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ADVANCES IN THE FIELD OF PHOSPHONITRILE POLYMERS

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I. INTRODUCTION

Hetero-chain organic-inorganic polymers have been widely studied lately. Of particular importance amongst them are organophosphorus compounds which possess a number of valuable properties, such as incombustibility, and fire- and heat-resistance.

Organophosphorus polymers containing the $-P=N-$ bond are especially interesting, owing to their heat-resistance. The compounds of this type which have been studied the most thoroughly are phosphonitrilic chloride and the polymers based on it; these have high elasticity and are known in the literature as "inorganic rubber"[1-6].

At present a homologous series of phosphonitrilic polymers has been prepared, proceeding from tri- and tetra-mer to macromolecular compounds. They have a number of important properties and are used industrially, *e.g.* in the electrical industry, as additives to lubricating oils, in fire-proofing textiles, and so on. The applications of phosphonitrilic chloride and its polymers have been reviewed by Rémond[4].

Polymeric phosphonitrilic chlorides are a class of inorganic hetero-chain linear macromolecular compounds which can exist as polymers both in the liquid and solid state[7].

Polymers which contain the $-P=N-$ bond and various organic branching groups are classified as organic-inorganic polymers. This review deals with phosphonitrilic derivatives and the polymers based on them.

II. METHODS OF PREPARATION

1. Phosphonitrilic Halides

The basic method for the preparation of phosphonitrilic chloride is the reaction of phosphorus pentachloride with ammonium chloride:

$$PCl_5 + NH_4Cl \rightarrow PNCl_2 + 4HCl.$$

This reaction can be carried out either in the presence or absence of organic solvents[8-11]. Audrieth, Steiman, and Toy[1] and Rémond[4] have reviewed the methods of preparation of phosphonitrilic chloride.

Liebig[12], in 1834, was the first to react phosphorus pentachloride with gaseous ammonia in an effort to prepare the amides of phosphoric acid. However, instead of the expected amides he obtained small quantities of a compound which was stable towards hydrolysis.

A number of workers showed later[13-16] that the compound obtained by Liebig was phosphonitrilic chloride and that its molecular formula was that of a trimer – $(PNCl_2)_3$. In order to prepare phosphonitrilic chloride, Stokes[8-10] reacted phosphorus pentachloride with ammonium chloride at 150°–200°, in a sealed tube. Liberation of hydrogen chloride during this reaction rendered the method dangerous and inconvenient. Stokes[8-10] isolated and characterised the cyclic trimer and tetramer of phosphonitrilic chloride.

Schenk and Römer[11] improved this method by using an autoclave instead of a sealed tube. A thorough study of this reaction showed that the yield of cyclic trimer and tetramer depended upon the weight ratio of the starting components, reaction temperature, and duration of heating[17]. The most favourable conditions, yielding about 95% of cyclic trimer, were: 52.1 g of phosphorus pentachloride and 50–100 g of ammonium chloride, heated 4–6 h at 145°–160°.

The use of organic solvents in this reaction is very advantageous, providing mild homogeneous conditions and minimising explosion risks. Schenk and Römer[11] used 1,1,2,2-tetrachloroethane as solvent. If the reaction is carried out with an excess of ammonium chloride at 135° for 20 h, a mixture of polymeric phosphonitrilic chloride homologues is obtained, consisting of 75% of trimer and 25% of tetramer.

Teja and Peters[18] recommend the use of $AlCl_3$, PCl_5, or quinoline as catalysts to obtain polymeric phosphonitrilic chloride homologues with polymerisation coefficient $n = 7$ or more. Under such conditions the yield of phosphonitrilic chloride heptamer reaches 55–60%.

The molar ratio of the starting components, the reaction temperature, and the duration of heating have the same significant effect upon the yield when organic solvents are used.

Yokoyama and Yamada[19] showed that when the temperature, duration of heating, and the excess of ammonium chloride are increased, the yield of cyclic trimer decreases owing to side reactions. The maximum yield of phosphonitrilic chloride trimer (40%) is obtained at 132°–134°, with a molar ratio of PCl_5 to NH_4Cl of 1 : 1.15.

If phosphorus pentachloride ammonolysis is not complete, large yields of linear polymers of the composition $(PNCl_2)_n.PCl_5$, which are insoluble in petroleum ether, are obtained. The same linear polymers are formed by the action of phosphorus pentachloride on cyclic polymers[20]. Individual members of this series have not been prepared in the pure state as they are unstable to heat and easily split off phosphorus pentachloride even in slightly polar solvents.

The linear polymers differ from the cyclic ones in being highly polar and more reactive. Polymers with small n are converted to a mixture of cyclic polymers when treated with ammonium chloride. When $n > 2$, chain formation predominates over cyclisation.

Yokoyama and Yamada[19] studied the effect of different solvents, such as chlorobenzene, chloroform, and carbon tetrachloride, on the synthesis of phosphonitrilic chlorides, and showed that no reaction took place in chloroform and carbon tetrachloride. Chlorobenzene can be used instead of tetrachloroethane. It is probable that the most important factor in the synthesis of phosphonitrilic chloride is not the nature of the solvent, but the reaction temperature.

The mechanism of the reaction of phosphorus pentachloride with ammonium chloride is still incompletely understood. Paddock and Searle[20] suggest that the reaction proceeds in stages, the first stage consisting of the formation of ammonium hexachlorophosphate,

$$NH_4Cl + PCl_5 \rightarrow NH_4PCl_6,$$

which subsequently decomposes into NH_2PCl_4 or, more probably, into $NH{=}PCl_3$.[1]

The latter compound can react either with itself, or with PCl_5, to yield $PCl_4{-}N{=}PCl_3$:

$$PCl_5 + \underset{(I)}{NH{=}PCl_3} \rightarrow \underset{(II)}{PCl_4N{=}PCl_3} + HCl.$$

Compounds (I) and (II) are the first members of the two series of polymers: $H(NPCl_2)_nCl$ and $PCl_4(NPCl_2)_nCl$. The higher polymers are formed by the successive reaction of such products with the starting components or with the intermediate compounds.

Among other methods of preparation of phosphonitrilic chlorides, the reaction of phosphorus pentachloride with NH_2HgCl may be noted[1]:

$$PCl_5 + NH_2HgCl \rightarrow PNCl_2 + HgCl_2 + 2HCl.$$

Moureu and Wetroff[21,22] showed that at temperatures above 700°, phosphorus nitrides react slowly with chlorine to form phosphonitrilic chlorides.

$$PN + Cl_2 \rightarrow PNCl_2.$$

Phosphonitrilic bromides and some phosphonitrilic halides containing both bromine and chlorine, can be prepared, in like manner to phosphonitrilic chloride, by the reaction of phosphorus pentabromide or pentachloride with ammonium bromide in organic solvents[23,24].

To prepare phosphonitrilic halides containing both bromine and chlorine, Rice, Daasch, Holden, and Kohn[23] reacted a mixture of phosphorus trichloride and bromine, or a mixture of phosphorus tribromide and pentachloride, with ammonium chloride. As a result they obtained the following phosphonitrilic halides: $P_3N_3Cl_5Br$, $P_3N_3Cl_4Br_2$, and $P_3N_3Cl_2Br_4$. Phosphonitrilic fluorides and fluorochlorides have also been reported in the literature[5,26-32].

Audrieth and his collaborators[1] did not succeed in obtaining a phosphonitrilic derivative by the reaction of phosphorus pentachloride with ammonium fluoride; in this reaction ammonium hexafluorophosphate was formed instead.

The reaction of trimeric phosphonitrilic chloride with silver fluoride resulted in products of indeterminate composition. By heating lead fluoride with phosphonitrilic chloride at 130°–180°, a mixture of liquid products was obtained, from which the following compounds were isolated: $P_4N_4Cl_2F_6$, $P_4N_4Cl_4F_4$, and $P_3N_3Cl_4F_2$,[1] and $P_3N_3F_6.2HF.2H_2O$.

Phosphonitrilic fluorides are also formed by the reaction of phosphonitrilic chloride (trimer and tetramer) with potassium fluorosulphinate at 120°–125°:

$$PNCl_2 + 2KSO_2F \rightarrow PNF_2 + 2KCl + SO_2.$$

The degree of polymerisation of the phosphonitrilic halide remains unaltered[25].

Of particular note among the new methods for the synthesis of phosphonitrilic fluorides is that of Mao, Dresdner, and Young[28], whereby $(PNF_2)_3$ and $(PNF_2)_4$ are prepared by heating P_3N_5 with nitrogen trifluoride or CF_3SF_5 to 700°.

Phosphonitrilic isothiocyanates are also known. Otto and Audrieth[33] prepared them by reacting phosphonitrilic chloride trimer with potassium isothiocyanate in acetone solution.

TABLE 1. Phosphonitrilic halides.

Formula	M.p., °C	B.p., °C		Reference
		at 13 mm Hg	at 760 mm Hg	
$(PNCl_2)_3$	114.0	127	265	1, 6, 12, 17, 34–38
$(PNCl_2)_4$	123.0	188	328.5	1, 6, 37, 38
$(PNCl_2)_5$	40.5	223	polymerises	6, 37
$(PNCl_2)_6$	91.0	261	»	6, 37
$(PNCl_2)_7$	—18.0	289	»	6, 37
$(PNF_2)_3$	26.8	—	50.9	25, 27–29 34–36
$(PNF_2)_4$	30.4	—	89.7	25–29, 34–36
$(PNF_2)_5$	—	—	120.1	37
$(PNF_2)_6$	—	—	147.2	37
$(PNF_2)_7$	—	—	170.7	37
$(PNF_2)_8$	—	—	192.8	37
$(PNF_2)_9$	—	—	214.4	37
$(PNF_2)_{10}$	—	—	230.8	37
$(PNF_2)_{11}$	—	—	246.7	37
$(PNF_2)_{18}$	—	—	—	6, 35
$(PNBr_2)_3$	191.0	—	—	24
$(PNBr_2)_4$	202.0	—	—	24
$P_3N_3Cl_5Br$	122.5	—	—	23
$P_3N_3Cl_4Br_2$	134.5	—	—	23
$P_3N_3Cl_4F_2$	165.5	—	—	23
$P_4N_4Cl_2F_6$	—12.1	—	106	1
$P_4N_4Cl_4F_4$	—24.9	—	130.5	1
$P_6N_7Cl_9$	237.0	—	—	34
$[PN(CNS)_2]_3$	42.0	—	—	33

All phosphonitrilic halides known at present are listed in Table 1.

As already mentioned, the reaction of phosphorus pentachloride with ammonium chloride yields a mixture of polymeric phosphonitrilic halide homologues, with the degree of polymerisation $n = 3$ or more. Crystallisation, sublimation, and distillation are usually employed for the separation of the mixtures.

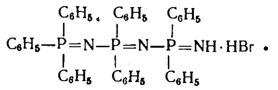
Trimer and tetramer are usually separated from the higher polymers by extraction with cold benzene[8-10], in which the latter are soluble ($n = 5$, 6, 7 or more). This method, however, is not suitable when large quantities of the higher polymers are present, as the viscosity of the solution increases considerably and makes filtration difficult. Glacial acetic acid was also used for the separation of trimer and tetramer from the higher polymers[1]. Steam distillation is recommended for the separation of the trimer only[1].

Good results were obtained in the separation of phosphonitrilic chlorides by gas chromatography. Gimblett[38] used a column packed with 30% E.301 Silicone on Celite 545, using nitrogen as carrier gas, at a flow rate of 1.5 litre h^{-1}.

2. Alkyl- and Aryl-Phosphonitriles

The synthesis of alkyl- and aryl-phosphonitriles can be carried out either by replacing the chlorine in phosphonitrilic chloride with alkyl or aryl radicals using the Grignard and Friedel-Crafts reactions (for phenyl radicals[2,39-42]), or by the reaction of trichlorodialkyl- and trichlorodiaryl-phosphoranes with ammonia[43-45]. Until recently the former method was the more widely used.

In 1929 Rosset[39] was the first to prepare hexaphenyltriphosphonitrile, from trimeric phosphonitrilic chloride and phenylmagnesium bromide, in molar ratio 1 : 4. The reaction was carried out in toluene at 110°–115°, and yielded 20–25% of hexaphenylphosphonitrile. Bode and Bach[40] repeated Rosset's experiments and made a thorough study of this reaction, including the effects of the component ratio, the temperature, and the nature of the solvent. In all cases they obtained the compound which corresponded to the formula $(C_6H_5)_7N_3P_3H.HBr$, m.p. 185°–187°, and to which they ascribed the following structural formula:


$$C_6H_5-\underset{C_6H_5}{\overset{C_6H_5}{P}}=N-\underset{C_6H_5}{\overset{C_6H_5}{P}}=N-\underset{C_6H_5}{\overset{C_6H_5}{P}}=NH\cdot HBr\ .$$

The yield of the cyclic trimer, hexaphenyltriphosphonitrile, was very low, regardless of the reaction conditions.

By allowing tetrameric phosphonitrilic chloride to react with phenylmagnesium bromide, Bode and Thamer[41] obtained two tetraphenyl derivatives, m.p. 176° and 205°, and two octaphenyl derivatives, m.p. 230° and 310°, which differed in their fluorescence.

In their attempt to prepare arylphosphonitriles, Bode and Bach[40] also allowed phosphonitrilic chloride to react with benzene in the presence of $AlCl_3$, and obtained products incompletely substituted by phenyl radicals. The quantity of the catalyst had no effect on the reaction rate. With ratios of aluminium chloride to trimeric phosphonitrilic chloride of 2 : 1 and 6 : 1, tetrachlorodiphenyltriphosphonitrile was obtained, m.p. 92.5°.

It is clear from these examples that Grignard and Friedel-Crafts' reactions are unsatisfactory for the preparation of aryl phosphonitrilic derivatives. Recent efforts of research workers have therefore been directed towards the alternative synthetic route, namely the reaction of tetrachloroarylphosphoranes, trichlorodiaryl-, and trichlorodialkyl phosphoranes with ammonia.

Bode and Bach[40] prepared the non-pairwise-substituted phenyl derivatives of trimeric phosphonitrilic chloride by reacting tetrachlorophenylphosphorane with ammonium chloride at 140° in tetrachloroethane. Haber, Herring, and Lawton[43] reacted trichlorodiphenylphosphorane with ammonium chloride in tetrachloroethane solution at 130°–135° and obtained very low yields of cyclic phosphonitrile derivatives (trimer and tetramer).

In the reaction in liquid ammonia, a white crystalline product was obtained, which upon heating under reduced pressure at 275° was converted in 65% yield to a polymer mixture. On fractional crystallisation, this product yielded 48% of cyclic tetramer and 7% of cyclic trimer. Searle[44] used this reaction for the synthesis of the alkyl derivatives of phosphonitrile. He reacted the components in tetrachloroethane at 120°–200°, and obtained very low yields of cyclic trimer and tetramer, and a mixture of linear polymers as the main reaction product. The linear polymers were converted to cyclic products in 70–75% yield on boiling with triethylamine or ammonium chloride in chloroform solution.

Korshak, Gribova, and their collaborators[45] reacted trichlorodibutyl- and trichlorodiethyl-phosphorane with ammonium chloride in dichlorobenzene solution and isolated linear products in which the molar ratio of phosphorus to nitrogen was 3 : 2 and 3 : 3 respectively.

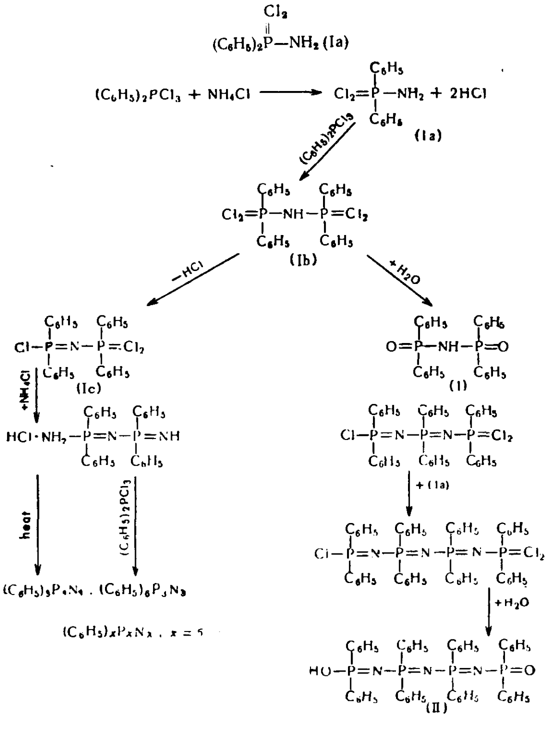
In order to study the mechanism of the reaction of trichlorodiaryl- and trichlorodialkyl-phosphorane with ammonium chloride in organic solvents, Korshak, Gribova, Artamonova, and Bushmarina[45] reacted trichlorodiphenylphosphorane with ammonium chloride in chlorobenzene or dichlorobenzene at 120°–180° for 8–20 h, with various molar ratios of the reactants. They carried out the reaction with gaseous ammonia in chlorobenzene at 0°.

The reaction of equimolar quantities of trichlorodiphenylphosphorane and ammonium chloride in chlorobenzene solution at 120°–125° for 12 h, results in 60% of a compound, m.p. 270°–272°, which corresponds to the formula $(C_6H_5)_4.$ $.P_2O_2NH$ (I). On hydrolysis it yields diphenylphosphinic acid. This reaction, carried out for 12–15 h at 160°–170° in dichlorobenzene, yields 70% of a compound which, on being recrystallised from benzene and alcohol, melts at 171°–171.5°. On the basis of analysis for the elements and ebullioscopic molecular weight determination in benzene, the formula ascribed to this compound is $(C_6H_5)_8.$ $.P_4N_3O_2H$ (II).

The reaction at 175°, for 20 h, of trichlorodiphenylphosphorane and ammonium chloride in molar ratio 1 : 5 results in the formation of 70% of octaphenyltetraphosphonitrile (III) and another compound which, after recrystallisation from dioxane, melts at 233°–235°, and whose formula is $(C_6H_5)_4P_2N_3H_4Cl$ (IV): the compound (IV) is formed in 60% yield in the reaction of trichlorodiphenylphosphorane with gaseous ammonia at 0° in organic solvents. It is unstable to heat, and when heated at 3–5 mm Hg and 270°–400° for 14 h, it is converted to octaphenyltetraphosphonitrile.

The authors assume the reaction to proceed in three main steps:

1. Chain initiation occurs as a result of the reaction of the NH_2 group with a chlorine atom in the trichlorophenylphosphorane molecule, giving rise to an intermediate compound:



2. The chain growth is thus a stepwise reaction, each stage giving rise to an independent compound. At the beginning the reaction consists basically of the interaction of the starting molecules with each other or with the molecules of the compounds formed, as is usual in polycondensations. Accordingly, the reaction product is a mixture of molecules with differing chain lengths. In principle, the chain growth can continue until all the reactive groups are used up. In fact, however, only small chains are formed at this stage (pentamers and hexamers) and the eight-membered cyclic product.

3. Chain rupture in this reaction is obviously connected with the tendency to form very stable eight-membered cyclic products. The predominant formation of the cyclic tetramer rather than the trimer is evidently to be accounted for by steric factors.

All the alkyl and aryl derivatives of phosphonitrile known at present are listed in Table 2.

3. Phosphonitrilamides and Their *N*-Substituted Derivatives

The synthesis of phosphonitrilamides from phosphorus pentachloride and gaseous or liquid ammonia in organic solvents is very widely known[1,6,46–50]:

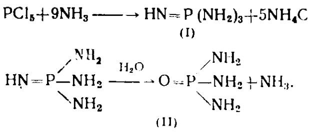
$$3PCl_5 + 24NH_3 \rightarrow [PN(NH_2)_2]_3 + 15NH_4Cl.$$

So is also the preparation from a solution of phosphonitrilic chloride (trimer or tetramer) and liquid ammonia[46]:

$$(PNCl_2)_3 + 12NH_3 \rightarrow [PN(NH_2)_2]_3 + 6NH_4Cl.$$

In the reaction of phosphorus pentachloride with liquid ammonia in different organic solvents a mixture of the polymeric homologues of phosphonitrilamides is usually formed[51].

Becke-Goehring and Niedenzu[50] studied the mechanism of the reaction of phosphorus pentachloride with ammonia in the presence of small quantities of water and suggested the following reaction scheme:

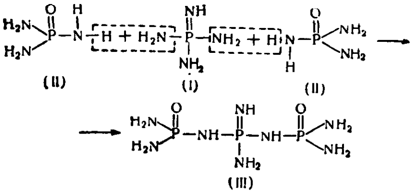


The triamide of imidophosphoric acid (I) formed in the early stages of the reaction is easily hydrolysed to phosphoramide (II). In the presence of very small quantities

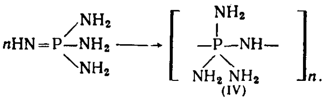
TABLE 2. Alkyl and aryl derivatives of phosphonitrile.

Formula	M.p., °C	Reference	Formula	M.p., °C	Reference
$(C_6H_5)_2P_3N_3Cl_4$	92.5	40	$(C_6H_5)_4P_2NO_2H$	270–272	45
$(C_6H_5)_7P_3N_3H\cdot HBr$	185.0	40	$(C_6H_5)_4P_2N_3H_4Cl$	233–235	45
$(C_6H_5)_3P_3N_3Cl(OH)_2$	294.0	40	$(C_6H_5)_6P_3N_3$	228–232	40, 43, 44
$(C_6H_5)_8P_4N_4$	310.0	41, 43, 45	$(CH_3)_6P_3N_3$	195–196	44
$(C_6H_5)_8P_4N_4$	230.0	41	$(CH_3)_8P_4N_4$	163–164	41
$(C_6H_5)_4P_4N_4Cl_4$	176.0	41	$(C_4H_9)_6P_3N_2ClO$	171–172	45
$(C_6H_5)_4P_4N_4Cl_4$	205.0	41	$(C_4H_9)_6P_3N_2O_2H$	86–87	45
$(C_6H_5)_8P_4N_3O_2H$	171–171.5	45	$(C_2H_5)_6P_3N_3HCl$	132–134	45

of water, the unhydrolysed compound (I) condenses with compound (II), forming the amide of triimidotriphosphoric acid (III):



Compound (I) can also polymerise:



The hydrolysis of the polymer (IV) results in the formation of ammonium polydiimidophosphate:

$$[-P(NH_2)_3-NH-]_n \rightarrow [-P(NH_2)_2(OH)-NH-]_n \rightarrow$$
$$\rightarrow [-P(NH)(ONH_4)-NH-]_n.$$

By carrying out the reaction of PCl_5 with an excess of liquid ammonia at -50° in chloroform solution, Audrieth and Sowerby obtained 36% of phosphonitrilamide trimer[46].

Another method for the synthesis of phosphonitrilamides is the ammonolysis of phosphonitrilic chlorides (trimer and tetramer). This reaction is slow, and, as shown by Audrieth and Sowerby[46], the complete substitution of chlorine atoms takes 48 h if an excess of liquid ammonia is used and the reaction is carried out under pressure at room temperature. The same result is obtained by slowly adding an ether solution of phosphonitrilic chloride to an excess of liquid ammonia at room temperature with vigorous agitation[46].

The products of partial ammonolysis are obtained by the reaction of aqueous or gaseous ammonia with the ether solution, or gaseous ammonia with the benzene solution of phosphonitrilic chloride trimer[1,6]. From the mixture of products obtained in this way, a diaminotetrachloro derivative, $P_3N_3(NH_2)_2Cl_4$, was isolated[6].

The ammonolysis of the ether solution of phosphonitrilic chloride tetramer with ammonia yields a mixture of products: diaminohexachlorophosphonitrile[52], tetraaminotetrachlorophosphonitrile[52], and phosphonitrilamide tetramer[46]. As in the case of phosphonitrilic chloride trimer, the reaction with liquid ammonia is very slow[1,46].

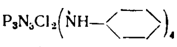
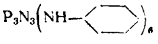
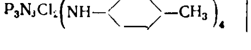
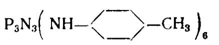
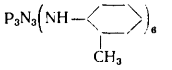
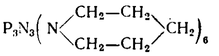
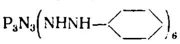
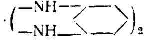
It can be seen from these examples that the ammonolysis of phosphonitrilic chlorides proceeds in stages: very harsh reaction conditions are required for the complete ammonolysis to take place.

N-Substituted phosphonitrilamides are prepared by ammonolysis of phosphonitrilic chlorides (trimer and tetramer) with aliphatic and aromatic amides[1,6,47,48,53,54,55].

$$(PNCl_2)_3 + 12RNH_2 \rightarrow [PN(NHR)_2]_3 + 6RNH_2HCl.$$

The reaction can be carried out either in the presence or absence of organic solvents[48]. Complete substitution of chlorine atoms in phosphonitrilic chloride is only achieved

TABLE 3. Phosphonitrilamides and their *N*-substituted derivatives.

Formula	M.p., °C	Reference
$P_3N_3(NH_2)_6$	161.5	1,46,47
$P_3N_3Cl_4(NH_2)_3$	—	10
$P_3N_3Cl_4[N(CH_3)_2]_2$	98—103	46,47,53
$P_3N_3Cl_3[N(CH_3)_2]_3$	107	47
$P_3N_3Cl_2[N(CH_3)_2]_4$	104	53
$P_3N_3[N(CH_3)_2]_6$	104	53
$P_4N_4[N(CH_3)_2]_8$	237	53
$P_3N_3Cl_3[N(CH_3)_2](NH_2)_2$	87	47
$P_3N_3Cl_2(NHCH_3)_2(NH_2)_2$	140	47
$P_3N_3[N(CH_3)_2]_2[NHCH_3]Cl_3$	82	47
$P_3N_3(NH_2)_2(NHCH_3)_4$	204	47
$P_3N_3(NH_2)_2(NHCH_3)_4$	161.5	47
$P_3N_3(C_6H_5)_2(NH_2)_4$	275	47
$P_3N_3(C_6H_5)_2[N(CH_3)_2]_4$	120	47
$P_3N_3(C_6H_5)_2(NHCH_3)_4$	174	47
$P_3N_3(C_6H_5)_2(NHCH_3)_2(NH_2)_2$	140	47
$P_3N_3(C_6H_5)_2(NH_2)_2[N(CH_3)_2]_2$	137	47
$P_3N_3Cl_4[N(C_2H_5)_2]_2$	134	53
$P_3N_3Cl_3[N(C_2H_5)_2]_3$	162	6
$P_3N_3(NHC_2H_5)_6$	119	6
$P_3N_3Cl_4(NHCH_2CH_2NH_2)_2$	188	48
$P_3N_3Cl[NHCH_2CH(CH_3)_2]_2$	—	1
$P_3N_3Cl_4(NHC_4H_9)_2$	—	6
$P_3N_3Cl_4[N(C_6H_{11})_2]_2$	200	1,53
$P_3N_3(NHC_6H_{11})_6$	166	50
	191	48
	268	1
	174	48
	249	48
	241	1
$P_3N_3Cl_4[(NH_2)C_6H_4CH_3]_2$	211	48
	231—266	1,48
$P_3N_3Cl_4[(NH)_2C_6H_4]$	350	52
	200	1
$P_3N_3Cl_2(C_6H_6)_2(NH_2)_2$	162	48
$P_3N_3Cl_2(C_6H_5)_2(NHC_6H_5)_2$	193	48
$P_3N_3(NH_2)_2(C_6H_5)_2(NHC_6H_5)_2$	218	48
$P_3N_3(NH_2)_2(NHC_6H_5)_4$	256	48
$P_3N_3(NH_2)_2(NHC_6H_5)_2\cdot$ 	160	48
$P_3N_3(N_3)_6$	oil	56
$P_3N_3(NHNH_2)_6$	360	57
$P_3N_3(NSC)_6$	42	33
$P_3N_3(NC_6H_5)_3$	—	54,57
$P_3N_3Cl_4(NHR)_2$ where RNH_2 = ester of amino-acid	—	1
$P_4N_4(NH_2)_2Cl_6$	—	52
$P_4N_4(NH_2)_4Cl_4$	—	52
$P_4N_4(NH_2)_2(NH_2)_2Cl_2$	—	52
$P_4N_4(NHC_6H_5)_8$	250	1
$P_3N_3(NHN=CHC_6H_5)_6$	250(decomp)	57
$P_3N_3(NHN=CHC_6H_4OH)_6$	255	57

under harsh reaction conditions[6]. The easiest to prepare are the disubstituted amino derivatives.

The preparation of aromatic phosphonitrilamides requires higher temperatures[48]. The reaction with aliphatic amines can occur under milder conditions if organic solvents are used. The *N*-substituted phosphonitrilamides reported in the literature are listed in Table 3. A large number of these compounds have been prepared lately.

It was believed until recently that the substitution at each phosphorus atom in phosphonitrilic chloride occurs in pairs. Becke-Goehring[47], however, showed that in the reaction of phosphonitrilic chloride with amines, substitution can occur simultaneously at different phosphorus atoms.

Ray and Shaw[53] obtained di- and tri-substituted phosphonitrilamides using secondary amines, diethylamine and dicyclohexylamine. With primary amines, ethylamine and cyclohexylamine, they succeeded in preparing the completely substituted products. In the reaction of phosphonitrilic chloride with diethylamine and dicyclohexylamine, the substitution obviously takes place at different phosphorus atoms. The rate of substitution in phosphonitrilic chloride and its derivatives depends on several factors, such as nucleophilic activity of the amine, steric effects, and the polarity of the substituent[48,53]. It should be noted that under identical conditions, the substitution in phosphonitrilic chloride tetramer proceeds faster than in the trimer[53]. Diamines, as well as monoamines, react with phosphonitrilic chloride, forming *N*-substituted phosphonitrilamides[6].

In the reaction with ethylenediamine, two chlorine atoms are substituted by *N*-aminoethylamino groups[6]. The reaction with aromatic diamines is similar[48]. If the substitution of halogen atoms attached to phosphorus does not proceed pairwise, di- and tri-substituted phosphonitriles are obtained in different stereoisomeric forms.

Audrieth[6] suggested the possible stereoisomers of the phosphonitrile trimer (see Fig. 1).

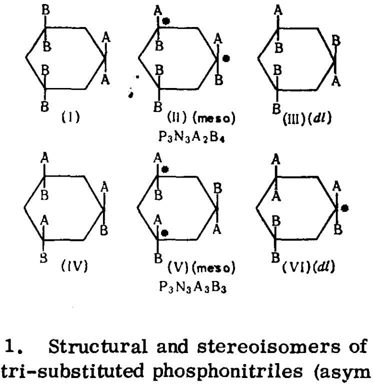
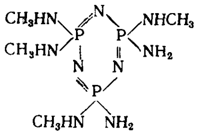
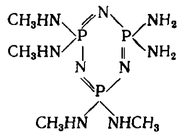


Fig. 1. Structural and stereoisomers of di- and tri-substituted phosphonitriles (asymmetric phosphorus atoms are indicated by an asterisk).

Becke-Goering[47] obtained two isomers, m.p. 161.5° and 204°, by the reaction of tetrachlorodiaminophosphonitrile and dichlorodiaminodimethylaminophosphonitrile, respectively, with methyl amine.



m.p. 161.5°



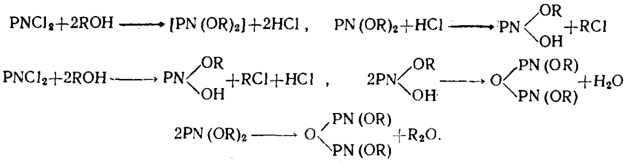
m.p. 204°

The products from the reaction of phosphonitrilic chloride and hydrazine[57] or sodium azide[56] also belong to *N*-substituted phosphonitrilamides.

The phosphonitrile trimer and tetramer react with esters of amino-acids yielding products in which some of the halogens are replaced with amino-ester radicals[1]. The trimer usually yields disubstituted derivatives, and the tetramer, tetrasubstituted ones.

4. Esters of Triphosphonitrilic Acids

The reaction of phosphonitrilic chloride — trimer and tetramer — with alcohols and phenols has been thoroughly studied[1,58-62]. Wissemann[1] studied the reaction with alcohols both in the presence and absence of proton acceptors such as pyridine, and showed the reaction to proceed in the following manner:



$$PNCl_2 + 2ROH \longrightarrow [PN(OR)_2] + 2HCl, \quad PN(OR)_2 + HCl \longrightarrow PN\begin{cases}OR\\OH\end{cases} + RCl$$

$$PNCl_2 + 2ROH \longrightarrow PN\begin{cases}OR\\OH\end{cases} + RCl + HCl, \quad 2PN\begin{cases}OR\\OH\end{cases} \longrightarrow O\begin{cases}PN(OR)\\PN(OR)\end{cases} + H_2O$$

$$2PN(OR)_2 \longrightarrow O\begin{cases}PN(OR)\\PN(OR)\end{cases} + R_2O.$$

The trimer and tetramer react with absolute methanol to form partially substituted products, the incomplete esters of tri- and tetra-phosphonitrilic acids.

Dishon[59] developed a method for the synthesis of phosphonitrilic esters in the presence of a proton acceptor at 0°. Hexamethyl and hexabutyl esters of triphosphonitrilic acid were prepared by this method. Phosphonitrilic esters can also be prepared by reacting phosphonitrilic chloride with alcoholates. In this way, Rätz and Hess[61] prepared the hexaethyl ester of triphosphonitrilic acid.

Aromatic esters of phosphonitrilic acids can be prepared by reacting phosphonitrilic chlorides with phenols, in the presence of pyridine[1], or with sodium phenoxide[62].

Table 4 lists all the phosphonitrilic esters known at present.

TABLE 4. Esters of tri- and tetra-phosphonitrilic acids.

Formula	M.p., °C	Ref.
$P_3N_3(OCH_3)_6$	127—128/0.1 mm	59
$P_3N_3(OC_2H_5)_6$		61
$P_3N_3Cl_2(OC_2H_5)_4$		61
$P_3N_3(OC_4H_9)_6$	170—171/0.3 mm	59
$P_3N_3(OCH_2—CH{=}CH_2)_6$	—	63
$P_3N_3[(OH)(OCH_3)]_6$	—	1
$P_4N_4[(OH)(OCH_3)]_8$	—	1
$P_3N_3(OC_6H_5)_6$	—	62
$P_3N_3(OC_6H_4CH_3)_6$	—	62
$P_3N_3(OC_6H_4NO_2)_6$		
$P_3N_3(OC_6H_4CH_2C_6H_5)_6$	—	62
$P_3N_3Cl_2(CH_2OCHOHCH_2OH)_2(OCH_3)_2 4C_5H_5N$	—	62
$P_4N_4Cl_2(CH_2OCHOHCH_2OH)_4(OCH_3)\cdot 4C_5H_5N$	—	1
$[PN(CCH_3)(OC_{10}H_{17})]$	—	1
$P_4N_4(OCH_3)_8$	41	36
$P_3N_3(OCH_2CHBrCH_2Br)_3$	—	63

5. Macromolecular Phosphonitrile Derivatives

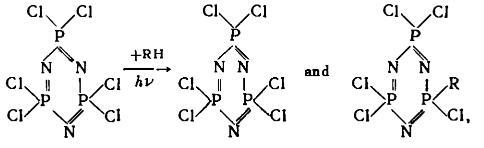
The usual method of preparing macromolecular derivatives of phosphonitrile is by polymerisation. Polymerisation of phosphonitrilic halides has been very widely studied[1,5,6,18,25-32,35,37,62,64-71]. The best known amongst the halogen derivatives of phosphonitrile is polyphosphonitrilic chloride, often called "inorganic rubber". In 1897 Stokes[9] showed for the first time that a mixture of phosphonitrilic chlorides was transformed on heating to 250°–350° into a rubber-like material. The polymerisation of phosphonitrilic halides can be carried out in the presence[66,67] or absence[66,68] of organic solvents.

Patat and Kollinsky[66] studied the polymerisation of phosphonitrilic chloride in the presence of solvents and showed the polymerisation rate to be determined by the reaction temperature, the monomer concentration, and the nature of solvent. During the polymerisation of phosphonitrilic chloride in solvents such as benzene, toluene, xylene, and hexane, at 280°–340°, an excess hydrogen chloride pressure was observed on opening the tube, whilst the viscosity of the solution was only slightly changed, thus indicating a possible reaction between the phosphonitrilic chloride and the solvent, according to the equation[67]

$$n\,\mathrm{RH} + (\mathrm{PNCl_2})_m \xrightarrow[\mathrm{O_2}]{\sim 300^\circ} \mathrm{P}_m\mathrm{N}_m\mathrm{Cl}_{2m-n}\mathrm{R}_n + n\mathrm{HCl}.$$

A more thorough study of the reaction of phosphonitrilic chloride trimer with toluene at 300° during 36 h showed that a mixture of products was formed, from which $P_3N_3Cl_5C_7H_7$, $P_3N_3Cl_4(C_7H_7)_2$, and others were isolated[66].

Dishon and Hirshberg[72] found that in the photochemical reaction of the phosphonitrilic chloride trimer and tetramer with benzene and decahydronaphthalene both soluble and insoluble products were formed. From the soluble part phenyl- and decahydronaphthyl-phosphonitrilic chlorides were isolated:



where R = phenyl and decahydronaphthyl. The percentage of carbon and hydrogen is higher in the insoluble part than in the soluble one, indicating stepwise substitution of chlorine atoms by R radicals.

Polymerisation in hydrocarbons and their derivatives is catalysed by oxygen. Patat and Kollinsky[66] showed that the polymerisation in these solvents did not take place in the absence of oxygen.

Polymerisation of phosphonitrilic chloride was studied in such solvents as tetrachloroethylene, hexachloroethane, tetrabromoethylene, hexachlorobenzene, hexabromoethane, phosphorus trichloride, phosphorus oxychloride, and concentrated H_2SO_4. The best results were obtained in a solution of carbon tetrachloride. In this solvent, colourless, high-molecular-weight polymers were obtained.

When the polymerisation is carried out in solution, its rate is substantially affected by the temperature and the monomer concentration. Fig. 2 shows the dependence of the reaction rate on temperature and concentration. The yield of polymer rises with increase of temperature and concentration. It is clear from Fig. 2 that the rate equation is of the second order. The activation energy is E = = 40 ± 3 kcal. The rate constant in carbon tetrachloride is $k = 4 \times 10^{14} \times 10^{-40\,000/2.3RT}$. The rate increases when oxygen is added (see Fig. 3), but when the reaction is carried out in an atmosphere of pure oxygen, a general fall in the reaction rate is observed. The molecular weight of the soluble part of the polymer reached 130 000. Table 5 shows that the molecular weight of the polymer depends on the concentration of the monomer in solution.

Polymerisation of phosphonitrilic chloride can also be carried out in bulk (block polymerisation), without organic solvents[68-71].

Patat and Frömbling[68] studied the kinetics of the polymerisation of phosphonitrilic chloride at 250°–300° in the absence of air. The reaction rate increases with increasing temperature (Fig. 4).

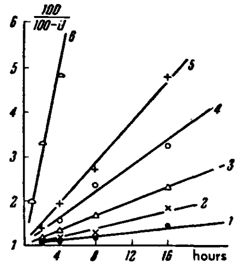


Fig. 2. Polymerisation of triphosphonitrilic chloride in solution at different temperatures: 1) 15% trimer at 270°; 2) 5% trimer at 300°; 3) 10% trimer at 300°; 4) 15% trimer at 300°; 5) 30% trimer at 330°; 6) 15% trimer at 330°. U = percentage conversion.

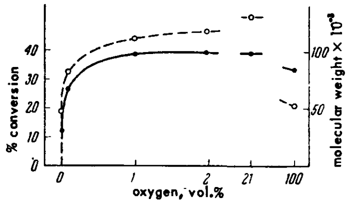


Fig. 3. Effect of oxygen on the polymerisation of triphosphonitrilic chloride in solution.

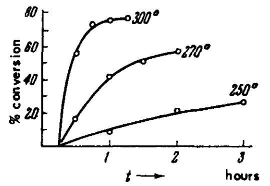


Fig. 4. Block polymerisation of triphosphonitrilic chloride at different temperatures.

This reaction can also proceed in the absence of oxygen, and is of the second order (see Fig. 5). Its activation energy is 42 ± 2.5 kcal. The addition of small quantities of carbon tetrachloride to the system causes a sharp drop in the polymerisation rate. Polymerisation of phosphonitrilic chloride in the absence of air is catalysed by alcohols, organic acids, and other compounds[69].

Konecny and Douglas[69] found that the following compounds initiated the polymerisation of phosphonitrilic chloride at 210° for a reaction time of 48 h (the weight of the catalyst used per gram of the sample is given in brackets): ether (2.1 mg), benzoic acid (10 mg), acetic acid (0.96 mg), chloroacetic acid (20 mg), nitromethane (1.6 mg), ethyl acetate (2.4 mg), n-butyl ether (40 mg), acetone (3.0 mg), methyl ethyl ketone (1.9 mg), ethanol (2.6 mg), di-t-butyl peroxide (2.3 mg), zinc (130 mg), tin (40 mg), and sodium (200 mg).

Fig. 6 shows the effect of different catalysts, ether, ethanol, and tin, on the polymerisation rate of phosphonitrilic chloride trimer. The results of the polymerisation of trimer, tetramer, and their mixture in the presence of 8.4 mg ether are given in Fig. 7, which shows that the trimer polymerises faster than the tetramer.

Manley[73] has shown that the polymerisation of phosphonitrilic chloride is not initiated by high-energy electrons.

The molecular weights of the samples of phosphonitrilic chloride polymers obtained by block polymerisation in the absence of air are of the order 1×10^6; if the polymerisation is carried out in solution in the presence of oxygen, the molecular weight reaches the values $1 \times 10^4 - 1 \times 10^5$ [68]. Block polymerisation in the absence of oxygen, as well as polymerisation in solution, gives an insoluble polymer in yields which depend on the reaction temperature and not on monomer concentration or reaction time[68]. With a rise in the polymerisation temperature the yield in macromolecular products is decreased.

TABLE 5. Dependence of the degree of polymerisation on concentration[68].

Concentration %	Mol.wt.
5	45600
10	108000
15	123000
30	131000

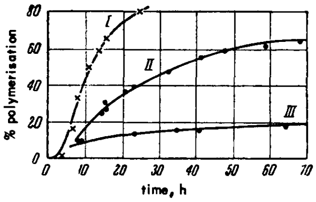


Fig. 6. Polymerisation of phosphonitrilic chloride (trimer, tetramer, and their mixture) catalysed by 8.4 mg of ether: I) trimer; II) trimer-tetramer mixture (initially containing 53% of trimer); III) tetramer.

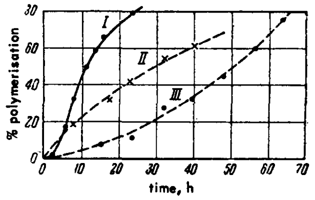


Fig. 7. Catalytic polymerisation of phosphonitrilic chloride trimer in the presence of: I) 8.4 mg of ether; II) 2.6 mg of ethanol; III) 20 mg of tin.

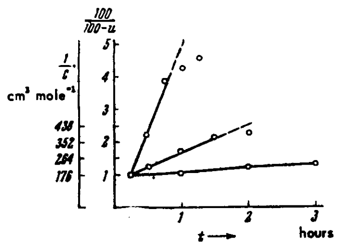
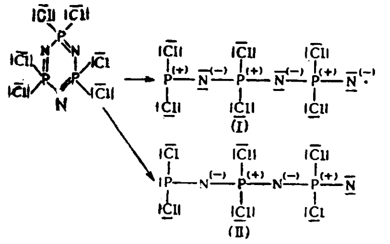


Fig. 5. Kinetics of the block polymerisation of triphosphonitrilic chloride. U = percentage conversion.

Patat and Frömbling[68] showed that thermal polymerisation of phosphonitrilic chloride followed a radical mechanism. The chain initiation is the result of the rupture of the P–N–bond of the trimer ring, which gives rise to a radical-like chain (I) or a chain in which the nitrogen atom is electron-deficient, but in which the phosphorus atom has an octet (II)*.



The chain growth is bimolecular, and chain termination is

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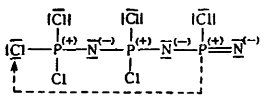
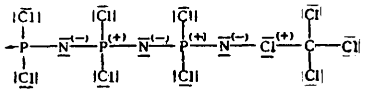
* The symbolism used in the next four formulae (a line to represent an electron pair is that of Patat and Frömbling[68] (Ed. of Translation).

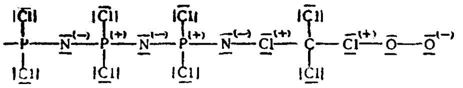
a result of monomolecular rearrangement, leading to the formation of the P=N–bond at the end of the chain:



Patat and Frömbling[68] explain the inhibiting effect of carbon tetrachloride by the deactivation of polymer radicals through the electron deficiency in nitrogen being made up:



The product formed by the addition of carbon tetrachloride to the growing chain becomes unstable in the presence of oxygen, and the polymerisation can consequently start again:



Phosphonitrilic halides containing bromine and fluorine can also polymerise[25,27,32,35]. Seel and Langer[25] found the phosphonitrilic fluoride trimer to polymerise on heating at 350° for 15 h into a rubber-like product. Meyer[27] heated phosphonitrilic fluoride in an autoclave at 260° and obtained a rubber-like polymer. The ability to polymerise remains even if the halogen in phosphonitrilic chloride is replaced by alkyl or aryl groups. Octaphenyltetraphosphonitrile and tetraphenyltetrachlorotetraphosphonitrile polymerise on heating to 300° [41]. Bode and Bach[40] showed that a solid white mass formed on heating diphenyltetrachlorotriphosphonitrile for 3 h at 250° in a sealed tube. Korshak, Gribova, Artamonova, and Bushmarina[45] studied the polymerisation of octaphenyltetraphosphonitrile by heating it in a sealed tube at 320°–500°. The time required for polymerisation varied from 6 to 127 h. The results of these experiments are given in Table 6. It is evident that at 320° the polymerisation of octaphenyltetraphosphonitrile is already taking place, yielding penta- and hexa-mers, which melt at 100°–140°. If the temperature is increased from 320° to 400°, the yield of these products rises from 6.0 to 50.5%. Hexaphenyltriphosphonitrile is formed as well as the mixture of penta- and hexa-mers.

If the heating is continued for 41 h at 400°, a product which does not melt up to 300°–400°, and which is insoluble in ordinary organic solvents, is also formed. Its yield rises with the rise in polymerisation temperature from 400° to 500°. The polymerisation of octaphenyltetraphosphonitrile is a result of the rupture of the eight-membered ring, which is subsequently transformed into a six-membered one.

Searle[44] showed that the methyl derivatives of phosphonitrile trimer do not polymerise to a rubber-like product when heated up to 350°–400°, but are decomposed instead.

Polymeric esters of triphosphonitrilic acid are obtained either by the polymerisation of the cyclic esters (trimer and tetramer) of phosphonitrilic acid, or by the alcoholysis of the phosphonitrilic chloride polymers[1,59–63]. Brown[62] polymerised the hexaphenyl triphosphonitrilic ester by heating it to 320°, and obtained a solid thermoplastic resin.

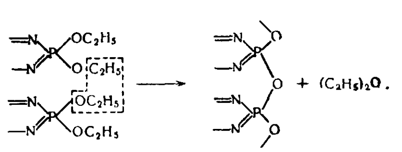
TABLE 6. The polymerisation of octaphenyltetraphosphonitrile.

Reaction temperature, °C	Time, h	Composition of polymers, %			
		trimer	tetramer	penta- and hexa-mer mixture	high-melting product
320	62.5	10.4	72.5	6.0	—
320	127.0	20.8	56.5	17.5	—
380	92.5	6.2	51.8	35.7	—
380	117.5	4.6	54.4	40.2	—
400	15.0	9.3	29.5	50.5	—
400	41.0	4.4	9.2	9.4	71.0
420	22.5	1.1	12.7	10.9	67.5
460	10.0	—	—	3.8	93.5
500	6.0	—	—	2.3	97.5

TABLE 7. Alcoholysis of polyphosphonitrilic chloride[75].

Alcohol	% substituted chlorine	% chlorine substituted by alkoxy groups	PO:P	C:H
Ethanol	99.5	79.5	1.59:1	2:5.1
Isopentanol	98.0	63.0	1.26:1	5:11.2
2-Ethylhexanol	88.0	68.5	1.37:1	8:17.1

Polymers of *p*-cresyl- and *o*-, *m*-, and *p*-nitrophenyl esters of triphosphonitrilic acid have been described[62]. According to Brown[62], the nitrophenyl phosphonitrilic esters are easier to polymerise. When heating the hexaethyl triphosphonitrilic ester to 125°, Rätz and Hess[61] observed the separation of ethyl ether and the formation of a polymeric, amorphous, hygroscopic product, barely soluble in water, but forming a strongly acid solution. They suggested the following scheme for this reaction:



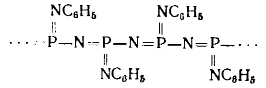
Dishon[59] prepared polymers from the hexamethyl, hexabutyl, and hexaallyl esters of triphosphonitrilic acid.

The polymerisation of triphosphonitrilic esters can be conducted in the presence of $AlCl_3$, $ZnCl_2$, and BF_3 as catalysts[61]. These polymers can also be obtained, as indicated above, by the alcoholysis of phosphonitrilic chloride polymers[63,74,76]. Goldschmidt and Dishon[75,76] made a thorough study of the alcoholysis of phosphonitrilic chloride polymers with several aliphatic alcohols in different solvents and in the presence of pyridine as a proton acceptor. Their results are given in Table 7, which shows that, under the stated conditions, the chlorine atoms in polyphosphonitrilic chloride can be almost completely replaced, partly by alkoxy groups and partly by oxygen. Goldschmidt and Dishon[75] observed a deterioration in the mechanical properties of polymers obtained by treating polyphosphonitrilic chloride with aliphatic alcohols in the presence of pyridine. They explained this by a difference in the properties of the layers of the polyester formed and those of the unreacted polyphosphonitrilic chloride. There is no deterioration in the mechanical properties of the polymer, and the alcoholysis proceeds faster, if carried out in toluene solution with a previously swollen polyphosphonitrilic chloride.

For the preparation of macromolecular phosphonitrilic polyesters soluble in organic solvents, the authors[75] recommended cautious heating of insoluble macromolecular polyesters with tetrachloroethane and other chlorine-containing solvents. The polymer dissolves as the cross-links between the parallel chains of the polymer are destroyed. Soluble phosphonitrilic polyesters are also formed by the alcoholysis of polyphosphonitrilic chloride previously swollen in a solvent.

Hamalainen[74] obtained phosphonitrilic polyesters by treating polyphosphonitrilic chloride with 2,3-dihalogeno alcohols in the presence of pyridine. Esterification of the phosphonitrilic chloride polymer can be carried out with sodium alcoholate in the corresponding alcohol[75], but the polyesters obtained by this method have a higher intrinsic viscosity and a smaller number of alkoxy groups than those obtained in the reaction with alcohol and pyridine.

Phosphonitrilamides and *N*-substituted phosphonitrilamides can polymerise to form resinous products[50,54,55,58,77]. Lipkin[55] obtained solid transparent polymers, insoluble in organic solvents, by heating to 200°–400° under reduced pressure the products of the reaction between phosphonitrilic chloride and butylamine. If the product of the reaction between phosphonitrilic chloride and acetanilide is heated, hydrogen chloride and acetyl chloride are liberated, and a thermoplastic solid is formed, which softens at 90°–110° and whose structure is probably that of a polyphenylphospham[54,58]:



$$\cdots-\overset{\overset{\displaystyle NC_6H_5}{\|}}{P}-N=\underset{\underset{\displaystyle NC_6H_5}{\|}}{P}-N=\overset{\overset{\displaystyle NC_6H_5}{\|}}{P}-N=\underset{\underset{\displaystyle NC_6H_5}{\|}}{P}-\cdots$$

Products of the reaction between phosphonitrilic chloride (trimer and tetramer) and chloroaniline, urea, guanylurea, guanidine, etc. have been described[77].

Among other polymers containing a $-\overset{|}{\underset{|}{P}}=N-$ bond may be mentioned phospham $[-N=P(=NH)-]_x$ [78,79], and phosphoryl nitride $(O=P\equiv N)_x$, a solid product which decomposes at 750°. [80]

Phosphoryl nitride polymer is formed on heating the triamide of phosphoric acid at 600°. Similarly, on heating at 100°, the triamide of thiophosphoric acid polymerises with the liberation of ammonia; at 800° impure phosphorus nitride is formed.

Audrieth and Sowerby[46] observed that after prolonged heating of phosphonitrilamide strong deamination occurred, and a high-molecular-weight compound, polyphospham, was formed. Polymeric phosphonitrilic thiocyanate, $[-N=P(NCS)_2]_x$, is also known[33].

III. PROPERTIES

1. Physical Properties

The physical properties of phosphonitrile derivatives, trimer and tetramer, as well as the higher polymeric homologues, have been widely studied[1,6,20,81-93]. Brockway and Bright[82] investigated the structure of phosphonitrilic chloride trimer by electron diffraction. They found the trimer to consist of a planar six-membered ring, with phosphorus and nitrogen alternating, and all P–N bonds equivalent. Two chlorine atoms are attached to each atom of phosphorus, at right angles to the plane of the P_3N_3 ring. Ketelaar and de Vries[94] showed phosphonitrilic chloride tetramer to possess an eight-membered non-planar ring, in which the P–N bonds are equivalent, as in the trimer.

Daasch[89,95], Shaw[90], and others[20,23,57] studied the infra-red spectra of phosphonitrilic chloride trimer and tetramer and their derivatives, and showed the absorption maximum at 1200–1350 cm^{-1} to be caused mainly by stretching vibrations of the P–N group. Daasch and Smith[95] studied the infra-red absorption spectra of phosphonitrilic esters and showed the frequency of the stretching vibrations of the P–N group to change insignificantly with change in the size of the alcohol radical from CH_3O to $C_8H_{17}O$. This frequency characterises the vibrations of the ring and depends mainly on the electronegative properties of the atoms attached to the ring; it increases with rising electronegativity, as shown in Table 8.

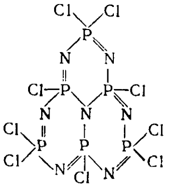
The structure of the higher polymeric homologues of phosphonitrilic chloride, pentamer, hexamer, and nitrilohexamer, is still little known. Audrieth and Toy[1] think that they have a linear structure. Kruse[34], on the basis of ultra-violet and infra-red spectra, and the dipole moments of the lower polymeric phosphonitrile homologues,

TABLE 8. Frequencies of the stretching vibrations of phosphonitrilic halides.

Compound	Frequency of stretching vibration, cm^{-1}	
$P_3N_3Cl_6$	1218[89]	1220[90]
$P_3N_3Br_6$	1170[20]	1184[90]
$P_3N_3(OMe)_6$	1242[95]	1275.1235[90]
$P_3N_3(NMe)_6$	1195[90]	
$P_3N_3Cl_2(NMe)_4$	1220. 1198[90]	
$P_3N_3Cl_4(NMe_2)_2$	1210[90]	
$P_3N_3Cl_4(NHMe)_2$	1215 (shoulder), 1205[90]	
$P_3N_3Cl_4(NEt_2)_2$	1255; 1226 (shoulder)[90]	
$P_3N_3Cl_4Ph_2$	1220, 1189[90]	
$P_3N_3F_6$	1287[90]	
$P_3N_3Cl_5Br$	1205[23]	
$P_3N_3Cl_4Br_2$	1202[23]	
$P_3N_3Cl_2Br_4$	1180[23]	
$P_3N_3(N_2H_3)_6$	1218[57]	
$P_4N_4Cl_8$	1305[89], 1315[90]	
$P_4N_4Br_8$	1277[90]	
$P_4N_4(OMe)_8$	1377[90]	
$P_4N_4Cl_4Ph_4$ (m.p. 248°)	1313, 1294, 1282[90]	
$P_4N_4Cl_4Ph_4$ (m.p. 148°)	1292[90]	
$P_4N_4(NMe_2)_8$	1265[90]	
$P_5N_5C_{10}$	1325[20]	
$P_6N_6C_{12}$	1324[20]	
$(PNCl_2)_{8-9}$	1291[20]	
$(PNCl_2)_{8-9}PCl_5$	1240[20]	
$(PNCl_2)_n$ (rubber)	1365—1380[20]	

attribute to them a non-planar ring, rather than a chain structure. There is very little difference in the infra-red absorption spectra of different phosphonitrilic chloride polymers.

Molar polarisation, P_{200} (cm^3) has been determined for trimer (84 ± 0.5), tetramer (148.5 ± 4.5), pentamer (145.5 ± ± 4.5), and hexamer (131.5 ± 6.5). The low P_{200} value, 44 ± 3, for the nitrilohexamer is accounted for by its structure — condensed rings with low electron mobility.



Phosphonitrilic halide trimers containing chlorine and bromine also have the structure of a planar six-membered ring[20]. The heat of formation of phosphonitrilic chloride trimer is ΔH_f = -196.3 ± 3 kcal mole^{-1}.[20] The energy of the P–N bond is approximately 75–80 kcal mole^{-1}.

A study has been made of the distribution curves of phosphonitrilic chloride (trimer, tetramer, pentamer, and hexamer) between solutions of sulphuric acid and n-hexane[20] to determine the acid–base equilibrium. The results are given in Fig. 8, which shows that the trimer is a stronger base than the other oligomers. The difference in basicities, and the corresponding difference in the partition coefficients for the distribution between sulphuric acid of a chosen concentration and an inert solvent, can be used as a basis for the separation of the phosphonitrilic chlorides.

Yokoyama and Yamada[96] determined the solubility of phosphonitrilic chloride trimer in benzene, toluene, xylene, hexane, trichloroethylene, tetrachloroethane, chloroform, carbon tetrachloride, methanol, ethanol, acetone, ethyl ether, acetic acid, and dioxane. The best solvents are found to be benzene, toluene, tetrachloroethane, and chloroform. The solubility of phosphonitrilic chloride trimer in these solvents increases as the temperature is increased from 20° to 80°.

Exceptional heat resistance and chemical stability are the main characteristics of the cyclic phosphonitrile derivatives. Like benzene, phosphonitrilic chloride trimer consists of a six-membered ring, with the length of all P–N bonds equal. The energy of that bond, determined thermochemically and spectroscopically, is higher than that of the single P–N bond[5,20,97,98].

The rings of cyclic phosphonitriles are apparently very flexible, as is borne out by the existence of 17-membered rings. The cyclic phosphonitrile derivatives can be regarded as aromatic compounds. The aromatic rings of the phosphonitrile series seem to be able to assume any dimensions as the aromatic bonds in them are formed by the overlapping of the *p*-orbital of nitrogen and the *d*-orbital of phosphorus, whereas in benzene they are formed by the overlapping of the *p*-orbitals of carbon[35,97,98].

The oily phosphonitrilic chloride polymer obtained by the incomplete ammonolysis of phosphorus pentachloride, of empirical formula $PCl_4(PNCl_2)_nCl$, has a linear structure, as is illustrated by a comparison of the ultra-violet spectra of this polymer with those of phosphonitrilic chloride trimer (see Fig. 9)[20]. Fig. 9 shows that the ultra-violet spectra of the linear polymer are characterised by two maxima, which are absent from the trimer spectra. The intensity of these maxima depends on the molecular weight of the polymer (see samples A and B) whereas their λ_{max} values remain unchanged. The linear structure of these polymers is confirmed by their preparation from cyclic derivatives by treatment with phosphorus pentachloride.

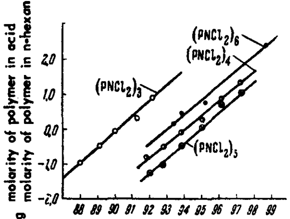


Fig. 8. Partition coefficients for the distribution of phosphonitrilic chlorides between sulphuric acid and n-hexane. The initial concentration of every polymer in n-hexane was 3.5 × 10^{-3} M.

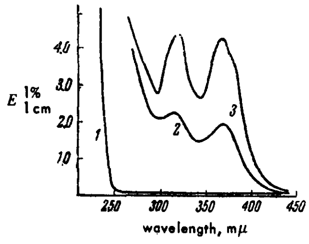
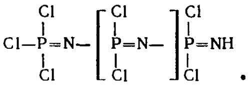


Fig. 9. Ultra-violet spectra of two samples of insoluble oil of the composition $PCl_4(NPCl_2)_nCl$ (of different molecular weight) and of phosphonitrilic chloride trimer: 1) cyclic trimer; 2) oil insoluble in petroleum ether (sample A); 3) insoluble oil (sample B).

Fig. 10. Nuclear magnetic resonance spectra of oily phosphonitrilic chloride.

Becke-Goehring and Koch[88] studied the structure of phosphonitrilic chloride polymers $(PNCl_2)_n$ (when n averaged from 10 to 15) from their nuclear magnetic resonance. There are two resonance maxima (Fig. 10) which indicate the presence of two different phosphorus atoms in the molecule. On the basis of these results Becke-Goehring and Koch[88] consider the oily polymer to have the linear structure, corresponding to the formula



$$\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{P}}{=}N{-}\left[\overset{Cl}{\underset{Cl}{P}}{=}N{-}\right]\overset{Cl}{\underset{Cl}{P}}{=}NH}\ .$$

The weak resonance maximum is ascribed to the phosphorus atom on the far left in the formula, whereas the very intense maximum corresponds to all the other phosphorus atoms.

Meyer, Lothmar, and Pankow[91] used X-ray diffraction in a thorough study of the structure of macromolecular phosphonitrilic chloride. They showed the chain in "inorganic rubber" to be spiral, as in Fig. 11.

Using the relation between the modulus of elasticity and the molecular weight ($M \simeq 3RTd/\epsilon$) for ideal rubbers, Specker[92,93] found the molecular weight of the macromolecular polyphosphonitrilic chloride to be 37 000 – 78 000.

Patat and Kollinsky[66] established the following relationship between the intrinsic viscosity Z_η and the osmotic molecular weight for phosphonitrilic chloride polymers prepared by polymerisation in solvents:

$$Z_\eta = 0.165 \times 10^{-4} M^{-0.69}.$$

Fig. 12 shows that there is good agreement between the experimental and calculated results. On the basis of these results the authors consider that in benzene or toluene solution phosphonitrilic chloride polymers are present in the form of entangled balls[66].

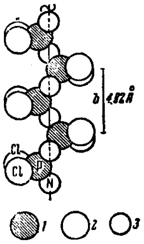


Fig. 11. The structure of the polyphosphonitrilic chloride chain: 1) phosphorus atoms; 2) chlorine atoms; 3) nitrogen atoms.

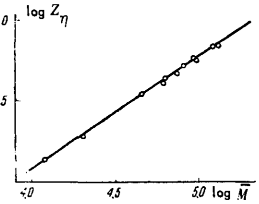


Fig. 12. The molecular weight and viscosity of phosphonitrilic chloride polymers.

From the polymerisation and depolymerisation data for polymeric phosphonitrilic chloride, Patat and Derst[99] consider its structure to resemble a series of interlocking rings. Such a structure would account for the limited solubility of polymeric phosphonitrilic chloride. The insoluble part swells to a certain extent only, as the interlocking rings cannot dissolve without breaking. Thus, the very high value obtained for the molecular weight of polymeric phosphonitrilic chloride is misleading. If the large rings were formed at low temperatures, and the small ones at higher temperatures, a relationship should exist between the overall rate [of dissolution? (Ed. of Translation)] and the temperature of polymerisation. In fact, the reaction rate constant depends solely on the concentration of the polymer. Patat and Derst[99] determined the solubility in benzene of polymeric phosphonitrilic chlorides obtained at different temperatures (see Table 9).

TABLE 9. Solubility of polymeric phosphonitrilic chlorides[99].

Temperature of polymerisation, °C	Fraction soluble in benzene, %	Reaction product
Below 250	100	no polymer formed
250—260	20—30	
300	20—30	
400	30—40	
500	40—50	
600	100	only low-molecular-weight homologues

2. Chemical Properties

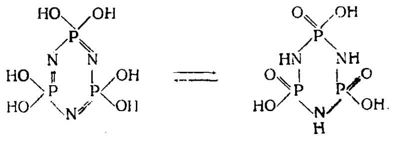
Owing to their structure, cyclic phosphonitrile derivatives are extremely stable chemically[1,6,20]. Their characteristic reactions are polymerisation, esterification, ammonolysis, substitution, hydrolysis, and others. The majority of these reactions proceed without ring rupture. We have already discussed polymerisation, ammonolysis, and esterification, and we shall now briefly mention another series of chemical transformations.

We must first note the hydrolysis of phosphonitrilic chlorides[1,8,10,20,100,101]:

$$(PNCl_2)_x \xrightarrow{H_2O} [PN(OH)_2]_x \xrightarrow{H_2O} H_3PO_4 + xNH_3 + xHCl.$$

phosphonitrilic acid
(metaphosphimic acid)

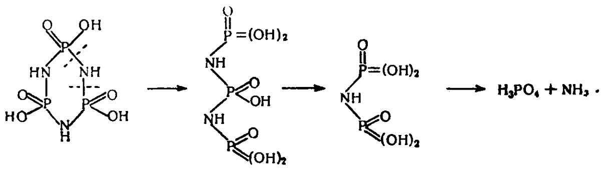
Stokes[8,10] obtained dihydroxytetrachlorotriphosphonitrile, $P_3N_3Cl_4(OH)_2$, as well as triphosphonitrilic acid, by the hydrolysis of phosphonitrilic chloride trimer in ether solution. Most of the authors call triphosphonitrilic acid metaphosphimic acid, and assume that it exists in two tautomeric forms[1,6]:



triphosphonitrilic acid trimetaphosphimic acid

Steger's work[102] on the infra-red spectra of this acid corroborates this hypothesis.

Triphosphonitrilic acid, $P_3N_3(OH)_6$, is a tribasic acid, very unstable, but forming stable salts (the hexasilver salt is also known). Its trisodium salt is easily formed by the extraction of the ether solution of phosphonitrilic chloride trimer with an aqueous solution of sodium acetate. The tetrasodium salt is also known, but it is evidently the derivative of the linear acid — $HO[PO(OH)NH]_3H$. Upon further hydrolysis of phosphonitrilic acid, imidophosphoric acids are formed, which are eventually transformed into phosphoric acid and ammonia[8,10]:



diimidotriphosphoric acid imidodiphosphoric acid

Using ion-exchange, paper chromatography, and other methods, Narath, Lohman, and Quimby[101] showed that the first step in the hydrolysis of sodium trimetaphosphimate is the gradual replacement of the P–N–P bond by P–O–P accompanied by the liberation of ammonia and the formation of the cyclic diimidotrimetaphosphate and imidotrimetaphosphate.

The cyclic phosphonitrilic chloride tetramer hydrolyses more easily than the trimer, and forms a very stable acid, $[NHP(O)OH]_4$.[8,10,100] The cyclic acid is tetrabasic.

Corbridge[100] obtained X-ray diffraction constants for dipotassium, dirubidium, and diammonium salts of tetrametaphosphimic acid. Octasilver tetrametaphosphimates are also known[8,10].

Infra-red spectra of tetraphosphonitrilates indicate the presence of hydrogen bonds (there is no maximum at 3620 cm^{-1}, corresponding to the free OH group, but there is intense absorption at 2600–3000 cm^{-1}, indicating the existence of hydrogen bonds between the P–OH groups). For this reason, Paddock[20] thinks that the difference between the tautomeric forms $NHPO(OH)-$ and $-N=P(OH)_2$ is less than might be expected from the formula. Yet the same salts of tri- and tetra-phosphonitrilic acids react with sodium hypochlorite to form *N*-chloro derivatives[61].

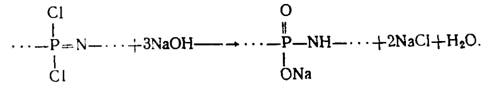
Seel and Langer[25] showed that the cyclic phosphonitrilic fluorides, trimer and tetramer, hydrolyse more easily to the corresponding acids than the chlorides; the trimer is more stable to hydrolysis than the tetramer. Tetraphosphonitrilic acid can be easily isolated from the products of hydrolysis.

Cyclic phosphonitrilic halides also react with nitrogen peroxide, forming an unstable complex[103]. Sulphur trioxide reacts with the chloride trimer at 40° forming a hygroscopic addition product of the composition $(PNCl_2.SO_3)_3$.[104] Bode, Bütow, and Lienau[48] reacted perchloric acid with a solution of phosphonitrilic chloride in acetic acid and isolated $(PNCl_2)_3.HClO_4$ and $(PNCl_2)_4.2HClO_4$.

The reaction of phosphonitrilic chlorides with a solution of sodium in liquid ammonia results in the rupture of the ring[6]. This reaction can be used for the quantitative determination of the halogen in phosphonitrilic halides.

Substitution, polymerisation, etc., proceed far more easily with linear derivatives of phosphonitrile, than with the cyclic ones, which is evidently connected with the loss of aromatic character by the former[88]. Thus, oily oligomers are so easily hydrolysed in water, that atmospheric moisture should be excluded during their preparation.

Polymetaphosphimic acid is formed by the hydrolysis of oily polymeric phosphonitrilic chloride (n = 10–15) with aqueous alkali:

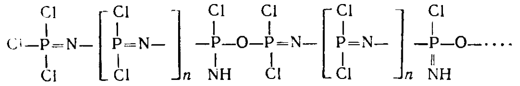


$$\cdots-\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{P}}=N-\cdots+3NaOH\longrightarrow\cdots-\underset{\displaystyle ONa}{\overset{\displaystyle O}{\overset{\|}{P}}}-NH-\cdots+2NaCl+H_2O.$$

During the hydrolysis of oily phosphonitrilic chloride with aqueous acid, in addition to the water-soluble products, a difficultly soluble material is also formed; this has acid properties and is a metaphosphimic acid hydrate.

Salts of the soluble polymetaphosphimic acid with the following cations have been prepared: Ag, Cu^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}.[88]

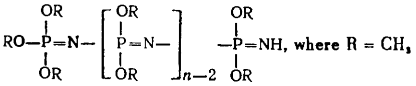
Becke-Goehring and Koch[88] showed that in the hydrolysis of polymeric phosphonitrilic chloride with insufficient quantities of water, hydrogen chloride splits off, and an oxygen bridge is formed:



$$Cl-\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{P}}=N-\left[\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{P}}=N-\right]_n-\underset{\displaystyle NH}{\overset{\displaystyle Cl}{P}}-O-\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{P}}=N-\left[\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{P}}=N-\right]_n-\underset{\displaystyle NH}{\overset{\displaystyle Cl}{\underset{\|}{P}}}-O-\cdots$$

The product obtained is rubber-like, and soluble in organic solvents.

Goldschmidt and Dishon[75,76] studied the esterification of phosphonitrilic chloride polymer, and we have covered it in detail in the present review (see p. 6). Becke-Goehring and Koch[88] made a study of the esterification of the oily phosphonitrilic chloride polymer. Its alcoholysis with sodium methoxide in absolute methanol yields a viscous colourless liquid of the composition



$$RO-\underset{\displaystyle OR}{\overset{\displaystyle OR}{P}}=N-\left[\underset{\displaystyle OR}{\overset{\displaystyle OR}{P}}=N-\right]_{n-2}-\underset{\displaystyle OR}{\overset{\displaystyle OR}{P}}=NH,\ \text{where } R = CH_3$$

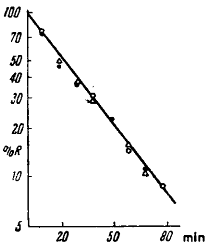
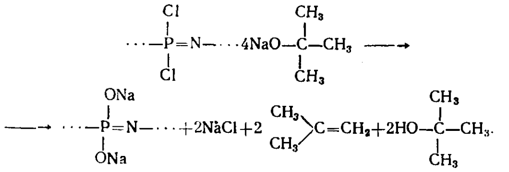


Fig. 13. Depolymerisation of phosphonitrilic chloride polymer samples obtained at 250°, 400°, and 500°. Depolymerisation temperature 350° [*R* = percentage of polymer? (Ed. of Translation)].

Mild alcoholysis with sodium t-butoxide yields sodium polymetaphosphimate and isobutylene[88].



$$\cdots-\overset{Cl}{\underset{Cl}{P}}=N-\cdots 4NaO-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \longrightarrow \cdots-\overset{ONa}{\underset{ONa}{P}}=N-\cdots+2NaCl+2\,(CH_3)_2C=CH_2+2HO-\overset{CH_3}{\underset{CH_3}{C}}-CH_3.$$

On being heated above 350° phosphonitrilic chloride polymer depolymerises[67,68,99]. Patat and Derst[99] studied the effect of various factors (such as temperature and time of polymerisation, and the presence of oxygen) on the destruction of polymeric phosphonitrilic chloride. The temperature of polymerisation has no effect on the depolymerisation rate, as is shown in Fig. 13, neither has the time of polymerisation. It is true, however, that there was some difference in the quantities of the soluble polymer owing to the incomplete conversion during the polymerisation in too short a time. The results of Patat and Derst's study[99] on the depolymerisation kinetics, are given in Table 10.

Depolymerisation of phosphonitrilic chloride polymers is a first-order reaction. The beginning of the reaction consists of the rupture of the larger rings, giving rise to two active chain ends at the rate $v_s = k_s[\mathrm{P}]$, where [P] is the concentration (weight) of the polymer. During depolymerisation, low-molecular-weight products, $(PNCl_2)_x$, with $x = 3-7$, are split off, according to a chain reaction with rate

$$v_{\mathrm{depolym}} = k_{\mathrm{depolym}}\,[\mathrm{P}^*],$$

where $[\mathrm{P}^*]$ is the concentration of "biactive" polymers; k_{depolym} is the depolymerisation rate constant. The reaction ends by the cyclisation of the low-molecular-weight residues from the initial ring.

The gross reaction rate,

$$v_{\mathrm{R}} = v_{\mathrm{depolym}} = k_{\mathrm{depolym}}[\mathrm{P}^*] = k_{\mathrm{R}}[\mathrm{P}],$$

depends only on the concentration of the high-molecular-weight phosphonitrilic chloride, and the gross reaction rate-constant is

$$k_{\mathrm{R}} = 7.5 \times 10^5\, e^{-26\,000/RT}\ \mathrm{sec}^{-1}\,.$$

The activation energy for depolymerisation is 26 ± 2 kcal × × mole^{-1}.

TABLE 10. Depolymerisation kinetics of phosphonitrilic chloride polymers[99].

Temp. of depolymerisation, °C	$t_{0.5}$, min *	Depolymerisation constant, sec^{-1}
250	1030	$1.1215 \cdot 10^{-5}$
300	99.5	$11.6105 \cdot 10^{-5}$
350	18.0	$64.1806 \cdot 10^{-5}$
275	350	$3.3007 \cdot 10^{-5}$
311	75	$15.4003 \cdot 10^{-5}$
330	32.5	$35.5462 \cdot 10^{-5}$

* $t_{0.5}$ = time of 50% depolymerisation.

3. Application

Rémond has made a thorough survey of the applications of phosphonitrilic chloride and its polymers[4]. Cyclic phosphonitrilic chlorides are of special interest because they form, on heating, macromolecular inorganic polymers with excellent elastic, heat- and fire-resistant qualities. These macromolecular compounds have functional groups which can be substituted by different organic radicals, thus making possible a combination of the properties of organic and inorganic polymers.

Phosphonitrilic chloride is used for the preparation of coatings and adhesive for glass, ceramics, asbestos, and metals[4]. Phosphonitrilic chloride polymers are used as additives to lubricating oils, and for the impregnation and fire-proofing of textiles. In combination with glass, asbestos, and other inorganic fibres, they are used for the preparation of insulating materials resistant to high temperatures[5].

Transparent solid materials have been obtained from the products of condensation of phosphonitrilic chloride with butylamine[55]. As a rule, the addition of phosphonitrilic chloride to polymers increases their heat-resistance[4]. The products of the reaction of phosphonitrilic chloride with alcohols, phenols, naphthols, mercaptans, and thiophenols are used as plasticisers for resins and varnishes[5].

Phosphonitrilic esters, prepared from the macromolecular phosphonitrilic chlorides and an alcohol in the presence of pyridine, can be used as plasticisers for nitrocellulose varnishes and films[75]. Allyl phosphonitrilates can be used to increase the adhesion of resins to glass fibres[4], and for fire-proofing textiles[63,74].

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THE CHEMISTRY OF β-KETOACETALS

N.K.Kochetkov and E.E.Nifant'ev

CONTENTS

I. INTRODUCTION

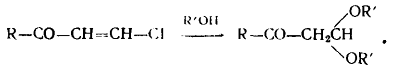
The study of β-dicarbonyl compounds has furthered the development of theoretical organic chemistry, and they and their derivatives are also versatile synthetic agents. While β-ketoesters, β-diketones, and similar compounds are readily accessible, syntheses and synthetic uses of β-ketoaldehydes have received relatively little attention for three reasons. Firstly, few β-ketoaldehydes of established structure are available. Until recently the main synthesis was the Claisen formylation[1-3], which gives unambiguous results only with symmetrical alkyl, alkyl aryl, and some other ketones. Most other ketones undergo side reactions[3-5] which make the isolation of the β-ketoaldehyde difficult or impossible. A number of hitherto inaccessible β-ketoaldehydes have been made by alkylation of β-aminovinyl ketones, a route which was recently proposed by Kochetkov, Ivanova, and Nesmeyanov[6]. Secondly, β-ketoaldehydes are very labile, except for formyl derivation of aryl methyl ketones and for those α-substituted by alkyl, nitro, or halogeno groups[3,7-14]; others exist only as the metal derivatives of the enols. Thirdly, β-ketoaldehydes often react simultaneously in different ways; syntheses of pyrazoles, isoxazoles, etc., nearly always give mixtures of isomers[15], which reduces their preparative value.

The β-ketoacetals are important as stable and accessible derivatives of β-ketoaldehydes, still retaining the high and diverse reactivity of those compounds.

II. SYNTHESIS OF β-KETOACETALS

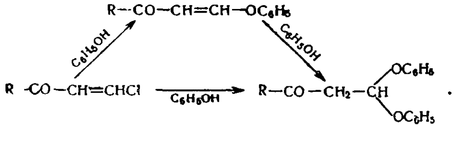
1. Synthesis from β-Chlorovinyl Ketones

This is the most important synthetic method, used in 1937 by Nells[16,17] and a group of German chemists[18] to obtain the first simple β-ketoacetals. Alcohols react with β-chlorovinyl ketones in the presence of bases such as alkali-metal hydroxides and carbonates, or tertiary amines:

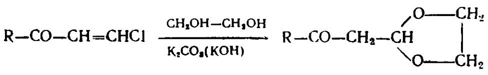


$$R-CO-CH=CH-Cl \xrightarrow{R'OH} R-CO-CH_2CH\begin{smallmatrix}OR'\\OR'\end{smallmatrix}\ .$$

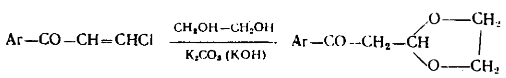
Since this synthesis was described only in patents, with little detail, β-ketoacetals attracted little attention at first*. In 1950 Nesmeyanov, Kochetkov, and Rybinskaya[19] and Price and Pappalardo[20] studied this method independently and simultaneously, and recommended it for the preparation of dialkylacetals of β-ketoaldehydes in 50–90% yield**. It has been suggested that an alkyl β-alkoxyvinyl ketone, R–CO–CH=CH–OR, is an intermediate[1], which reacts with a second alcohol molecule, in the presence of a base, to give a β-ketoacetal. This is a general reaction of α,β-unsaturated ketones. The suggestion is supported by the reaction between β-chlorovinyl ketones and phenol to give β-phenoxyvinyl ketones, which under suitable conditions can react with more phenol to give diphenylacetals[19]:



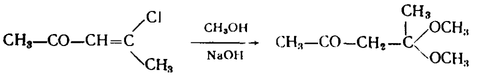
By recent modifications of the dialkylacetal synthesis, higher β-ketoacetals[22-24] and β-ketoacetals with a functional group in the alkyl radical[25] have been prepared. In 1957 Kochetkov, Nifant'ev, and Nesmeyanov[26] synthesised cyclic ethyleneacetals by the reaction between β-chlorovinyl ketones and ethylene glycol in alkaline media:



These products are widely applicable synthetic agents, being very stable relative to the dialkylacetals. While syntheses of dialkylacetals of aromatic β-ketoaldehydes have been limited to the unstable dimethylacetal of benzoylacetaldehyde[28], the analogous cyclic derivatives are readily made[27]:

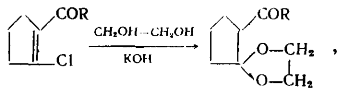


Recently acetals of heterocyclic aldehydes, such as α-furoylacetaldehyde and its sulphur and selenium analogues[29], have been made. Alcohols and α-glycols also react with β-alkyl-β-chlorovinyl ketones in the presence of alkali to give the monoketals of β-diketones[30-33]:

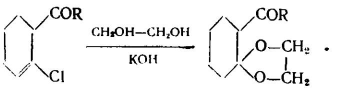


$$CH_3-CO-CH=C\begin{smallmatrix}Cl\\CH_3\end{smallmatrix} \xrightarrow[NaOH]{CH_3OH} CH_3-CO-CH_2-\overset{CH_3}{\overset{|}{C}}\begin{smallmatrix}OCH_3\\OCH_3\end{smallmatrix}\ .$$

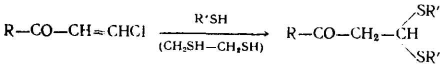
Ethylene glycol reacts in this way with 1-chloro-2-acylcyclopent-1-enes to give ethyleneketals of 2-acylcyclopentanones[31]:



and with 2-chloro-3-acylcyclohexenes[32-33]:



Very recently, mercaptans have been converted in this way to the hitherto almost unknown β-ketomercaptals[34]:

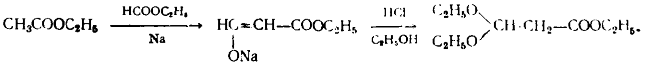


$$R-CO-CH=CHCl \xrightarrow[(CH_2SH-CH_2SH)]{R'SH} R-CO-CH_2-CH\begin{smallmatrix}SR'\\SR'\end{smallmatrix}\ .$$

Ethanedithiol, giving cyclic ethylenemercaptals, was more effective than simpler mercaptans.

2. Synthesis from β-Ketoaldehydes and Their Sodium Derivatives

In 1927 Sugasawa[35] first converted the enol form of a β-dicarbonyl compound to an acetal, using the sodium derivative of malonic monoaldehyde ethyl ester:



$$CH_3COOC_2H_5 \xrightarrow[Na]{HCOOC_2H_5} \underset{ONa}{\underset{|}{HC}}=CH-COOC_2H_5 \xrightarrow[C_2H_5OH]{HCl} \begin{smallmatrix}C_2H_5O\\C_2H_5O\end{smallmatrix}CH\cdot CH_2-COOC_2H_5.$$

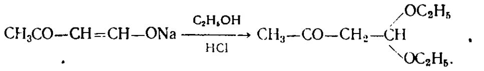
---

* The use of β-ketoacetals was impeded by lack of a suitable synthesis of β-chlorovinyl ketones. The latter are now well known and accessible[21].

** The reaction between β-chlorovinyl ketones and alcoholic hydrogen chloride also gives β-ketoacetals but in small yield[19].

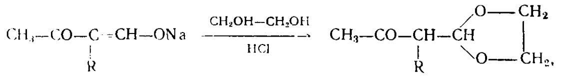
This was later developed into a general synthesis of acetals from derivatives of that ester[36,37].

In the 1950's Sugasawa, Yamada, and other Japanese chemists described syntheses of acetals from acetoacetaldehyde ; Sugasawa[38] converted the sodium derivative to the diethylacetal:

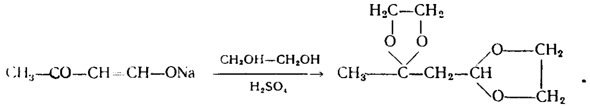


$$CH_3CO{-}CH{=}CH{-}ONa \xrightarrow[HCl]{C_2H_5OH} CH_3{-}CO{-}CH_2{-}CH(OC_2H_5)_2.$$

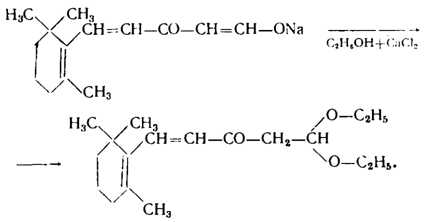
The dimethylacetal was obtained in the same way in 45% yield[39]. Chlorosulphonic acid, phosphorus trichloride, thionyl chloride, and hydrogen chloride, were later shown to catalyse this reaction[40]. Later, Richmond[41] studied these reactions and improved the conditions and the yield in the synthesis of acetoacetaldehyde diethylacetal. The same synthesis was applied to the ethyleneacetals of acetoacetaldehyde and α-methylacetoacetaldehyde[42,43]:



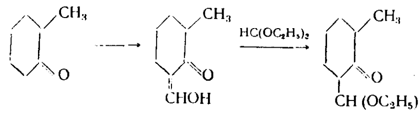
where R = H or CH_3. Yields of the latter were usually small; in the former case, some of the bisethylene acetal-ketal was also formed, which Sugasawa et al.[44] obtained pure in 1950 by using sulphuric acid as catalyst:



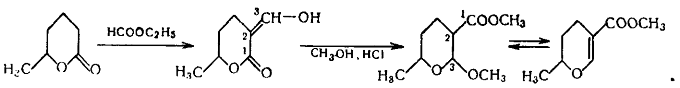
Royals and coworkers[45-47] studied the formylation of ketones, and showed that the reaction between sodium derivatives thus formed of β-ketoaldehydes and alcoholic hydrogen chloride give β-ketoacetals or, more often, β-alkoxyvinyl ketones, depending on the initial compound. Cyclohexanone-2-aldehyde and benzoylacetaldehyde give only vinyl ethers, other compounds give mixed products, and only some of the simplest β-ketoaldehydes give β-ketoacetals alone. Schanz[48] obtained an acetal from the sodium derivative of ω-formyl-β-ionone and ethanolic calcium chloride:



Ružicka and coworkers[49] synthesised β-ketoacetals of the cyclohexane and cycloheptane series from the free parent enol and orthoformic ester:



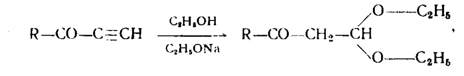
Cyclohexanone-2-aldehyde has recently been shown to form a β-ethoxyvinyl ketone, not a β-ketoacetal, under similar conditions[50]. Korte[51-53] recently discovered a related conversion of lactones and thiolactones to acids of the dihydropyran, dihydrofuran, and dihydrothiophene series, e.g.:



It is therefore clear that β-ketoaldehydes cannot always be converted to β-ketoacetals, on account of the diversity of the products and the subsequent difficulty of isolation.

3. Other Methods

Bowden, Braude, and Jones[54] reported the addition of ethanol across the triple bond of benzoyl and n-butyryl acetylene in the presence of sodium ethoxide:

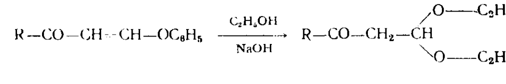


$$R{-}CO{-}C{\equiv}CH \xrightarrow[C_2H_5ONa]{C_2H_5OH} R{-}CO{-}CH_2{-}CH(O{-}C_2H_5)_2,$$

where R = C_6H_5 or C_3H_7.

The oxidation of β-hydroxyacetals[55] is not a widely applicable synthesis, since these compounds are not readily available; since they are useful synthetic agents, they are in fact made by reducing β-ketoacetals, as is shown below.

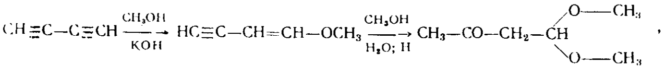
The preparation of β-ketoacetals from β-phenoxyvinyl ketones[56],



$$R{-}CO{-}CH{=}CH{-}OC_6H_5 \xrightarrow[NaOH]{C_2H_5OH} R{-}CO{-}CH_2{-}CH(O{-}C_2H_5)_2,$$

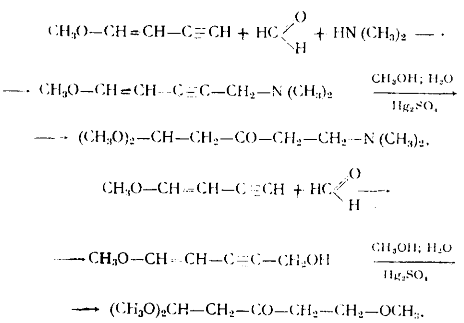
is of theoretical interest only, as are the other two syntheses described above.

In 1953 Franke, Kraft, Teitejen, and Weber[57] developed an industrial synthesis of acetoacetaldehyde dimethylacetal from butadiyne,



$$CH{\equiv}C{-}C{\equiv}CH \xrightarrow[KOH]{CH_3OH} HC{\equiv}C{-}CH{=}CH{-}OCH_3 \xrightarrow[H_2O;\ H]{CH_3OH} CH_3{-}CO{-}CH_2{-}CH(O{-}CH_3)_2,$$

based on earlier detailed studies of the reactions of butadiyne and its derivatives[58-62]. This synthesis has not been applied generally, but some β-ketoacetals bearing other functional groups have been prepared[63,64]:



$$CH_3O{-}CH{=}CH{-}C{\equiv}CH + HC{\left\langle{}^{O}_{H}\right.} + HN(CH_3)_2 \longrightarrow$$

$$\longrightarrow CH_3O{-}CH{=}CH{-}C{\equiv}C{-}CH_2{-}N(CH_3)_2 \xrightarrow[Hg_2SO_4]{CH_3OH;\ H_2O}$$

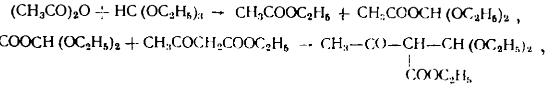
$$\longrightarrow (CH_3O)_2{-}CH{-}CH_2{-}CO{-}CH_2{-}CH_2{-}N(CH_3)_2.$$

$$CH_3O{-}CH{=}CH{-}C{\equiv}CH + HC{\left\langle{}^{O}_{H}\right.} \longrightarrow$$

$$\longrightarrow CH_3O{-}CH{=}CH{-}C{\equiv}C{-}CH_2OH \xrightarrow[Hg_2SO_4]{CH_3OH;\ H_2O}$$

$$\longrightarrow (CH_3O)_2CH{-}CH_2{-}CO{-}CH_2{-}CH_2{-}OCH_3.$$

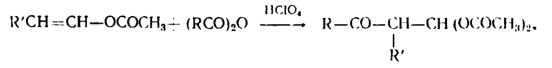
α-Ethoxycarbonyl-β-ketoacetals[65], such as α-ethoxycarbonylacetoacetaldehyde acetal,



$$(CH_3CO)_2O + HC(OC_2H_5)_3 \rightarrow CH_3COOC_2H_5 + CH_3COOCH(OC_2H_5)_2,$$

$$CH_3COOCH(OC_2H_5)_2 + CH_3COCH_2COOC_2H_5 \rightarrow CH_3{-}CO{-}\underset{COOC_2H_5}{CH}{-}CH(OC_2H_5)_2,$$

are compounds of great interest, but no general synthesis has been suggested for them. A related reaction was recently described giving the hitherto unknown β-ketoaldehyde diacetates[66]:



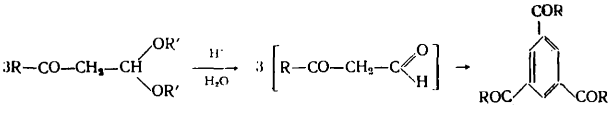
$$R'CH{=}CH{-}OCOCH_3 + (RCO)_2O \xrightarrow{HClO_4} R{-}CO{-}\underset{R'}{\underset{|}{CH}}{-}CH(OCOCH_3)_2.$$

III. PROPERTIES OF β-KETOACETALS

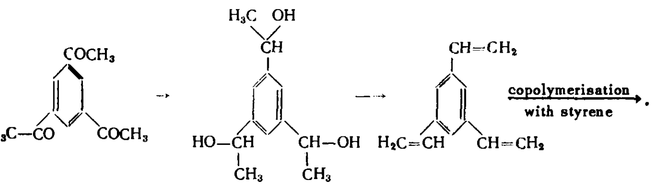
β-Ketoacetals contain two functional groups, show many of the reactions of β-dicarbonyl compounds, and possess a reactive methylene grouping. Their reactions are conveniently classified in this way.

1. Reactions of the Acetal Group

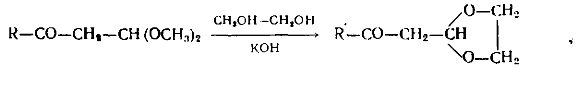
Almost all the reactions typical of acetals are undergone by β-ketoacetals. They are hydrolysed by traces of mineral acid or by acetic acid, the resultant β-ketoaldehydes polymerising spontaneously to *sym*-triacylbenzenes[19]:



1,3,5-triacetylbenzene has recently been converted to trivinylbenzene on an industrial scale, and hence to synthetic resins[67]:



Dialkyl-β-ketoacetals undergo the usual transacetalisation with ethylene glycol[26]:



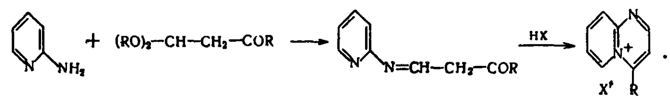
where R = n-C_3H_7 or C_6H_5. A molecule of alcohol is lost in the presence of alkaline catalysts to give β-alkoxyvinyl ketones[47]:

$$R{-}CO{-}CH_2{-}CH(OR')_2 \xrightarrow[-R'OH]{OH'} R{-}CO{-}CH{=}CH{-}OR'.$$

Aromatic β-ketoacetals undergo this reaction readily, but aliphatic analogues only with difficulty. Reaction with ammonia and primary and secondary amines is exceptionally ready[68]:

$$R{-}CO{-}CH_2{-}CH(OR')_2 \xrightarrow{HNR''R'''} R{-}CO{-}CH{=}CH{-}NR''R''',$$

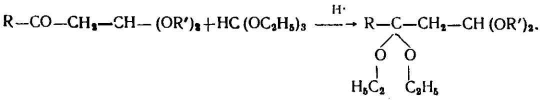
where R″, R‴ = H or an alkyl group. The resultant β-aminovinyl ketones are usually more conveniently obtained, however, direct from β-chlorovinyl ketones[69-71]. Nesmeyanov, Rybinskaya, and Kel'skii[72] recently obtained 4-alkylpyrido[1,2-e]pyrimidinium salts from β-ketoacetals and 2-aminopyridine, and also isolated the intermediate aminovinyl ketones:



Later, the improved synthesis was carried out in one stage[73].

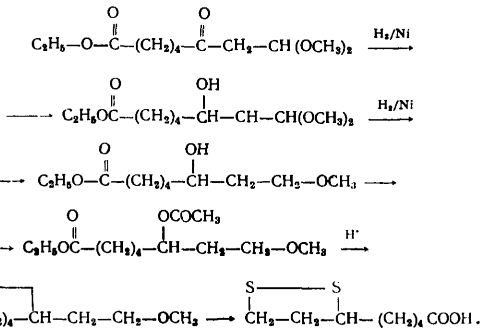
2. Reactions of the Carbonyl Group

Orthoformic ester reacts with β-ketoacetals in the presence of acidic catalysts to give acetal-ketals in high yield[74]:

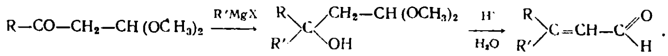


$$R{-}CO{-}CH_2{-}CH{-}(OR')_2 + HC(OC_2H_5)_3 \xrightarrow{H^{\cdot}} R{-}\underset{\substack{O\quad O\\ |\quad\ |\\ H_5C_2\ \ C_2H_5}}{C}{-}CH_2{-}CH(OR')_2.$$

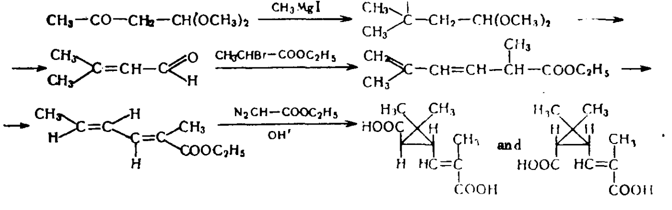
The carbonyl group is readily reduced by lithium aluminium hydride[4,42], aluminium isopropoxide[23], and sodium and ethanol[49]. The resulting secondary alcohols are readily dehydrated and hydrolysed to α,β-unsaturated aldehydes. A recent synthesis of α-lipoic acid has as its first stage the catalytic reduction of ω-ethoxycarbonylpentanoylacetaldehyde dimethylacetal[25]:



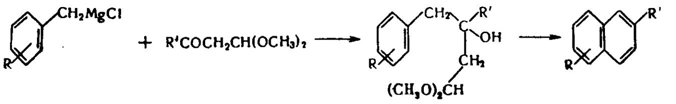
Grignard reagents react smoothly with β-ketoacetals; Price and Pappalardo[20] synthesised a series of α,β-unsaturated aldehydes related to the terpenes:



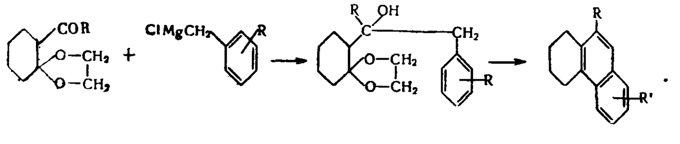
Crombie[75] used similar aldehydes to prepare naturally occurring acids derived from cyclopropane:



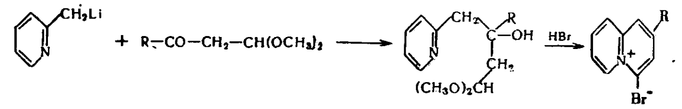
The tertiary alcohols obtained from β-ketoacetals and Grignard reagents have recently been cyclised to aromatic and heterocyclic compounds. Kochetkov, Nifant'ev, and Nesmeyanov[26,76] readily obtained alkylnaphthalenes from derivatives of benzylmagnesium chloride:



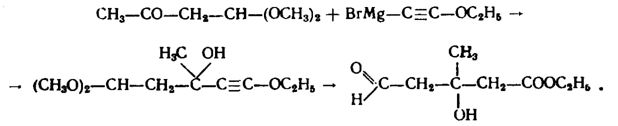
A general synthesis of alkyltetrahydrophenanthrenes from cyclohexane β-ketoacetals afforded hitherto unknown compounds[32,33]:



Palladium dehydrogenation readily converted these into alkylphenanthrenes in almost quantitative yields. Nesmeyanov and Rybinskaya[77] and Richards and Stevens[78] obtained 2-alkyldehydroquinolizinium salts from β-ketoacetals and α-picolyllithium:

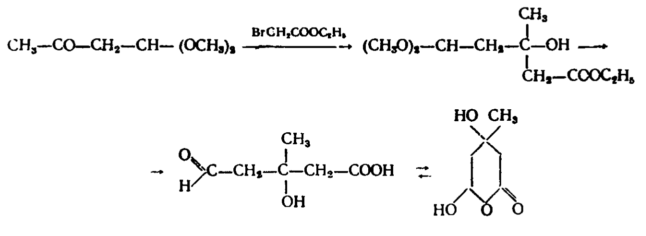


Compounds have been synthesised related to β,δ-dihydroxy-β-methylvaleric (mevalonic) acid, a growth factor for microorganisms such as *Lactobacillus acidophilus*. In 1957 Birch, Pride, and Smith[79] synthesised a related aldehydo-ester from acetoacetaldehyde dimethylacetal and ethoxyethynylmagnesium bromide:

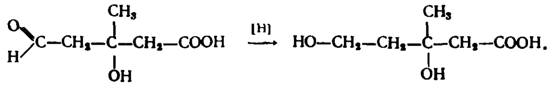


$$CH_3{-}CO{-}CH_2{-}CH{-}(OCH_3)_2 + BrMg{-}C{\equiv}C{-}OC_2H_5 \rightarrow$$
$$\rightarrow (CH_3O)_2{-}CH{-}CH_2{-}\overset{H_3C\ \ OH}{C}{-}C{\equiv}C{-}OC_2H_5 \rightarrow \overset{O}{\underset{H}{>}}C{-}CH_2{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_2{-}COOC_2H_5\,.$$

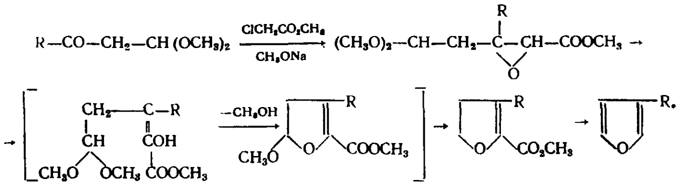
Almost simultaneously Folkers and coworkers[80] synthesised (±)-β-hydroxy-β-methylglutaric monoaldehyde by the Reformatsky reaction:



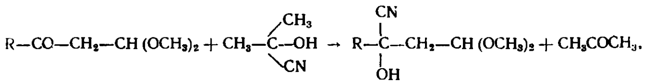
Sodium borohydride or platinum and hydrogen reduced the product to mevalonic acid[80]:



In 1956 Burness first applied the Darzens condensation to β-ketoacetals, and cyclised the glycidic esters produced to furan derivatives[81]:

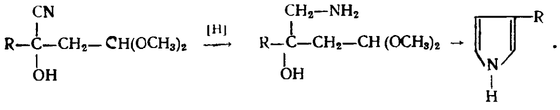


Although of great potential value, this reaction has not been investigated further. Acetone cyanhydrin converts β-ketoacetals to cyanhydrins[82]:



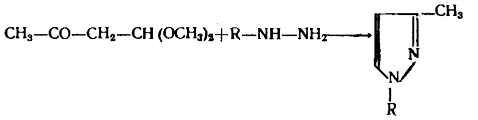
$$R{-}CO{-}CH_2{-}CH(OCH_3)_2 + CH_3{-}\overset{CH_3}{\underset{CN}{C}}{-}OH \rightarrow R{-}\overset{CN}{\underset{OH}{C}}{-}CH_2{-}CH(OCH_3)_2 + CH_3COCH_3.$$

From these, 3-alkylpyrroles may be made[82]:

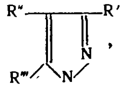


3. Reactions Typical of β-Dicarbonyl Compounds

Like other β-dicarbonyl compounds, β-ketoacetals may be used to synthesise heterocyclic compounds. In 1951 Nesmeyanov, Kochetkov, and Rybinskaya[19] obtained N-substituted 3-methylpyrazoles from acetoacetaldehyde dimethylacetal:

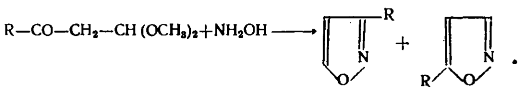


where R = C_6H_5 or p-$C_6H_4NO_2$. In this way, other authors[22,64,83,84] obtained 50–85% yields of pyrazoles of general formula

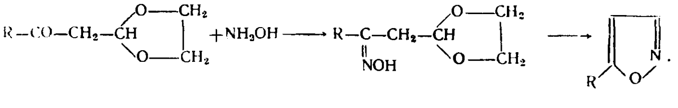


where R = H, alkyl, C_6H_5, p-$C_6H_4NO_2$, 2,4-$C_6H_3(NO_2)_2$, $CONH_2$, or $CSNH_2$; R′, R″, and R‴ = H or alkyl. The expected hydrazone is clearly an intermediate, and was isolated in some cases.

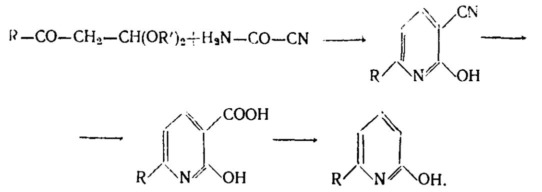
Dimethylacetals may be converted into mixtures of 3- and 5-alkylisoxazoles[83]:



The stabler ethyleneacetals yield only 5-derivatives[85]; an intermediate oxime can be isolated:

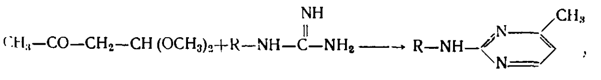


In 1952 Kochetkov[86] published a general synthesis of 6-alkyl-3-cyano-2-hydroxypyridines, which he used to prepare the relatively inaccessible 6-alkyl-2-hydroxypyridines:

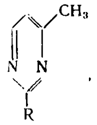


Franke and Kraft[83] recently prepared highly substituted pyridine derivatives by this method.

One of the most important pyrimidine sulphonamides, sulphamerazine or 2-sulphanilamido-4-methylpyrimidine, and its N-substituted derivatives were made by Japanese chemists[39,42,43,87] from acetoacetaldehyde dimethylacetal or methyl β-methoxyvinyl ketone, in 70–80% yield:

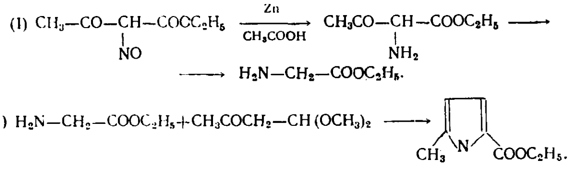


where R = H, p-$NH_2C_6H_4SO_2$, p-$CH_3CONHC_6H_4SO_2$, or p-$(CH_3)_2NC_6H_4SO_2$. The same authors, as well as Franke and Kraft[83], synthesised other 2-derivatives of 4-methylpyrimidine, of general structure



where R = OH, SH, Cl, NH_2, NH–CN, or C_6H_5. An 85% yield of the important pharmaceutical 2-amino-4-methylpyrimidine was obtained.

Fischer and Fink[88] used acetoacetaldehyde dimethylacetal in the Knorr pyrrole synthesis, but obtained 2-methyl-5-ethoxycarbonylpyrrole and not the expected 2,4-dimethyl-5-ethoxycarbonylpyrrole-3-aldehyde. This they explained by the elimination of acetic acid from α-aminoacetoacetic ester, formed by reduction of the corresponding isonitroso compound; the resultant glycine ester reacts with the β-ketoacetal:



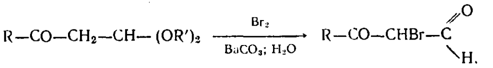
The formation of the same product from isonitroso-n-butyroacetic acid lends support to the above mechanism. The reaction has been recently re-examined[89].

The ready ketonic hydrolysis of other β-dicarbonyl compounds applies to β-ketoacetals[90,91], and has been used by Wakayama and Maekana[92] as a source of methyl ketones:

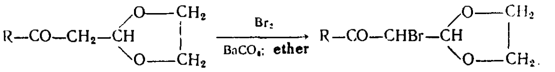
$$R-CO-CH_2-CH(OCH_3)_2 \xrightarrow[NaOH]{CH_3OH} R-CO-CH_3.$$

4. Reactions of the α-Methylene Group

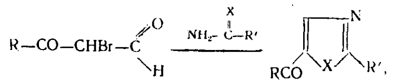
Substitution in this group was discovered only recently when bromination of β-ketoacetals with N-bromosuccinimide, dioxan dibromide, and bromine itself, was carefully examined[93,94]. Bromination is most effective when bromine is used together with hydrogen bromide acceptors; the solvent also influences the reaction. Aqueous bromine and barium carbonate cause monosubstitution in the α-CH_2 group and hydrolysis of ethylene- or dialkyl-acetal groups, giving α-bromo-β-ketoaldehydes:



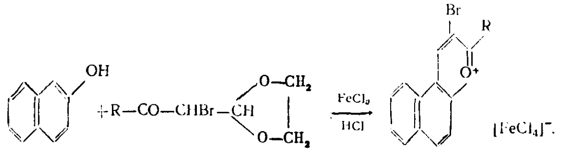
where R = CH_3, C_2H_5, or n-C_3H_7; R' = CH_3; R'–R' = = CH_2-CH_2. Ethyleneacetals alone withstand hydrolysis when dry ether is the solvent:



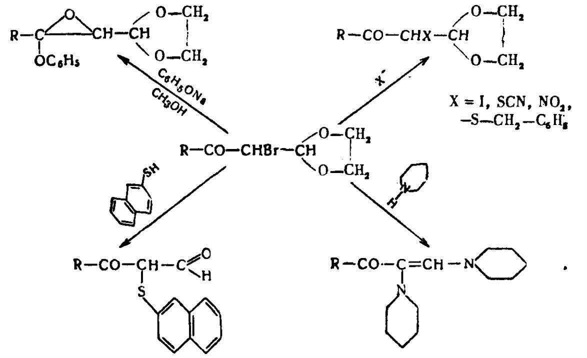
where R is an alkyl or aryl group. Mild treatment of the product with acid effects hydrolysis. The exclusive bromination of the α-methylene group indicates activation by the acetal group. The products are useful synthetic agents; α-bromo-β-ketoaldehydes react readily with urea, thiourea, and thioamides to give the hitherto inaccessible oxazole and thiazole ketones[94]:



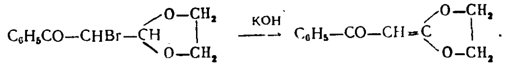
where R = an alkyl group; R' = NH_2, H, or C_6H_5; X = O or S. Corresponding acetals will also yield heterocyclic compounds, such as brominated pyrylium derivatives[94]:



Other syntheses depend on the ready replacement of the bromine atom[95]:



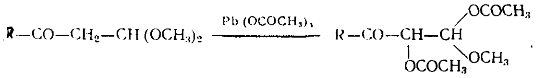
Dehydrobromination of α-bromo-β-acetals with powdered potassium hydroxide in benzene gives the acetal of an acylketene[93]:



Excess of alcoholic alkali gives a β-ketoester[93]:

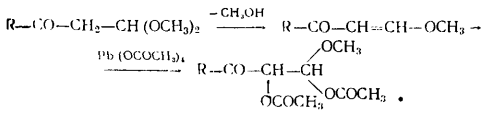
$$CH_3CO{-}CHBr{-}CH(OCH_3)_2 \xrightarrow[CH_3OH]{KOH} CH_3COCH_2{-}COOCH_3.$$

The action of lead tetraacetate on β-ketoacetals was shown by two groups of chemists[93,95,97] to give the acylals of α-acetoxy-β-ketoaldehydes:



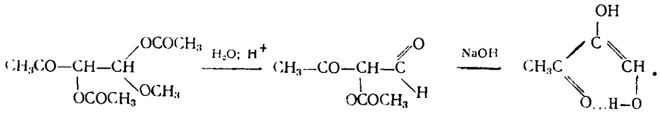
$$R{-}CO{-}CH_2{-}CH(OCH_3)_2 \xrightarrow{Pb(OCOCH_3)_4} R{-}CO{-}\underset{OCOCH_3}{CH}{-}CH\begin{smallmatrix}OCOCH_3\\OCH_3\end{smallmatrix}$$

where R = CH_3, C_2H_5, n-C_3H_7, or C_6H_5. The double bond of the β-methoxyvinyl ketone, formed by β-elimination of alcohol[98], is attacked as in other vinyl ethers[99]:

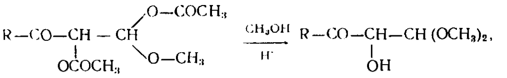


$$R{-}CO{-}CH_2{-}CH(OCH_3)_2 \xrightarrow{-CH_3OH} R{-}CO{-}CH{=}CH{-}OCH_3 \rightarrow \xrightarrow{Pb(OCOCH_3)_4} R{-}CO{-}\underset{OCOCH_3}{CH}{-}CH\begin{smallmatrix}OCH_3\\OCOCH_3\end{smallmatrix}.$$

Stepwise hydrolysis of the simplest product gave a high yield of methylreductone[100]:

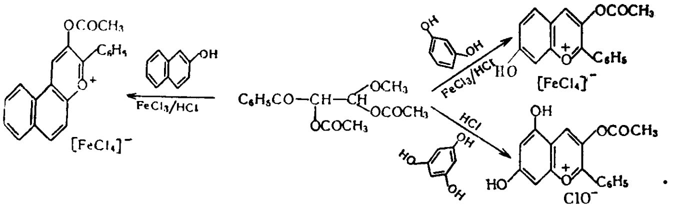


Other alkylreductones may be made similarly. Alcoholic hydrogen chloride yields acetals of α-hydroxy-β-ketoaldehydes[97,98]:



$$R{-}CO{-}\underset{OCOCH_3}{CH}{-}CH\begin{smallmatrix}O{-}COCH_3\\O{-}CH_3\end{smallmatrix} \xrightarrow[H^+]{CH_3OH} R{-}CO{-}\underset{OH}{CH}{-}CH(OCH_3)_2,$$

where R = CH_3, C_2H_5, n-C_3H_7, or C_6H_5. Acylals of α-acetoxy-β-ketoaldehydes react with phenols to give acetoxy-substituted pyrylium derivatives[98]. Ferric chloride catalyses the condensation with β-naphthol and resorcinol, but is unnecessary with phloroglucinol:



The flavilium salts produced are monoacetyl derivatives of anthocyanins.

The β-ketoacetals are readily available, versatile synthetic reagents, from which natural and pharmacologically active products have been made, as well as others difficult or impossible to obtain earlier. Much doubtless remains to be discovered about the uses of these recently developed compounds.

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POLYMERIC COMPOUNDS OF BORON

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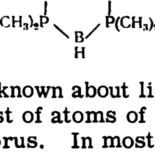
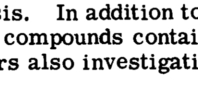
Little information is available in the scientific and patent literature about polymers of boron, although it is known[1] that they are of great importance because of their resistance to heat and the action of hydrocarbons. Of special interest are polymers containing in the main chain atoms of boron and nitrogen, −B−N−B−N−, or boron and phosphorus, −B−P−B−P−[2], although up to the present the only systematic descriptions of such compounds which have been published are of cyclic representatives with low molecular weights, namely the borazoles,

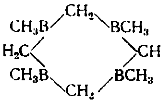


(where R and R′ can be H, alkyl, or aryl), and the phosphinoborines,



Very little is as yet known about linear polymers whose molecular chains consist of atoms of boron and nitrogen or of boron and phosphorus. In most cases the properties of polymeric compounds of boron have been inadequately described, and often no information is given on their molecular weight, melting points, solubility, or resistance to oxidation and hydrolysis. In addition to work on the preparation of polymeric compounds containing boron, the following review covers also investigations concerned with monomeric compounds of boron during the course of which the formation of polymers has been observed.

Polymers containing B–B bonds in the main chain are unknown, apart from the polyboranes[3], although the possibility of their preparation has been suggested[4,5]. Only a few organic polymers whose main chain consists of boron and carbon atoms are known. Thus Goubeau and Epple[6], who heated trimethylboron in an autoclave to 400°–600° and observed the elimination of methane, obtained, in addition to 1,3,5,7-tetramethyl-1,3,5,7-tetraboracyclooctane,

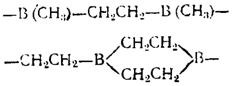


a coloured solid of the composition $(B_2C_3H_6)_x$. At 600° it splits off further methane and hydrogen, forming a polymer of the empirical composition $(BCH_2)_x$, to which these workers ascribe a cross-linked structure. The disproportionation of other trialkylborons is also accompanied by the formation of polymers; thus tri-n-hexylboron on being boiled under reflux undergoes the following reaction:

$$xB(C_6H_{13})_3 \rightarrow [B(C_6H_{13})]_x + 2xC_2H_{12} + xH_2.$$

The polymer $[B(C_6H_{13})]_x$ proved to be a mixture of solid substance having the composition $[BHB(C_6H_{13})]_x$, containing 20% of boron, and a liquid $[B_2(C_6H_{13})_2(C_6H_{12})]_x$ with a molecular weight of ~600 [7].

Schlesinger *et al.* [8] obtained a quantitative yield of *B,B'*-tetrachloroethylenediborine $Cl_2BCH_2CH_2BCl_2$ by the action the action of ethylene on tetrachlorodiborane. On treatment with dimethylzinc, this compound is converted into the corresponding *B,B'*-tetramethyl compound, $(CH_3)_2BCH_2.CH_2B(CH_3)_2$, which on pyrolysis splits off trimethylboron to form vitreous polymers of the type



Pyrolysis of the original *B,B'*-tetrachloroethylenediborine yields hydrogen, methane, ethane, boron, trichloride, and a solid polymeric boron subchloride $(BCl)_n$ [9]. Similar observations have recently been published by Holliday and Massey[10].

By heating the tetrahydrofuran compound of triphenylethynylboron, Krüerke[11] isolated a reddish-violet polymeric solid stable to the action of water:

$$B(C{\equiv}CC_6C_5)_3.OC_4H_8 \xrightarrow{85°} C_4H_8O + \text{polymer}.$$

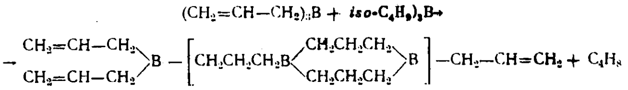
Its molecular weight and structure were not determined.

The formation of polymeric products was observed also in the synthesis of bisdi-n-butylborylacetylene $(n\text{-}C_4H_9)_2B{-}C{\equiv}C{-}B(n\text{-}C_4H_9)_2$. [12]

Pyrolysis of diphenylboron chloride in the presence of aluminium chloride yielded a solid polymer which did not melt below 300° [13]. The pyrolysis was accompanied by the formation of an equivalent amount of benzene:

$$m(C_6H_5)_2BCl \rightarrow C_6H_5(BClC_6H_4)_{m-1}BClC_6H_5 + (m-1)C_6H_6.$$

During the sublimation of boron tricyanide $B(CN)_3$, Chaigneau[14] observed the formation of a polymer which became darker at 130°. The action of an electric discharge on a mixture of boron trichloride and carbon monoxide led to the formation of a polymeric film with a softening temperature of 115° [15]. Mikhailov and Tutorskaya[16] observed the formation of polymeric derivatives of 1,5-diboracyclooctane by the interaction of triallylboron and triisobutylboron:



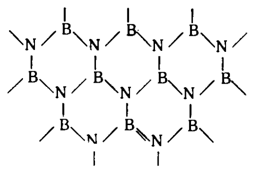
The polymer formed a gelatinous mass, which was swollen by ether and benzene. The same workers noted that the anhydride of 2-propeneboronic acid can be polymerised by slow distillation[17]. Topchiev *et al.* suggested a new method for synthesising triallylboron and trivinylboron[18]. They investigated the chemical changes undergone by these compounds, and proposed using the resulting monomers, in particular 2-propeneboronic esters, as starting materials for the synthesis of boron-containing polymers[19].

Normant and Braun synthesised substituted ethyleneboronic and ethyleneborinic acids of the types $>C{=}\overset{|}{C}{-}B(OH)_2$ and $(>C{=}\overset{|}{C}{-})_2BOH$ and a substituted trivinylboron, $(>C{=}\underset{|}{C}{-})_3B$. They note that compounds containing the vinyl groups $CH_2{=}CH{-}$ and $CH_2{=}C(CH_3){-}$ rapidly polymerise in the air[20]. β-Chloroethyleneboronic acid, which has been known for some time[21,22], is recommended for copolymerisation with vinyl monomers[23].

The synthesis of *p*-vinylbenzeneboronic acid, its esters, and its anhydride has been described. These compounds polymerise readily in the presence of the ether compound of boron trifuloride and of peroxides, as well as in the liquid state[24,25]. Lennarz and Snyder report that the polymer of *p*-vinylbenzeneboronic acid is a white powder slightly soluble in aqueous alkali; it does not melt below 300°, but at 300°–350° it decomposes slightly and darkens[26]. Bis(*p*-vinylbenzene)borinic acid $(CH_2{=}CHC_6H_4)_2BOH$ was copolymerised with styrene and other vinyl compounds; the resulting insoluble resins could be used to extract aminoethyl alcohol from solutions. It was readily regenerated in aqueous media, releasing free aminoethyl alcohol[27].

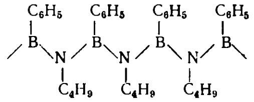
Considerably more work has been published describing polymers containing B–N links in their structure. The simplest polymer of boron and nitrogen is boron nitride, which has been known for a long time. Wöhler and St. Deville[28] as well as Moissan[29] established that boron combines with nitrogen at 1230° to form a white solid having the composition BN. This compound can be obtained also by the action of urea[30] or ammonia[31] on boron trioxide at red heat. The purest boron nitride is obtained by the pyrolysis of boron imide $B_2(NH)_3$ [32], as well as by the action of ammonia on boron tribromide[33] or trichloride[34]. Soviet investigators have suggested preparing boron nitride by the action of ammonia on boric acid in the presence of ammonium chloride at 1200° [35]. The kinetics of the formation of boron nitride by the action of nitrogen on elemental boron have been studied by Sleptsov and Samsonov[36].

Boron nitride is a white powder melting at about 3000° under pressure; it is slowly hydrolysed on boiling with water, forming boric acid and ammonia; like graphite it has a hexagonal structure:



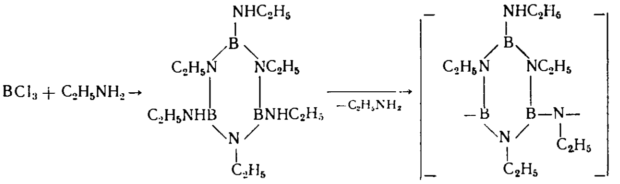
Until recently boron nitride found no great practical use. However, interest in this compound increased rapidly when it became known[37] that the hexagonal form passes into a cubic form on heating to 1800° under a pressure of 85 000 atm, the change being from a solid resembling graphite to a hard crystal surpassing diamond in mechanical strength. Cubic boron nitride withstands heating to 2000°, being only slightly oxidised at the surface; it is a good dielectric.

Numerous attempts to prepare a linear polymer with a main chain consisting of boron and nitrogen atoms have generally led to the formation of the cyclic trimer borazole. However, a polymer of this type has now been prepared by Gerrard. Using phenylboron dichloride and n-butylamine or isobutylamine as starting materials, he was able to prevent ring formation by steric hindrance, and obtained a linear polymer containing 20–40 atoms of boron and nitrogen in the chain:

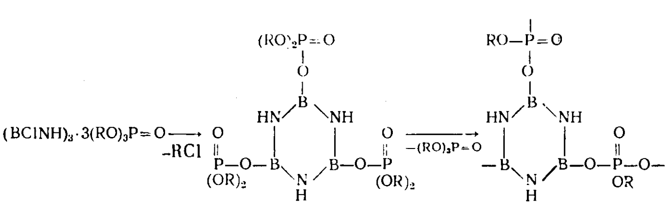


This polymer melts at about 150°, and remains stable on heating to 400°, but is readily hydrolysed[38].

The view has been expressed[1,39,40] that borazole and its *N*- and *B*-substituted derivatives, being very heat-resistant substances, might be used to synthesise polymers of high melting point which are heat resistant. Hexaphenylborazole, for example, melts at 413°–415° without decomposition[41–43]. Some polymers of this type have already been obtained; Lappert obtained a brittle substance of high melting point, sensitive to hydrolysis, by the interaction of boron trichloride and ethylamine[44]:

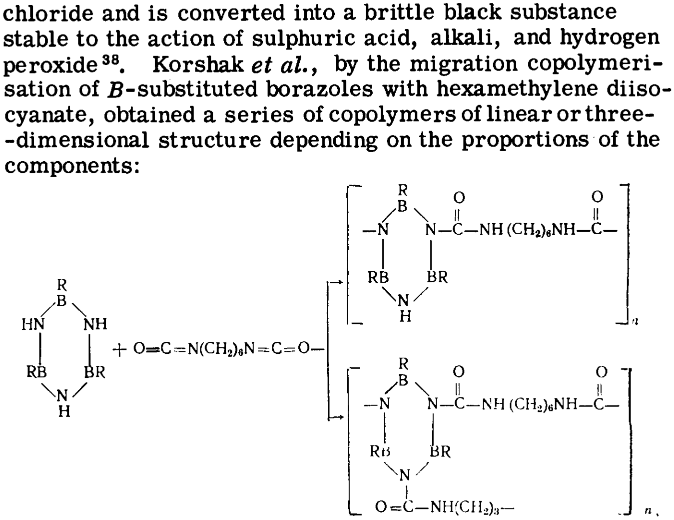


Analogous syntheses have been described by other workers[45,46]. A similar type of polycondensation is the elimination of alkyl chloride and alkyl phosphate from the complex of trichloroborazole with a trialkyl phosphate:



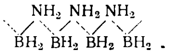
The poly(alkyl borazole orthophosphate) which is obtained does not dissolve in the usual organic solvents, is slowly hydrolysed in water, and is stable up to 400°. At higher temperatures breakdown of the borazole rings occurs[38].

Another type of condensation is observed on the prolonged heating of *B*-trichloro-*N*-triphenylborazole to 600°. This compound loses nearly all its chlorine as hydrogen chloride and is converted into a brittle black substance stable to the action of sulphuric acid, alkali, and hydrogen peroxide[38]. Korshak *et al.*, by the migration copolymerisation of *B*-substituted borazoles with hexamethylene diisocyanate, obtained a series of copolymers of linear or three-dimensional structure depending on the proportions of the components:



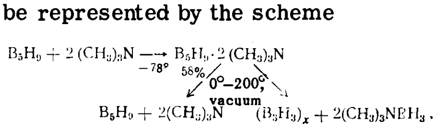
The copolymers are transparent vitreous substances with softening temperatures depending on the nature of the substituent attached to the boron[47].

In a study of the reaction of diborane with ammonia, Burg *et al.*[48], as well as other investigators[49,50], obtained in addition to borazole an insoluble solid with the composition $(BNH_4)_x$, which may possibly have the structure

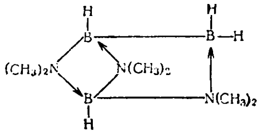


This polymeric aminoborine was isolated also by Schaeffer and Basile[51] when studying the reaction between lithium amide and diborane. The properties of the polymer were not described. However, no mention is made of this polymer in subsequent papers either by these authors or by other investigators; and it is possible that its linear structure has not been confirmed[52]. Pyrolysis of the complex of borazole with methanol led to the isolation of a polymeric material with a composition close to $[(CH_3O)BNH]_x$ together with trimethoxyborazole[53].

With the aim of preparing aminopolyboranes, Burg[54] investigated the reaction of pentaborane with trimethylamine, which can be represented by the scheme



The polymer $(B_3H_3)_x$ includes a small amount of excess trimethylamine which, in Burg's opinion, is responsible for its thermoplastic properties above 100°. At ordinary temperatures the polymer is a hard and brittle material in conformity with its cross-linked structure. Burg studied also the reaction between pentaborane and bisdimethylaminoborine, $[(CH_3)_2N]_2BH$, which yields, together with other products, triaminotriborane, a coordination compound consisting of one molecule of dimethylaminodiborane and a molecule of bisdimethylaminoborine:



Triaminotriborane melts at 95°, boils at 220°, and remains unchanged on being heated to 300°. On being heated to 360°, it becomes still more stable, and apparently polymeric. Zhigach *et al.* investigated the pyrolysis of the complex of pentaborane and di- and tri-alkylamines, and found that formation of alkylamino derivatives of diborane and borine is accompanied by that of a solid polymer containing B, H, C, and N [55].

Goubeau and Zappel[56], heated trimethylboron with ethylenediamine and trimethylenediamine in sealed tubes to 250°. In addition to cyclic borazans and borazens, they obtained polymeric oils and solids soluble in water with decomposition. On further heating these were converted into a vitreous mass unaffected by air, water, or acids. These authors write the reaction as follows:

$$2(CH_3)_3B + NH_2CH_2CH_2NH_2 \xrightarrow[250°]{-2CH_4} (CH_3)_2B \leftrightharpoons NHCH_2CH_2NH \rightleftharpoons B(CH_3)_2 \xrightarrow[-2CH_4]{450°} \textbf{polymer}.$$

It has been reported also that a vitreous polymer having the composition C_3H_7NBH, which is stable in the air, can be obtained by heating monoisopropylaminoborine to 300° [57]. This polymer does not dissolve in water or dilute acids, and is a good dielectric. The results in the earlier patents [58,59], which describe the preparation of boron-containing resins by heating boric or phenylboronic acid with diisocyanates in a non-aqueous solvent, were not subsequently confirmed[60]. The resins proved to be formed by reaction of the diisocyanates with the water eliminated by the dehydration of the boric or boronic acids, and contained boron only as impurity.

Unusually high thermal stability is shown by organic boron–phosphorus polymers, which have been prepared and investigated by Burg and his collaborators[61]. By the interaction of diborane and dimethylphosphine, they obtained a cyclic trimer, $[(CH_3)_2PBH_2]_3$, which is stable up to 400° and is very inert chemically. According to Burg[62], the great thermal stability of such compounds is explained by the boron–phosphorus bond being strengthened by some interaction between the electrons of the B–H bond and neighbouring phosphorus atoms. In an attempt to strengthen this delocalisation of electrons, Burg and Brendel[63] replaced the methyl groups attached to the phosphorus by the more electronegative fluorocarbon groups. The stronger inductive effect was accompanied, however, as these authors had foreseen, by a weakening of the ordinary σ bond between boron and phosphorus, which resulted in the weakening of the ring. The trimer and tetramer of bis(trifluoromethyl)phosphinoborine $(CF_3)_2P.BH_2$, obtained by these workers, were stable only up to 200°; above this temperature pyrolysis occurred with the formation of BF_3, H_2, and solids containing no boron.

In his later work[64] Burg evidently obtained both cyclic and linear polymers starting from the borine complexes of tetramethyldiphosphine. Pyrolysis of the diborine complex $(CH_3)_4P_2.2BH_3$ (170°–200°) gave a 75% yield of the cyclic trimer $[(CH_3)_2P.BH_2]_3$ and a 15% yield of the polymer $[(CH_3)_2PBH_2]_x$. The monoborine complex $2(CH_3)_4P_2.2BH_3$ under similar conditions eliminated hydrogen and dimethylphosphine to form cyclic trimers and tetramers in 42.3% yield. The thermoplastic white residue was stable up to 300°, but when heated at 330° for 20 h, it was largely converted into the trimer and tetramer. In an attempt to increase the yield of polymer, Wagner and Caserio[65] carried out the pyrolysis in the presence of triethylamine (10% and more). They put forward the following reaction scheme:

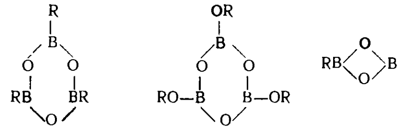
$$(CH_3)_2HP\cdot BH_3 \xrightarrow{200°} (CH_2)_2PBH_2 + H_2\ ,$$
$$(CH_2)_2PBH_2 + (C_2H_5)_3N \rightarrow (CH_3)_2P\cdot BH_2\cdot N(C_2H_5)_3\ ,$$
$$(CH_3)_2PBH_2\cdot N(C_2H_5)_3 + n\,(CH_3)_2PBH_2 \rightarrow [(CH_3)_2PBH_2]_n\,(CH_3)_2P\cdot BH_2\cdot N\,(C_2H_5)_3.$$

The end group of the triethylamine complex is not conducive to cyclisation, and the yield of polymer was therefore increased to 49%. Its molecular weight was 6000, and its melting point 170°. These workers ascribe a linear structure to the polymer; they regard a macrocyclic structure with an eighty-membered ring as improbable.

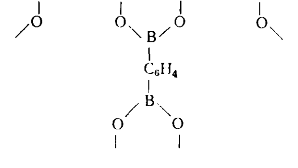
In 1959 a patent was granted to Burg and Slota in which they proposed to obtain cyclic phosphinoborines by heating disubstituted phosphinyl chlorides with sodium tetrahydroborate in the dimethyl ether of diethylene glycol[66]. These starting materials are considerably more readily available and more convenient to handle than phosphines and diborane. Detailed investigations in this field have already been described[67]. Burg studied also the reaction of pentaborane with trimethylphosphine, aminophosphines, and diphosphines. He obtained several transparent polymers of complex composition, which after removal of volatile impurities were found to be high-melting and thermostable[68].

Polymeric compounds containing boron–oxygen links in the main chain include polyanhydrides and polyesters. These materials are very stable to heating, but the overwhelming majority of them are readily hydrolysed, which hinders their practical application. Synthetically they form the most easily accessible and the cheapest class of boron-containing polymers, and therefore research in this field is being tenaciously pursued. Individual representatives of this group which are quite stable to hydrolysis have been obtained.

Boron oxide is a polymer[69], vitreous B_2O_3 having a tetrahedral structure. Linear polyanhydrides containing a $-\overset{|}{B}-O-\overset{|}{B}-O-$ chain, resembling the chain of siloxanes, have not yet been obtained. The anhydrides of alkane- and arene-boronic acids or of alkylboric acids ["*O*-alkyl-" (Ed. of Translation)], the boroxoles, are usually cyclic trimers or dimers [70-75]:

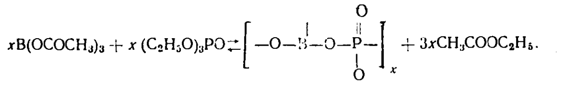


Boroxoles are very stable to heating. Thus, for example, tri-n-butylboroxole, which boils at 259°, remains unchanged on being heated to 600°. Above this temperature it evolves ethylene and gives a non-volatile product containing $>BCH_2-CH_3$ groups [76]. The action of heat on benzene-1,4-diboronic acid yielded a polymeric anhydride with the structure



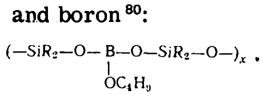
It does not melt, does not sublime, and remains unchanged on being heated in air to 350° or in a vacuum to 450° [77]. A similar polymer was obtained from benzene-1,3-diboronic acid [78].

An infusible but strongly hygroscopic and readily hydrolysed mixed polyanhydride of boric and phosphoric acids obtained by the reaction of boron triacetate with triethyl phosphate has been described [79]:



$$xB(OCOCH_3)_3 + x(C_2H_5O)_3PO \rightleftarrows \left[-O-\overset{|}{B}-O-\underset{O}{\overset{O}{\overset{\|}{\underset{|}{P}}}}- \right]_x + 3xCH_3COOC_2H_5.$$

Heterofunctional polycondensation of alkyl- or aryl-dialkoxysilanes with triacetoxyboron, and of alkyl- or aryl-diacetoxysilanes with butyl borate, yielded organoborasiloxanes, the molecular chains of which contained silicon, oxygen, and boron [80]:

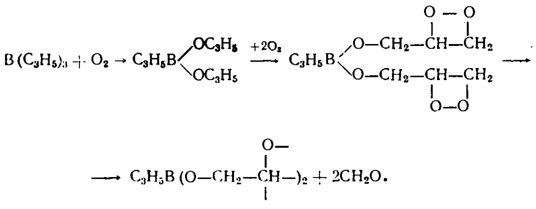


$$(-SiR_2-O-\underset{OC_4H_9}{\underset{|}{B}}-O-SiR_2-O-)_x .$$

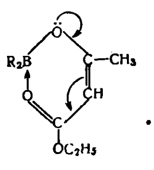
These polymers are stable on heating, but are readily hydrolysed by water with the formation of boric acid and an organosilicon polymer. Other investigators [81,82] have also studied the preparation of such polyanhydrides.

Polyesters of boric and substituted boric acids have been known for a comparatively long time, being readily prepared by simple esterification or "transesterification". Several of them are used as adhesives, plasticisers, and textile sizes. Reaction of ethyl borate with methylene glycol diacetate yielded polyborylformal [83], a solid which hydrolyses in the air. Similar instability in the presence of moisture is shown by poly(ethylene glycol borate) [84,85], the polyester obtained by heating glyceryl borate in a vacuum [86], and by the products of the polycondensation of boric acid with catechol, resorcinol, and pyrogallol [87,88].

Topchiev *et al.* [89] obtained a branched polyester of 2-propeneboronic acid by the oxidative polymerisation of triallylboron:

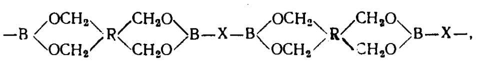


A polyester resistant to hydrolysis was synthesised by Kamenskii *et al.* [90] by condensing trisdiacetonyl borate with furfural. After being hardened in the presence of alkali, the polymer did not melt below 400°. The resistance of this polyester to the action of water may be explained by the formation of a coordinate link between the carbonyl of the diacetonoxy group and a boron atom. An example of this type of stability is provided by the esters formed by dialkylborinic acids with ethyl acetoacetate [91]:

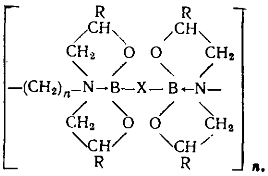


A broad investigation of the hydrolysability of boric esters was carried out by Steinberg and Hunster [92]. They synthesised a large number of alkyl and aryl borates, including many for the first time, and studied their rates of hydrolysis in water and in aqueous dioxan. These workers derived several rules which could be utilised in the synthesis of polyesters of boric acid.

Several new polyesters are described by Bamford and Fordham [93], some of which are quite stable in moist air. Polyesters of *p*-phenylene- and polymethylene-diboronic acids with pentaerythritol and tetrakishydroxymethylcyclopentanone of general formula



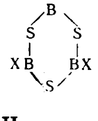
are infusible and stable to heat and hydrolysis when X = $= p\text{-}C_6H_4$. If, however, X = $[CH_2]_n$, fibre-forming polyesters obtained are of relatively low melting point and less resistant to hydrolysis. Chelate polyesters of diboronic acids with tetrakishydroxyalkylated polymethylenediamines have also been described:



When $n = 2$, R = CH_3, and X = $p\text{-}C_6H_4$ the polyester remains unchanged in boiling water, and darkens slightly on being heated to 300°. The intramolecular coordination between boron and nitrogen atoms in this polymer is probably responsible for its great stability to the action of water [94].

Several hydroxylated carbon-chain polymers modified with boric acid are known, *e.g.* poly(vinyl borate) [95], and the products obtained by the reaction of boron oxide with hydroxylated polymers of conjugated dienes or hydroxylated natural rubber [96]. These products are employed in the manufacture of moulding powders, sealing compounds, and varnishes.

Polymeric compounds of boron containing sulphur and arsenic have been obtained. Thus the reaction between diborane and hydrogen sulphide yielded a polymer of composition $(BHS)_n$, containing the B–S bond and probably having a linear structure. It forms a colourless transparent film, readily hydrolysed by water [97]. Wiberg and Sturm [98,99] synthesised several cyclic borasulpholes with the structure



where X = H, Cl, Br, OCH_3.

Pyrolysis of the addition product of diborane and dimethylarsine yielded trimers, tetramers, and polymers having the composition $[(CH_3)_2AsBH_2]$, analogous to phosphinoborines, but less stable to heat and chemical reagents [100].

The above brief review of polymeric compounds of boron shows that this branch of high-polymer chemistry has only just begun to evolve. Synthetic methods have been little developed, the properties of the polymers are not always described, and the polymers themselves are rarely available, since many of them have been prepared only in gram quantities. The requirements of modern technology, however, demand that research shall be continued on the polymeric compounds of boron, as theoretical considerations suggest that it may be possible to make materials of high melting point, which are stable to heat and to chemical agents. The most promising compounds are evidently the phosphinoborines, which are expected to have good mechanical properties.

Polymers containing borazole rings in the main molecular chain will probably have very rigid three-dimensional structures. It would appear from individual examples that linear polymers containing –B–N– and –B–P– chains do not have high melting points, are less heat resistant, and in the case of phosphinoborines tend to change into cyclic compounds of low molecular weight at high temperatures.

The properties of polymers containing the –B–C– bond have hardly been described at all; the fundamental disadvantage of many of them is the readiness with which they are oxidised by atmospheric oxygen. Although the polyanhydrides and polyesters of boric and substituted boric acids show a general tendency to be readily hydrolysed, isolated representatives of these polymers are completely stable both to hydrolysis and to oxidation and the action of high temperatures.

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THE CHEMISTRY OF RARE-EARTH AND ACTINIDE SULPHIDES

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CONTENTS

INTRODUCTION

The rare-earth and actinide sulphides are of interest on account of the combined effects on the outer *s* and *d* electrons (in the metal) of the electronegative sulphur atom and of the incomplete metal 4*f* and 5*f* orbitals, which are themselves unable to take part in bonding. As a result, the bonds in these compounds are always heterodesmic and sometimes even predominantly ionic, rather than covalent or metallic, and this leads to important and useful physical properties. Sulphides with metallic bonding and structure have the hardness, high melting point, and large heat of formation characteristic of interstitial compounds. Those rich in sulphur have semiconductor properties and relatively low melting points, are less hard, and dissociate more readily on heating in a vacuum. Some sulphides, inert to molten metal, are used as refractory materials; others will be used as high temperature semiconductors, large resistances, and anti-emission materials. This article reviews the electronic structure, chemical and physical properties, and applications of these compounds, in order to facilitate further study of them.

STRUCTURE AND PROPERTIES

The rare-earth and actinide sulphides have the general formulae MS, M_5S_7, M_3S_4, M_2S_3, and MS_2; the rare earths and plutonium form oxysulphides M_2O_2S, and the remaining actinides form oxysulphides MOS. These resemble sulphides in their properties, structure, and bonding. X-Ray investigation of the structures of the lanthanum, cerium, and actinide sulphides and oxysulphides is due to Zachariasen[1-3]. Makarov[4] has studied the sulphides of Th, U, Np, and Pu by optical crystallography. All the compounds of type MS have the face-centred cubic lattice of sodium chloride, while M_5S_7 is monoclinic, and M_3S_4 and MS_2 have the cubic Th_3P_4 and the $PbCl_2$ structures respectively. Th_2S_3, Y_2S_3, and Np_2S_3 have the orthorhombic Sb_2S_3 structure[1]. Ac_2S_3, Pu_2S_3, and Am_2S_3, and the rare-earth sesquisulphides, apart from Y_2S_3 and the δ modifications of Dy_2S_3, Er_2S_3, and Yb_2S_3, form defect cubic lattices deficient in sulphur. The unit cell contains 16 sulphur atoms and $10\frac{2}{3}$ metal atoms, randomly distributed among the 12 available positions. As a result of the low proportion of metal atoms in relation to the available positions, every ninth lattice position remains empty, on the average.

The rare-earth oxysulphides are isomorphous with Pu_2O_2S, their structure being derived from the hexagonal Ce_2O_3 lattice (Fig. 1), in which the oxygen atoms are cubically close packed with cerium atoms in the octahedral holes, two full layers alternating with one empty one. The replacement of one oxygen by sulphur causes distortion of the Ce_2O_3 lattice. In the unit cell each metal atom is linked to four oxygen and three sulphur atoms. Th, Pa, U, and Np form oxysulphides, MOS, of tetragonal structure.

The ratios of sulphur's atomic radius (1.04 Å) to those of the rare earths and actinides (Table 1) are generally near to or less than the critical Hägg value 0.59 for formation of interstitial compounds. In nearly all the monosulphides the sulphur atoms are packed interstitially in the tetragonal or octahedral holes of the metal lattice; high melting points and hardness result.

Scandium and yttrium, *d* transition metals, have been included for historical and geochemical reasons in the rare earths; the lanthanides are *f* transition metals (4*f* level unfilled), although lanthanum and lutetium also resemble the *d* metals. The behaviour of scandium and yttrium compounds is largely determined by the number of electrons in the *d* orbital (n) and the so-called acceptor capacity[5] of this orbital, expressed as $1/Nn$, where N is the principal quantum number of the orbital. The values of 0.33 for Sc and 0.25 for Y exceed those for the remaining *d* transition metals, even Ti, Zr, V, and Hf. Sc and Y should therefore have great polarising power; the effect is insignificant in compounds with elements such as nitrogen, which has a high first ionisation potential (14.51 eV). In compounds with phosphorus, sulphur, and carbon (ionisation potentials respectively 10.43, 10.42, and 11.24 eV), there should be electron displacement towards the metal atom and a consequent tendency towards metallic bond formation, although with partial conservation of the ionic bond. Scandium and yttrium sulphides should therefore be heterodesmic, with both metallic and ionic bonding, the degree of the latter increasing with increase in the number of sulphur atoms per molecule.

The well-screened 4*f* electrons of the lanthanides and the 5*f* electrons of the actinides, in contrast to *d* electrons, cannot participate directly in the bonding with sulphur, but their influence on the *s* electrons is indicated by the magnetic properties of the metals[6-8], and results in relatively strong attraction of the *s* electrons. Bonds with sulphur, which is fairly difficult to ionise, should therefore be both metallic and ionic; the asymmetric distribution of electron density causes energy gaps, characteristic of semiconductors. This effect on the *s* electrons should be larger, the more incomplete the *f* orbital; the consequence of Hund's rule[9] must be taken into account, namely that the ions La^{3+}, with the xenon configuration, Gd^{3+}, with a half complete *f* orbital, and Lu^{3+}, with a complete *f* orbital, are the most stable. The $5f^16s^2$ valency electrons of these three atoms should be loosely bound in the sulphides. Conductivity data (Table 6) support this in that La_3S_4, at least, has a lower resistivity than most analogous lanthanide sulphides. The resistivities of pure specimens of thorium sulphides (Table 2) illustrate that as the proportion of sulphur increases, so do the extent of covalent bonding between sulphur atoms, the asymmetry of electron-density distribution in the lattice, and the percentage ionic character of the metal–sulphur bond. ThS is reported to be a metallic conductor, and the other semiconductors[10]; the sharp increase in resistivity from Th_2S_3 to Th_4S_7 is evidently due to increasing covalent character of the bonds, which rises to a maximum for ThS_2.

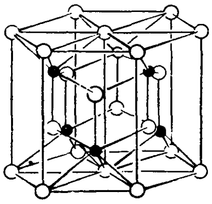

Fig. 1. The Ce_2O_3 structure.

TABLE 1. Radius ratios for rare-earth and actinide sulphides.

Metal	$r_S : r_M$	Metal	$r_S : r_M$	Metal	$r_S : r_M$
Sc	0.64	Eu	0.50	Lu	0.60
Y	0.58	Gd	0.58	Ac	—
La	0.56	Tb	0.59	Th	0.58
Ce	0.57	Dy	0.59	Pa	0.64
Pr	0.57	Ho	0.59	U	0.68
Nd	0.57	Er	0.59	Np	0.69
Pm	—	Tm	0.60	Pu	0.65
Sm	0.56	Yb	0.54	Am	0.57

TABLE 2.

Sulphide	Sulphur content, at.%	Resistivity, ohm cm
ThS	50.0	0.2
Th_2S_3	60.0	10
Th_4S_7	63.5	$25 \cdot 10^3$
ThS_2	66.7	$10 \cdot 10^9$

TABLE 3.

Sulphur	Sulphur content, at.%	Heat of formation per g-atom of sulphur, kcal
CeS	50.0	117.9
Ce_3S_4	57.0	105.2
Ce_2S_3	60.0	100.2
ThS	50.0	120
Th_2S_3	60.0	102
Th_4S_7	63.5	95
ThS_2	66.7	85

TABLE 4.

Oxysulphide	Distance, Å				
	observed			calculated from ionic radii	
	M—1O	M—3C	M—3S	M—4O	M—3S
La_2O_2S	2.41	2.38	3.06	2.44	2.92
Ce_2O_2S	2.39	2.36	3.04	2.42	2.90
Pu_2O_2S	2.37	2.33	2.99	2.41	2.89

TABLE 5.

metal	Effective magnetic moment in Bohr magnetons					
	M	MS	M_2S_3	M_3S_4	MO_2	M_2O_2S
La	0	0.8	0.22	0,25	0,35	~0
Ce	2.56	2.34	2.50	2.30	2.39	2.31
Pr	3.62	—	3.65	—	—	—
Nd	3.68	3.30	3.71	3.48	—	3.48
Pm	2,83	—	—	—	—	—
Sm	1,55	3.51	1.60	2.42	—	1.57
Eu	3.51	7.71	—	—	—	—
Gd	7.94	—	8.3	—	—	—
Tb	9.7	—	—	—	—	—
Dy	10.6	—	10.8	—	—	—
Ho	10.6	—	—	—	—	—
Er	9.5	—	9.8	—	—	—
Tm	7.6	—	—	—	—	—
Yb	4.5	—	4.8	—	—	—
Lu	0	—	—	—	—	—

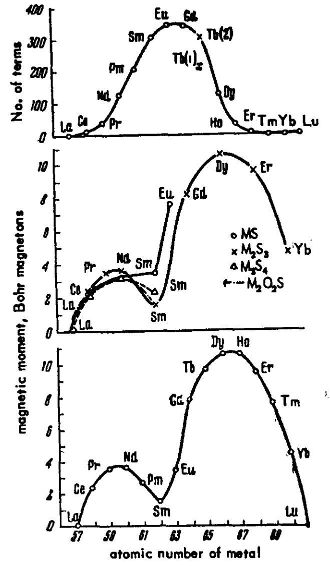

Fig. 2. Number of terms and effective magnetic moments of lanthanides and their sulphides.

The transition from highly conducting monosulphides to semiconductor polysulphides, with forbidden gaps and a significant proportion of ionic bonding, is also marked by a decrease in the heat of formation per g-atom of sulphur (Table 3). As the proportion of sulphur rises electrons are transferred from the M–S to the S–S bond, as with the borides of transition metals[11], and the M–S bond length increases. The Ce–S bond length is 2.88 Å in CeS, 2.97 Å in Ce_3S_4, and 2.98 Å in Ce_2S_3. In the oxysulphides the high ionisation potential of the oxygen atom causes greater participation in bonding of the outer electrons of the *f* transition metals, so that the average heat of formation per g-atom of non-metal rises, reaching 143 kcal for Ce_2O_2S. When a sulphur atom is substituted in the Ce_2O_3 lattice, the Ce–O bond becomes stronger and shorter, the Ce–S bond being relatively long and weak[3] on account of electron deprivation caused by the more electronegative oxygen atom. This is true of other oxysulphides (Table 4); they are even more metallic than monosulphides. Their conductivity should be high, but has not yet been studied.

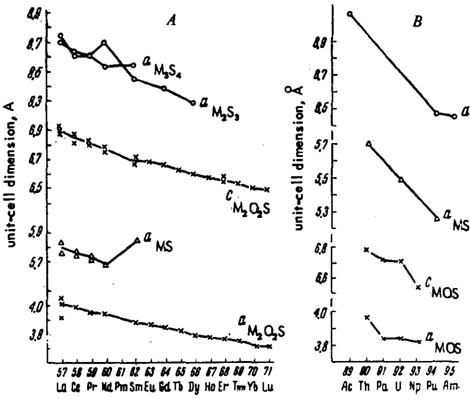

Fig. 3. Effect of atomic number on the lattice constants of sulphides and oxysulphides of lanthanides (*A*) and actinides (*B*).

The effective magnetic moments of trisulphides of the lanthanum series (Table 5) approximate to those of the ion[9] M^{3+}, indicating a significant degree of ionic bonding; they are also close to the values for the atoms[8], indicating that the *f* electrons take no direct part in bonding. The magnetic moments of the sulphides were calculated by means of the van Vleck formula from magnetic susceptibility values taken from Foex's handbook[12] and sources referred to in Table 6. The magnetic moment of Sm_3S_4, as well as its resistivity, is extremely high. The moments of other sulphides are less than that of M_2S_3, on account of either the pooling of electrons or the formation of covalencies; exceptions are SmS and EuS, the unusually high magnetic moments of which are difficult to explain. On account of the small energy gap between 4*d* and 5*d* orbitals (the latter being unoccupied in free lanthanide atoms), *f* → *d* transitions may occur in lanthanide compounds, as data on thermionic emission from lanthanide borides show[13,14]. Assuming the

TABLE 6. Physical properties of the rare-earth and actinide sulphides.

Metal	Formula of sulphide	Colour	Crystal structure and properties							M.p.	Heat of formation, kcal mole^{-1}	Electromagnetic properties	
			structure	lattice constants, Å			c/a	density, g cm^{-3}				resistivity, ohm cm	magnetic susceptibility × × 10^6, at 20°
				a	b	c		by pyknometer	by X-ray analysis				
Sc	Sc_2S_3	yellow	—	—	—	—	—	2.89[18]	—	—	—	—	—
Y	YS	ruby red[19]	cubic[19]	5.466[19]	—	—	—	4.51[19]	4.92[19]	2040[19]	—	—	100[19]
	Y_5S_7	—	monoclinic[20]	12.67[20]	3.81[20]	11.43[20]	β=74[20]	4.10[20]	4.18[20]	1630[20]	—	—	39.3[20]
	Y_2S_3	yellow[18]	monoclinic[21]	10.17[21]	4.02[21]	17.47[21]		3.87[18,21]	3.87[21]	1600[20] 1900—1950[27]	—	—	83.4[20]
	YS_2	brown violet[20]	tetragonal[20]	7.71[20]	—	7.89[20]	1.02[20]	4.25[20]	4.35[20]	converted to Y_2S_3 above 600° in a vacuum[20]	—	—	125[20]
	Y_2O_2S	grey white[21]	hexagonal[22]	3.78[22]	—	6.56[22]	1.73[22]	4.89[22]	4.95[22]	2120[22]	—	—	⩾0[22]
La	LaS	gold[23, 24]	cubic[23, 15]	5.788[23]	—	—	—	5.75[23]	5.86[23]	1970[23]	—	—	281[23]
		tinged with green[15]		5.842[15] 5.84[24]	— —	— —	— —	— —	5.70[15] 5.36[24]	— —	— —	— —	— —
	La_3S_4	blue black[25]	cubic[25]	8.748[25]	—	—	—	5.34[25]	5.44[25]	—	—	0.24[25]	27.2[25]
	La_2S_3	yellow[18]	cubic[2]	8.723[2]	—	—	—	4.90[18]	5.00[2]	2750[18]	342[16, 28]	0.2	−18.5[12]
		vermilion[24] black[27]						4.93[25] 4.997[27]	4.98[25] —	— 2100—2150[27]			−19[18]
	LaS_2	yellow-brown[18]	—	—	—	—	—	4.77[18]	—	dissociates to La_2S_3 and S at 620°[18]	180[16]		−50[12] −52[18]
	La_2O_2S	pale yellow[26]	hexagonal[26]	4.020[26] 3.927[3] 4.051[29]	— — —	6.906[26] 6,894[3] 6.943	1.71[25] 1.76[3] 1.71[29]	5.77[26] — —	— 5.81[3] 5.73[29]	1940[26]	—	—	⩾0[12.26]
Ce	CeS	brassy to bronze[30]	cubic[30]	5.76[30] 5.778[1] 5.765[15] 5.763[19]	— — — —	— — — —	— — — —	— — — 5.88[19]	5.96[30] 5.93[1] 5.98[15] 5.98[19]	2450[30]	117.9[30]	$9\cdot10^{-6}$[30] $4.5\cdot10^{-4}$	2140[30] 2110[12.19]
	Ce_3S_4	black[30]	cubic[2, 30]	8.623[2] 8.626[25] 8.606[30]	— — —	— — —	— — —	— 5.51[25] —	5.67[2,25] — 5.72[30]	2050[30]	421.5[30] 483.6[16]	$4\cdot10^{-4}$[30]	2125[25]
	Ce_2S_3	red[30]	cubic[1, 30]	8.635[2] 8.618[30]	— —	— —	— —	— 5.25[30]	5.19[2] —	1840[30]	300.5[30] 347.1[16]	>1000[30] 0.3	2520[30] 2540[12]
	CeS_2	black-brown[31]	cubic[31]	8.12[31]	—	—	—	4.96[31]	5.07[31]	decomposes above 720°[31]	—	—	2290[12]
	Ce_2O_2S	brown to black[32]	hexagonal[3, 32]	4.00[3] 4.008[32] 4.00[22]	— — —	6.82[3] 6.833[32] 6.87[22]	1.71[3] 1.71[32] 1.72[22]	— — —	5.99[3] 6.02[32] 6.01[22]	1950[22]	430[32]	—	2139[12.22]
Pr	PrS	dark gold[23]	cubic[15, 23]	5.727[15]	—	—	—	—	6.80[15]	—	—	—	—
		tinged with green[15]		5.747[23]	—	—	—	—	6.08[23]				
	Pr_3S_4	blue black[25]	cubic[25]	8.611[25]	—	—	—	5.57[25]	5.77[25]	—	—	—	—
	Pr_2S_3	dark brown[18]	cubic[25]	8.611[25]	—	—	—	5,27[25] 5.23[18]	5,27[25]	—	—	—	5385[12.18]
	Pr_2O_2S	black[26]	hexagonal[26, 29]	3.96[26] 3.974[29]	— —	6.82[26] 6.825[29]	1.72[26] 1.72[29]	— —	6.22[26] 6.16[29]	—	—	—	—
Nd	NdS	gold[23]	cubic[23]	5.690[23]	—	—	—	6.24[23]	6.36[23]	2140[23]	—	—	4370[23]
		tinged with green[15]		5.681[15]	—	—	—		6.27[15]				
	Nd_3S_4	black	cubic[25]	8.541[25]	—	—	—	5.91[25]	6.02[25]	—	—	1.2[25]	4849[25]
	Nd_2S_3	brown[18]	cubic[25]	8.699[25]	—	—	—	5.49[25]	5.50[25]	2200[27]	342[16]		5545[18]
		green yellow[27]					—	5.39[27]					5650[12]
	Nd_2O_2S	pale blue[26]	hexagonal[26, 29]	3.934[26] 3.946[29]	— —	6.759[26] 6.790[29]	1.71[26] 1.72[29]	6.22[26] —	6.47[26] 6.40[29]	1990[26]	—	—	4846[26]
Sm	SmS	black[23]	cubic[23]	5.863[23]	—	—	—	5.64[23]	6.01[23]	1940[23]	—	—	4970[23]
	Sm_3S_4	black[25]	cubic[25]	8.563[25]	—	—	—	6.11[25]	6.14[25]	—	66.4[25]		2350[25]
	Sm_2S_3	brown[18] black[27]	cubic[25]	8.465[25]	—	—	— — —	5.82[18] 5.87[25] 5.73[27]	— 5.83[25]	1900[27]	—	—	1690[18] 1650[12] 1020[25]
	Sm_2O_2S	light brown[26]	hexagonal[26, 29]	3.884[26] 3.893[29]	— —	6.673[26] 6.717[29]	1.72[26] 1.73[29]	6.90[26] —	6.95[26] 6.87[29]	1980[26]			993.9[18] 994[12]

TABLE 6 (contd.)

Metal	Formula of sulphide	Colour	Crystal structure and properties							M.p.	Heat of formation, kcal mole^{-1}	Electromagnetic properties	
			structure	lattice constants, Å			c/a	density, g cm^{-3}				resistivity, ohm cm	magnetic susceptibility × × 10^6, at 20°
				a	b	c		by pyknometer	by X-ray analysis				
Eu	EuS	black[33]	cubic[33, 34]	5.970[34]	—	—	—	5.71[34]	5.75[34]	—	—	—	22600[34] 35400 195°K 81000 90°K
	Eu_3S_4	black[34]	cubic[34]	8.537[34]	—	—	—	6.26[34]	6.27[34]	—	—	—	11500[34]
	$Eu_2S_{3.31}$		tetragonal[34]	7.86[34]	—	8.03[34]	1.02[34]	5.70[34]	5.70[34]	—	—	—	5800[34]
	Eu_2O_2S	pink[34]	hexagonal[29, 34]	3.872[29] 3.87[34]	— —	6.686[29] 6.68[34]	1.72[29] 1.72[34]	— —	7.04[29] 7.04[34]	—	—	—	
Gd	GdS	yellow[35]	cubic[35]	—	—	—	—	—	—	—	—	—	—
	α-Gd_2S_3	red brown[35]	—	—	—	—	—	—	—	—	—	—	—
	γ-Gd_2S_3	brown[35]	cubic[35]	8,387[35]	—	—	—	6.06[35]	6.15[35]	1885[35]	—	—	27750[12,18]
	GdS_2	brown violet[35]	hexagonal[35]	7.85[35]	—	7.96[35]	1.01[35]	5.90[35]	5.98[35]	—	—	—	—
	Gd_2O_2S	pale brown[35]	hexagonal[29, 35]	3.851[29] 3.850[35]	—	6.667[29] 6.668[35]	1.73[29] 1.73[35]	—	7.34[29]	—	—	—	—
Tb	Tb_2O_2S	—	hexagonal[29]	3,825[29]	—	6.626[29]	1.73[29]	—	7.56[29]	—	—	—	—
Dy	DyS	red violet[21]	cubic[21]	—	—	—	—	—	—	—	—	—	—
	Dy_5S_7	black[35]	monoclinic[35]	12.84[35]	3.81[35]	11.61[35]	—	6.14[35]	6.35[35]	1540[35]	—	—	—
	α-Dy_2S_3	red brown[35]	—	—	—	—	—	5.97[35] 6.08[18]	—	—	—	—	47600[18] 45700[12]
	γ-Dy_2S_3	black[21]	cubic[21]	8.292[21]	—	—	—	6.48[21]	6.54[21]	1490[21]	—	—	—
	δ-Dy_2S_3	green[21]	monoclinic[21]	10.17[21]	4,02[21]	17.57[21]	—	5.75[21]	5.91[21]	1470° (passes into γ-Dy_2S_3)	—	—	—
	DyS_2	red brown[35]	tetragonal[35]	7.69[35]	—	7.85[35]	1.02	6.11[35]	6.48[35]		—	—	—
	Dy_2O_2S	pale grey[35]	hexagonal[29, 35]	3.803[29] 3,792[35]	— —	6,603[29] 6.587[35]	1.73[29] 1.73[35]	— 7.84[35]	7.81[29] 7.88[35]	—	—	—	—
Ho	Ho_2O_2S	—	hexagonal[29]	3.782[29]	—	6.580[29]	1.74[29]	—	8.02[29]	—	—	—	—
Er	ErS	red violet[21]	cubic[21]	5.424[21]	—	—	—	—	—	—	—	—	—
	$ErS_{1,18}$	red violet[21]	cubic[21]	5.452[21]	—	—	—	6.75[21]	7.10[21]	—	—	—	—
	Er_5S_7	black[35]	monoclinic[35]	12.63[35]	3.77[35]	11.47[35]	—	6.39[35]	6.71[35]	1620[35]	—	—	—
	δ-Er_2S_3	pale brown[35]	monoclinic[35]	10.07[35]	4.00[35]	17.33[35]	—	6.07[35]	6.21[35]	1630[35]	—	—	38600[12,18]
	Er_2O_2S	pale pink[35]	hexagonal[29, 35]	3.760[1] 3.774[35]	— —	6.552[29] 6.571[35]	1.74[29] 1.74[35]	— 7.92[35]	8.25[29] 8.16[35]	—	—	—	—
Tm	Tm_2O_2S	—	hexagonal[29]	3.747[29]	—	6,538[29]	1.75[29]	—	8.59[29]	—	—	—	—
Yb	Yb_2S_3	yellow[18]	orth.[36]	6.78[36]	9.95[36]	3.61[36]	—	—	6.02[36]	—	—	—	9150[18]
	Yb_2O_2S	—	hexagonal[29]	3.723[29]	—	6.503[29]	1.75[29]	—	8.72[29]	—	—	—	—
Lu	Lu_2O_2S	—	hexagonal[29]	3.709[29]	—	6.486[29]	1.74[29]	—	8.89[29]	—	—	—	—
Ac	Ac_2S_3	—	cubic[2]	8.99[2]	—	—	—	—	6.75[2]	—	—	—	—
Th	ThS	silver[37]	cubic[1]	5.682[1]	—	—	—	—	9.56[1]	>2200[38] >2500[39] ~2400—2450[40]	120[16]	0.2[10]	diamagnetic[39]
	Th_2S_3	brown[31]	orth.[1]	10.99[1]	10.85[1]	3.96[1]	—	9.57—9.69[38]	7.87[1]	~2300[16] 1900—2000[39]	306[16]	10^{10}	diamagnetic[39]
	Th_4S_7 or Th_7S_{12}	red[38]	hexagonal[37]	11.041[37]	—	3.983[37]	0.36[37]	6.91[38]	7.65—7.85[37]	~2300[16] 1770[39]	665[16]	25·10^8 [10]	—
	ThS_2	purple, brown violet[41, 42]	orth.[1]	4.268[1]	7.264[1]	8.617[1]	—	7.3[38]	7.36[1]	1905[41.42] 2203[16]	170[16]	10·10^9 [10]	—
	ThOS	yellow[39]	tetragonal[1]	3.963[1]	—	6.747[1]	1.70[1]	—	8.78[1]	—	—	—	—
Pa	PaOS	yellow[43]	tetragonal[44]	3.832[44]	—	6.704[44]	1.75[44]	—	9.44[44]	>2000[39]	—	—	—
U	US	grey[39] yellow[45]	cubic[1]	5.484[1]	—	—	—	10.51[45]	10.87[1]	>2000[39]	—	—	4180[16] 4603[45]
	U_2S_3	black[39]	orth.[1]	10,41[1] 10.34[46]	10.65[1] 10.58[46]	3.89[1] 3.86[46]	— —	— 8.94[46]	8.78[1] 9.01[46]	—	—	—	5206[46]
	U_3S_5		orth.[46]	7.41[46]	8.05[46]	11,70[46]	—	8.30[46]	8.34[46]	—	—	—	11220[46]
	α-US_2	greyish black[39]	tetragonal[47]	10,26[47]	—	6.30[47]	0.61[47]	7.60[47]	7.57[47]	—	—	—	3137[47]
	β-US_2	greyish black[39]	orth.[47]	4,12[47] 4.22[39]	7.11[47] 7.08[39]	7.46[47] 7.45[39]	— —	8.07[47] —	8.09[47] 7.90[39]	— —	— 1850[39]	— —	3470[47] —

TABLE 6 (contd.)

Metal	Formula of sulphide	Colour	Crystal structure and properties							M.p.	Heat of formation, kcal mole^{-1}	Electromagnetic properties	
			structure	lattice constants, Å			c/a	density, g cm^{-3}				resistivity ohm cm	magnetic susceptibility × × 10^6, at 20°
				a	b	c		by pyknometer	by X-ray analysis				
	γ-US$_2$		hexagonal[48]	7.238 [48]	—	4.059 [48]	0.56 [48]	8.12 [48]	8.18 [48]	transition to β-US$_2$ at 425° [48]	—	—	—
	UOS	blue black[39]	tetragonal[1]	3.843 [1]	—	6.694 [1]	1.74 [1]	—	9.60 [1]	—	—	—	—
Np	Np$_2$S$_3$	black[49]	orth.[1]	10.32 [1]	10.62 [1]	3.86 [1]	—	8.8 [1]	—	—	—	—	—
	NpOS	black[49]	tetragonal	3.824 [1]	—	6 554 [1]	1.74 [1]	9.71 [1]	—	—	—	—	—
Pu	PuS	golden bronze[50]	cubic[1]	5 536 [1]	—	—	—	10.61 [1]	—	—	—	—	—
	Pu$_2$S$_3$	black[50]	cubic[2]	8.454 [2]	—	—	—	8.41 [2]	—	—	—	—	—
	Pu$_2$O$_2$S	—	hexagonal[3]	3.926 [3]	—	6.769 [3]	1.72 [3]	9.95 [3]	—	—	—	—	—
Am	Am$_2$S$_3$	—	cubic[2]	8.445 [2]	—	—	—	8.50 [2]	—	—	—	—	—

Note. orth. = orthorombic.

lanthanide 4*f* orbitals to be little perturbed by bond formation, Hund's rule[9] may be applied in the form which states that the greater the spin multiplicity, the greater the stability of the orbital and the more firmly are its electrons held. The resultant calculation (Fig. 2) shows that electrons are most firmly held, and $f \rightarrow d$ transitions are least probable, for Sm, Eu, and Gd. The small proportion of sulphur in the monosulphides exerts little polarising effect and induces no transitions, so that the probability of hybridisation and mutual spin compensation is reduced. This effect is absent in the rare-earth hexaborides, on account of the extensive polarisation of the metal atoms by the covalent octahedral groups (closed octahedra) of boron atoms, to the structure of which the metal's electrons are necessary. The improbability of $f \rightarrow d$ transitions may account for the high magnetic moment of Sm_3S_4, since it counteracts the increasing covalency due to the high number of sulphur atoms relative to Sm_2S_3.

Makarov[4] showed that $5f \rightarrow 6d$ transitions in actinides, on compound formation, are more important than $f \rightarrow d$ transitions in lanthanides, since the 5*f* and 6*d* energy levels are so close. The actinides consequently display several valencies, as exemplified by the thorium and uranium sulphides.

The lanthanide and actinide contractions are reflected in the dependence of sulphide and oxysulphide lattice constants on atomic number (Fig. 3). The effect is more pronounced for the less ionic oxysulphides. The graphs indicate the +2 state for Nd in Nd_2S_3 and Sm in SmS. The M–S distance and the sum of the ionic radii in lanthanide sulphides decrease as the atomic number of M increases[15]:

Sulphide	M–S distance, Å	Sum of ionic radii, Å
LaS	2.92	2.97
CeS	2.88	2.93
PrS	2.86	2.91
NdS	2.84	2.89

The vapour pressures of sulphides with a high degree of metallic bonding are low — *e.g.* 10^{-3} mm for CeS at 1900°, and for Ce_3S_4 at 1840°. When a larger proportion of covalently bonded sulphur is present, some is lost fairly readily on heating through thermal decomposition as in M_2S_3 and especially in MS_2.

The M–S bonds in the lanthanide and actinide sulphides are therefore ionic or metallic, and the S–S bonds covalent. From a study of interatomic distances, Zachariasen[1] also concludes that all three bond types are present.

Little is known of the chemical properties of these sulphides and oxysulphides. They are mainly stable at room temperature in dry air, but in moist air some are very slowly hydrolysed and evolve hydrogen sulphide. They are oxidised in air at 200°–300° to basic sulphates and oxides; the monosulphides are less stable to atmospheric oxidation[15] than MSe or MTe. The sulphides are inert towards nitrogen, hydrogen, and carbon dioxide even at high temperature. La_2S_3, LaS_2, CeS, Ce_3S_4, Ce_2S_3, Nd_2S_3, ThS, Th_2S_3, Th_4S_7, and ThS_2 are insoluble in water[16]. The sulphides react with mineral acids and acetic acid, evolving hydrogen sulphide and hydrogen; the M_3S_4 sulphides react least readily. The oxysulphides react less readily, being difficultly soluble in acetic acid, or even in concentrated hydrochloric acid (*e.g.* Yb_2O_2S); at high temperatures they are converted by aluminium to sulphides. A useful property of the sulphides is their stability towards fused metals and salts, although they form intermetallic compounds with the noble metals.

Physical and structural data for the rare-earth and actinide sulphides and oxysulphides appear in Table 6. Serebrennikov's monograph[17] also gives data on rare-earth sulphides.

METHODS OF PREPARATION

1. From the elements. Almost any sulphide may be made from suitably pure metal powder and sublimed sulphur, heated together in a sealed tube, which is often evacuated. Despite other stoichiometric proportions, M_2S_3 is generally formed at 400°–600° and is slowly converted to MS at 1000°–1100°. Iandelli[15] obtained LaS, CeS, PrS, and NdS in this way.

2. From the metal powder and hydrogen sulphide. The metal hydride is often used, since the metal powders are sometimes pyrophoric, and oxysulphides may arise from them.

3. From the metal oxide and hydrogen sulphide. Sulphur or carbon may be added to reduce the oxide. The reaction occurs between 1200° and 1600°. The sesquisulphides of cerium[51,52], lanthanum, and other metals have been made thus; MS is difficult to make in this manner, even if reducing agents are used. Oxysulphides are generally formed at lower temperatures and when the quantity of reducing agent is insufficient[30].

4. Thermit reduction by metals. M_2S_3 mixed with an oxysulphide or oxide, is generally reduced by aluminium to MS:

$$3M_2S_3 + 3M_2O_2S + 4Al = 12MS + 2Al_2O_3$$

$$2M_2S_3 + M_2O_3 + 2Al = 6MS + Al_2O_3.$$

The reaction proceeds in a vacuum at 1300°–1500°, excess Al and Al_2O_3 vaporising as AlO at 1600°.

5. Preparation from the sesquisulphides. These are readily obtained, and may be reduced with the metal: $M_2S_3 + M = 3MS$. The powdered metal hydride is normally used, however, at 1600°–2250° in a vacuum, or briquettes of sesquisulphide are impregnated in a vacuum with very hot molten metal[24]. Higher sulphides may be obtained by reactions such as[78] $M_2S_3 + S = 2MS_2$, and at 1500°–1600° in a vacuum by the reaction $M_2S_3 + MS = M_3S_4$.

6. Reaction of metal salts with hydrogen sulphide. The dry gas reacts with anhydrous chlorides and sulphates at 600°–1000° to give various products, often contaminated with oxysulphide. Ce_2S_3 was obtained thus[53,54], by treating cerium chloride, bromide, or iodide in a quartz tube for periods of the order of several dozen hours. The colour change often indicates the course of the reaction; a rapid temperature increase is avoided since the resultant sintering and fusion of the halide slows down the reaction.

7. Thermal dissociation of higher sulphides. Vapour pressure measurements for the metal-sulphur systems are based on this[38].

Oxysulphides. Rare-earth and actinide oxysulphides may be obtained from oxides and a deficiency of hydrogen sulphide, by partial oxidation of sulphides, by the reaction between oxides and sesquisulphides in a vacuum at 1200°–1500°:

$$M_2S_3 + 2M_2O_3 = 3M_2O_2S,$$

by heating metal oxides in carbon disulphide vapour at 700°–800° (for La, Nd, Sa, and Eu), and from the oxides and excess thioacetamide (for the remaining rare earths). Thiosulphates, which are salt-like compounds, are obtained from the soluble chlorides and sodium thiosulphate[55]:

$$2MCl_3 + 3Na_2S_2O_3 = M_2(S_2O_3)_3 + 6NaCl.$$

Scandium and Yttrium Sulphides and Oxysulphides

Scandium sulphide. Only the preparation of Sc_2S_3 has been described; $ScCl_3$ is heated in a current of hydrogen sulphide for several hours at 500°–600°, the temperature is raised to 600°–700° over 10–12 h, and then to 800°–1000° over several hours, and the product finally cools in a stream of the gas[18].

Yttrium sulphides and oxysulphides. Yttrium forms the compounds YS, Y_5S_7, Y_2S_3, YS_2, and Y_2O_2S. Flahaut and Guittard[19] first obtained YS by heating equal quantities of Y_2S_3 and aluminium for 4 h in a vacuum at 1350°. The chemical individuality of Y_5S_7 is very doubtful; it was obtained by heating Y_2S_3 rapidly in a graphite crucible, in a vacuum, by slow fusion of YS_2 in a vacuum[20], and by heating a mixture of 1 mole of YS and 2 moles of Y_2S_3 for 2 h at 1600°[20]:

$$YS + 2Y_2S_3 = Y_5S_7.$$

Y_2S_3 is made by heating the oxide at 1460° for $2\frac{1}{2}$ h in a current of dry hydrogen sulphide[20], or by heating the chloride in the same gas[18], as described above for Sc_2S_3. YS_2 is formed when Y_2S_3 and sulphur are heated in a sealed tube, first for 24 h at 400° and then for 5 days at 500°–600°[20]. It behaves like a polysulphide, and evolves sulphur on heating. The oxysulphide is made by heating Y_2S_3 with Y_2O_3 in a graphite boat for 3 h at 1350° in a vacuum[22], or by treatment of Y_2O_3 with dry hydrogen sulphide at 1000°[56]; the small proportion of sulphide produced is washed out with dilute (1 : 10) hydrochloric acid.

YS dissolves in dilute acetic and mineral acids, and is oxidised by permanganate and iodine solutions and, slowly, by heating in air. Y_2O_2S dissolves with difficulty in dilute hydrochloric acid, but readily in the concentrated acid; iodine and permanganate solutions do not oxidise it, but air at 200° converts it to Y_2O_3.

Little is known of the physical properties of yttrium sulphides; YS is metallic in that its resistivity approaches that of CeS, 9×10^{-5} ohm cm.

Sulphides and Oxysulphides of the Lanthanum Series

Lanthanum. This forms the compounds LaS, La_3S_4, La_2S_3, LaS_2, and La_2O_2S. La_2S_3 is most readily obtainable; the sulphate or chloride may be treated with hydrogen sulphide at 800°–1000°[18,25], or H_2S may be allowed to react directly with the oxide. Zvereva[24] treated $La(NO_3)_3$ with carbon tetrachloride vapour in a sealed quartz tube, and treated the resultant $LaCl_3$ with dry hydrogen sulphide in the same tube at 800°. We prepared La_2S_3 by heating La_2O_3 in a current of dry hydrogen sulphide for 1–2 h at 1000°–1200°. LaS was prepared by Zvereva[24] by sintering at 1800° and 10^{-4}–10^{-5} mm Hg pressure porous crucibles of the sesquisulphide, made at a compression of 1 ton cm^{-2}, filling them with a small stoichiometric excess of lanthanum, and heating in a vacuum. The molten metal penetrated the pores by capillarity and began to react very slowly at 1250°; the reaction was completed after 10 min at 1600°. Picon and Patrie[23] compressed an equimolecular mixture of La_2O_2S and La_2S_3 with aluminium powder and heated it in an alumina crucible for 4 h at 1350° in a vacuum furnace, and then for 2 h at 1600° in a graphite crucible to remove excess aluminium and alumina as AlO.

$$3La_2O_2S + 3La_2S_3 + 4Al = 12LaS + 2Al_2O_3.$$

We used the reaction

$$2La_2S_3 + La_2O_3 + 3C = 6LaS + 3CO$$

by heating briquettes of the required stoichiometric composition at 1650° and 10^{-1}–10^{-2} mm Hg in a vacuum furnace with a graphite heater[76]. The product was ground and reheated in order to obtain a full yield of the correct composition, 81.2% La and 18.7% S (and C, a trace). Iandelli[15] prepared pure LaS by the fusion of lanthanum and sulphur at 400°–500° in a sealed tube, and subsequent prolonged heating at 1000°–1100°.

La_3S_4 has been prepared by means of the reaction[25]:

$$La_2S_3 + LaS = La_3S_4,$$

heating at 1600° being prolonged for 2 h. LaS_2 (or La_2S_4) has been obtained by heating $La_2(SO_4)_3$ at 580°–600° in a current of dry hydrogen sulphide[18,57]:

$$La_2(SO_4)_3 + 12H_2S = La_2S_4 + 11S + 12H_2O.$$

In 16 h, 2–3 g of sulphate were converted. The reaction is too slow at lower temperatures, while La_2S_4 decomposes to La_2S_3 and sulphur at 620°. La_2S_4 is a polysulphide, concentrated hydrochloric acid liberating H_2S_2 from it.

Flahaut and Guittard[56] prepared La_2O_2S by means of the reaction

$$2La_2O_3 + La_2S_3 = 3La_2O_2S,$$

a mixture containing a 20% excess of sulphide being compressed and heated in a graphite boat at 1350° for 3 h in a vacuum. Excess sulphide is dissolved in acetic acid, and the product vacuum-dried. Eick[29] heated the oxide at 750°–800° for 2–8 h in carbon disulphide vapour; traces of the latter were removed in a vacuum, and other impurities oxidised at 800°–1200° for 1 h in an oxygen current. The basic sulphate formed was reduced to oxysulphide at 1200°–1300° in a current of hydrogen. The sulphate itself can be reduced thus at 800° [57]:

$$La_2(SO_4)_3 + 12H_2 = La_2O_2S + 10H_2O + 2H_2S.$$

The melting point of La_2S_3 is variously recorded as 2100° [27] and 2750° [18]; the sulphide is described as a black glass[27], as shiny, pale yellow or orange hexagonal platelets[18], and as a vermilion crystalline powder[24]. We obtained a yellow powder. These variations are probably due to differences in particle size. La_2S_3 is a semiconductor with thermo-e.m.f. of 270 μV deg^{-1}. We found it readily soluble in cold inorganic or organic acids, but inert towards boiling water and solutions of alkalis. Heating in a vacuum at 1800° causes loss of sulphur and formation of the La_2S_3–La_3S_4 eutectic, melting between 1800° and 2000°. The traces of oxygen present convert the vapour of the volatile La_3S_4 to La_2O_2S, which is harder to fuse and volatilise.

The physical properties of LaS are given in Table 6; it is unstable and is readily decomposed by dilute organic and inorganic acids. La_3S_4 is even less stable towards acids than LaS, and air converts it to the basic sulphate at 600°. LaS_2 dissociates at 660° to La_2S_3. La_2O_2S dissolves in dilute inorganic acids, but only with difficulty in acetic acid, unlike other lanthanum sulphides; it is oxidised above ~680° in air to the basic sulphate.

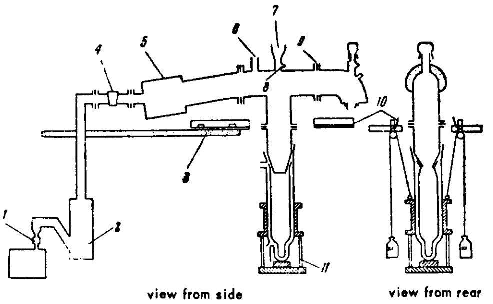

Fig. 4. Vacuum furnace for preparing CeS: 1) rubber tubing; 2) booster pump; 3) support; 4) tap; 5) oil diffusion pump; 6) connection to manometer; 7) detachable Pyrex window; 8) Pyrex T-piece; 9) screw flange; 10) iron bracket; 11) centre guide.

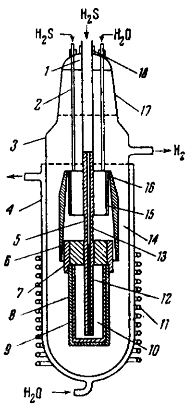

Fig. 5. Graphite furnace for preparing Ce_2S_3 and Ce_2O_2S: 1) Pyrex inlet tube for H_2S; 2) copper tube; 3) Pyrex tube; 4) water jacket; 5) graphite tube; 6) porous graphite support; 7) detachable graphite lid; 8) fixed graphite crucible; 9) detachable graphite crucible; 10) reaction mixture; 11) water-cooled induction heater; 12) graphite inlet tube; 13) threaded graphite parts; 14) carbon insulation; 15) copper partition; 16) porous graphite collar; 17) Pyrex cap; 18) seals.

Cerium. There has been much work on the sulphides and oxysulphides of this element, which are refractory materials suitable for use in the fusion and casting of high-melting metals. The compounds CeS, Ce_3S_4, Ce_2S_3 (α, β, and γ forms), CeS_2, and Ce_2O_2S are known. CeS is made by the reaction[30]

$$2Ce_2S_3 + 2CeH_3 = 6CeS + 3H_2.$$

The hydride, prepared from its elements at a little over room temperature, is mixed with Ce_2S_3 in a molybdenum vessel, and the powder is heated slowly at first in a vacuum furnace (Fig. 4) to remove hydrogen. The temperature and pressure are adjusted after a few minutes to 2200° and 10^{-4} mm Hg, when alkali metal and alkaline-earth impurities, oxygen, possibly evaporating as CeO, iron, and excess cerium are removed. Flahaut and Guittard[19] used the thermit reaction

$$Ce_2O_3 + 2Ce_2S_3 + 2Al = 6CeS + Al_2O_3,$$

the oxalate acting as a source of oxide. A mixture containing a fivefold excess of aluminium was compressed and heated for 2 h at 1600° in a vacuum, the aluminium evaporating as AlO. Samsonov and Radzikovskaya[52] reduced an oxide–sulphide mixture with carbon at 1500°–1700°, in a vacuum:

$$Ce_2S_3 + CeO_2 + 2C = 3CeS + 2CO.$$

The product contained 1.3–1.6% of carbon and up to 3% of oxygen, reduced to 0.2–0.3% and 0.1–0.2% respectively by the addition of 70% of the initial weight of Ce_2S_3 and subsequent vacuum heating at 1650°–1700° for 1 h. The use of all the sesquisulphide in one stage raises the impurity levels to 0.7–0.9% and 0.2–0.3% respectively. Iandelli[15] prepared CeS by prolonged heating of the elements in a sealed tube at 1000°–1100° after a short period at 400°–500°.

Very pure Ce_2S_3 may be prepared directly from its elements, and from the dioxide and hydrogen sulphide[51,52]. Picon[51,58] heated CeO_2 at ~1500° in a graphite boat, in hydrogen sulphide. Strotzer and coworkers[53] obtained a fairly pure specimen by heating CeO_2 for 2–3 h at 1200°–1300° in a current of hydrogen sulphide. Eastman and coworkers[30] used an unnecessarily complicated method, based on the reactions

$$6CeO_2 + 4H_2S = 3Ce_2O_2S + 4H_2O + SO_2,$$

$$Ce_2O_2S + 2H_2S + 2C = Ce_2S_3 + 2CO + 2H_2.$$

Hydrogen sulphide was passed through a graphite tube, at 25–50 litre per h, into an induction-heated reaction vessel inside a water-cooled Pyrex container (Fig. 5). The temperature was raised slowly to 1200°–1400°, and reaction was complete after 2–3 h. Flahaut and Guittard[31] prepared oxygen-free Ce_2S_3 by heating CeO_2 in a graphite boat in a current of hydrogen sulphide, dried over calcined Al_2S_3. Heating at 1000° for 10 h gave β-Ce_2S_3, which the authors considered idential with Eastman's product[30]. On heating CeS_2 in a vacuum at 850°–1100°, α-Ce_2S_3 is formed[31], described earlier[18]. The passage of very dry hydrogen sulphide for several dozen hours over cerium halides at 600°–1000°, in a quartz tube, yields Ce_2S_3 [18,54].

Ce_3S_4 is prepared from Ce_2S_3 and CeS, in Eastman's apparatus[30], for example. The important refractory "black cerium", a solid solution of Ce_2S_3 and Ce_3S_4, is formed when Ce_2S_3 is heated almost to its melting point[30]; Ce_2S_3 is heated in a molybdenum container to 1800° at 10^{-4}–10^{-5} mm Hg, and then, slowly, to 2200°. The composition of the product after several hours is $CeS_{1.40}$.

CeS_2 is prepared by heating γ-Ce_2S_3 with an excess of very dry sulphur at 600° in a sealed tube[31], and also from hydrogen sulphide and anhydrous cerium sulphate at 720°–750°.[59]

Ce_2O_2S is prepared[32] by passing hydrogen sulphide over CeO_2 at 1300°, in a refractory tube ($4CeO_2 + 4H_2S = 2Ce_2O_2S + 4H_2O + S_2$), by the reaction between ceric oxide and sulphur vapour ($CeO_2 + S_2 = Ce_2O_2S + SO_2$), and by the action of hydrogen sulphide on CeO_2 at 1000°–1300° in Eastman's apparatus, for less than 2 h. At higher temperatures Ce_2S_3 is formed in 2–3 h. Cerium oxalate may be heated with Ce_2S_3 in a vacuum, initially at 200° and then at 1350° ($2Ce_2O_3 + Ce_2S_3 = 3Ce_2O_2S$) [22]. The product is washed with cold 10% acetic acid to remove the sulphide. Partial oxidation of Ce_2S_3 with moist hydrogen sulphide at 500° also yields the oxysulphide[56].

A review by Samsonov, Popova, and Tikhomirova[60] describes most fully the preparation and properties of cerium sulphides. The hypothetical Ce–S phase diagram[30] shows two maxima corresponding to the congruently melting CeS and Ce_3S_4 (Fig. 6). These form a eutectic with S : Ce = = 1.14, melting near 2000°. CeS has the highest melting point of these sulphides, 2450°, a low vapour pressure at high temperatures, and metallic conductivity (thermo-e.m.f. 10 μV deg^{-1}). Very strong heating causes loss of sulphur and subsequent lattice defects. CeS is fairly stable to water, but dilute acetic and inorganic acids decompose it readily. With graphite at 1900° it yields the carbide; air begins to oxidise it at 200°–300°. Like other lanthanide and actinide sulphides, CeS has a metallic conductivity; it also has a small temperature coefficient of expansion, and articles made from it withstand heating at a rate of 1000° min^{-1}.

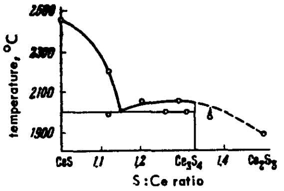

Fig. 6. Part of the Ce-S phase diagram.

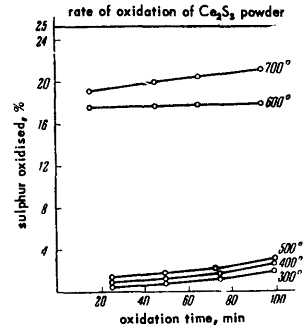

Fig. 7. Rate of oxidation of Ce_2C_3 powder.

TABLE 7. Melting points of cerium sulphides and oxysulphide and their mixtures.

Initial compound	Added components			
	CeS	Ce_3S_4	Ce_2S_3	Ce_2O_2S
CeS	2450±100	2000—75	—	1900±100
Ce_3S_4	—	2050±75	1900±2000	1650
Ce_2S_3	—	—	1890±50	1650
Ce_2O_2S	—	—	—	2000±20

Ce_3S_4 melts and vaporises more readily, but is oxidised by air only at 700°. Chlorine reacts with it at 200°, and water vapour above 300°.

Ce_2S_3 is stable in air at normal temperatures, but burns with a blue flame on heating. An air current begins to oxidise it slowly at 300° and rapidly at 600° (Fig. 7). Ce_2S_3 is unaffected by boiling water or alkali solutions, but dissolves in dilute inorganic and organic acids. It is very brittle, like all sulphides; it has a low enough temperature coefficient to withstand heating at 100° min^{-1}. Its semiconductor properties have long been suspected because of its high resistivity; its thermo e.m.f. is 430 μV deg^{-1}. It has long been suggested that Ce_2S_3 and Ce_3S_4 form solid solutions melting between 1900° and 2000° (Fig. 6), or even near 2200°[18]. Above 2300° the mixtures give off sulphur rapidly. Zachariasen[2] showed by X-ray analysis that the region of homogeneity of these solutions is bounded by Ce_3S_4, in the cubic unit cell of which cerium atoms occupy all the vacant places, and by Ce_2S_3, in the disordered structure of which every ninth metal-atom site is vacant. The lattice constants change regularly with the S : Ce ratio:

S : Ce	a, kX	Density from X-ray analysis, g cm^{-3}
1.495 (~Ce_2S_3)	8.6173	5.186
1.45	8.6131	5.313
1.40	8.6123	5.455
1.33 (Ce_3S_4)	8.6076	5.675

Zachariasen correctly relates the decrease of lattice constant, as the extent of the lattice defect decreases, to the transition from the largely ionic bond in Ce_2S_3 to the largely metallic one in Ce_3S_4.

CeS_2 is unstable towards air and water, and may be considered a polysulphide since sulphur separates when it dissolves in hydrochloric acid. Cerium sulphides are pyrophoric when finely divided. Additon of Ce_2O_2S to the sulphides lowers their melting points by 200°–400°, so that refractories of this type must be free of oxygen (Table 7).

Ce_2O_2S is insoluble in water, and dissolves with difficulty in acetic acid but readily in inorganic acids, evolving hydrogen sulphide. It reacts with cerium only above 1300°, the equation evidently being[32]

$$Ce_2O_2S + Ce = CeS + 2CeO.$$

Ce_2O_2S is the only rare-earth oxysulphide to be oxidised at room temperature[56]; the colour changes from brown to dark green, and the lattice constants decrease. It gains weight rapidly above 180°, but loses it above 650° as the basic sulphate is formed.

CeS, and solid solutions of Ce_2S_3 and Ce_3S_4, are important refractory materials, being resistant to fused metals (Tables 8 and 9[61]).

Praseodymium, neodymium, and samarium. These form the compounds MS, M_3S_4, M_2S_3, and M_2O_2S. PrS and NdS were prepared by prolonged heating of the elements in a sealed tube at 1000°–1100°, to ensure homogeneity, after a preliminary period at 400°–450°[15]. Iandelli[62] prepared SmS in this way. PrS, NdS, and SmS are also prepared by reducing a sesquisulphide–oxysulphide mixture with aluminium, at 1350° in a vacuum[23]:

$$2M_2S_3 + 3M_2O_2S + 4Al = 12\ MS + 2Al_2O_3.$$

A mixture of MS and M_2S_3, heated for 2 h at 1600°, gives M_3S_4 [25]:

$$M_2S_3 + MS = M_3S_4.$$

The sesquisulphides are prepared, like those of La and Ce, from hydrogen sulphide and the oxides at 1500°–1550°[27] or the chlorides or sulphates at 1000°[16]; the oxysulphides are prepared by the method used for lanthanum[29,56]. The monosulphides react with dilute acids, evolving two volumes of hydrogen sulphide to one of hydrogen with hydrochloric or acetic acid. Solution in nitric or concentrated sulphuric acid is accompanied by separation of sulphur. Hydrogen peroxide oxidises PrS, NdS, and SmS, but dilute permanganate only SmS; slow atmospheric oxidation begins at 200°. Pr_3S_4, Nd_3S_4, and Sm_3S_4 are decomposed by acids, evolving eight volumes of hydrogen sulphide to one of hydrogen.

TABLE 8. Effect of molten metals on CeS.

Metal	Temp., °C	Time, min	Atmosphere	Type of interaction
U	1300	5	vacuum	none; shining ingot produced
U	1400	30	»	ditto
U	1900	4	»	golden efflorescence on ingot surface
Ce	1500	15	»	none
Th	1825	6	—	pure ingot firmly attached to crucible
Mg	900	5	vacuum	good ingot, readily leaving crucible
Bi	1400	5	»	as for Th
Bi	1500	10	»	ditto
Al	1500	10	»	fine black film on ingot
Ti	1500	10	»	as for Th
Pt	1900	10	»	crucible destroyed by formation of CePt
Sn	1200	3	»	ingot firmly attached to crucible; grey film on surface
Zn	500	1	»	as for Mg
Zn	700	5	»	ditto

TABLE 9. Effect of molten metals on Ce_2S_3–Ce_3S_4 alloy.

Metal	Temp., °C	Time, min	Type of interaction
U	1475	30	black efflorescence on ingot surface
Ce	1500	15	black ingot, readily leaving crucible; bronze efflorescence crucible
Th	1825	6	ingot readily leaves crucible; fine layer of CeS on crucible surface
Mg	1900	5	good ingot; crucible partly reduced to CeS by magnesium vapour
Be	1400	5	good ingot, not adhering to crucible; crucible not destroyed
Be	1500	10	slight* reduction of crucible to CeS
Bi	1200	5	good ingot; some metal attached to crucible, but latter not destroyed
Al	1500	10	ditto
Fe	1500	10	ditto, but no adhesion to crucible
Ti	1500	10	good ingot with a film of CeS, adhering to crucible
Sn	1200	3	pure ingot, not reacting with crucible but adhering lightly to it
Zn	900	5	no reaction with crucible; slight adhesion to crucible

* Russian ambiguous; could mean "ready reduction ..." (Ed. of Translation).

Air oxidises them slowly at 500°, forming the basic sulphates $(MO)_2SO_4$, at 600°. Sm_3S_4 sublimes at 600°. The oxysulphides dissolve more slowly than the sulphides in dilute inorganic acids; Sm_2O_2S alone is insoluble in cold dilute acetic acid. Iodine and permanganate solutions do not oxidise the oxysulphides.

Picon and Flahaut showed the magnetic susceptibilities per metal atom of M_3S_4 and M_2S_3 to be almost identical, and inferred that the metals are trivalent[25]. The high value for Sm_3S_4, 2350 × 10^{-6}, they attributed to the composition $Sm_2S_3.SmS$.

Europium. EuS, Eu_3S_4, $Eu_2S_{3.81}$, and Eu_2O_2S are known. EuS is prepared from $EuCl_2$ and excess sulphur, heated up to 600° over several hours in a rapid stream of pure hydrogen:

$$EuCl_2 + S + H_2 = EuS + 2HCl.$$

Excess sulphur is removed by prolonged heating at 820° in a stream of hydrogen. Domange, Flahaut, and Guittard[34] prepared EuS by heating Eu_2O_3 at 1000°–1200° for 1 h in oxygen-free hydrogen sulphide. Eu_3S_4 is prepared by heating a mixture of composition 3EuS + S at 600° in a sealed tube. If sulphur is in excess, $Eu_2S_{3.81}$ is formed under those conditions [34]. At 600° a mixture of composition $2EuS + 2Eu_2O_3 + S$ yields Eu_2O_2S, excess sulphur being removed with carbon disulphide [34]. Eick[29] obtained Eu_2O_2S by heating Eu_2O_3 in carbon disulphide vapour at 750°–800°.

Gadolinium. GdS, α- and γ-Gd_2S_3, GdS_2, and Gd_2O_2S are known. GdS is prepared from aluminium and an equimolar mixture of Gd_2S_3 and Gd_2O_2S [35]:

$$3Gd_2S_3 + 3Gd_2O_2S + 4\ Al = 12GdS + 2Al_2O_3.$$

Gd_2O_3 and hydrogen sulphide yield α-Gd_2S_3 and a little oxysulphide at 800° [35], and γ-Gd_2S_3 at 1000°. Purer α-Gd_2S_3 is obtained by the thermal dissociation of GdS_2 at 800°. Gd_2S_3 is obtained in an unknown modification from the sulphate and hydrogen sulphide at 1000° [18]. At 600°, Gd_2S_3 reacts with sulphur in a sealed tube, yielding GdS_2 [35]. Gd_2O_2S is obtained by the most general method for rare earths, described above for La_2O_2S:

$$2Gd_2O_3 + Gd_2S_3 = 3Gd_2O_2S.$$

Eick[29] prepared the oxysulphides of gadolinium and other rare earths by heating the oxide with excess thioacetamide in a sealed tube for 4–6 h at 1200°. At 800° impurities were burned in the tube by a stream of air, and the product was then reduced again in a stream of hydrogen.

Terbium. Only Tb_2O_2S is known, prepared by Eick[29] in the same way as Gd_2O_2S.

Dysprosium. Flahaut, Guittard, Loriers, and Patrie prepared Dy_5S_7, α-, γ-, and δ-Dy_2S_3, DyS_2, and Dy_2O_2S. DyS, prepared by heating δ-Dy_2S_3 with a large excess of aluminium in a vacuum at 1450° [21], contains a variable excess of sulphur. The cubic unit cell dimension increases as the sulphur content falls. Dy_5S_7 is obtained by heating a mixture of δ-Dy_2S_3 and 20–50% of aluminium for 4 h at 1300°–1350° in a vacuum [21]. Hydrogen sulphide and Dy_2O_3 yield α-Dy_2S_3 and a little Dy_2O_2S at 800°, and δ-Dy_2S_3 at 1000°–1300°. γ-Dy_2S_3 is formed from α-Dy_2S_3 at 1250°, in a stream of hydrogen sulphide [21]. DyS_2 is prepared, like GdS_2, from the sesquisulphide and sulphur at 600° in a sealed tube. Dy_2O_2S is obtained in the same way as La_2O_2S and Gd_2O_2S [29,56].

Holmium. Eick[29] prepared Ho_2O_2S in the same way as Gd_2O_2S.

Erbium. Like dysprosium, this forms the compounds ErS, Er_5S_7, Er_2S_3, ErS_2, and Er_2O_2S. At 1450° in a vacuum a large excess of aluminium reduces Er_2S_3 to ErS, the composition of which varies. The cubic unit-cell dimension increases from 5.424 Å to 5.452 Å as the sulphur content falls [21]. Er_5S_7 is prepared in the same way as Dy_5S_7. Er_2O_3 reacts less readily than Gd_2O_3 and Dy_2O_3 with hydrogen sulphide, giving only the oxysulphide at 1000° and Er_2S_3 only at higher temperatures; at 1250° the last traces of oxygen disappear. At 1000° hydrogen sulphide converts erbium chloride to Er_2S_3 [18]. ErS_2 and Er_2O_2S are prepared in the same way as the gadolinium and dysprosium compounds [29,35,56].

Thullium. Eick[29] prepared Tm_2O_2S by the general method of heating Tm_2O_3 with excess thioacetamide.

Ytterbium. Domange, Flahaut, Guittard, and Loriers[36] prepared $YbS_{1.14}$, $YbS_{1.33}$, $YbS_{1.48}$, and Yb_2S_3. The sulphide $YbS_{1.14}$ was formed on heating $YbS_{1.33}$ and $YbS_{1.48}$ for several hours at 1450° in a vacuum. At 1000°–1100° in a vacuum, Yb_2S_3 forms $YbS_{1.33}$. At 1350°–1400°, Yb_2O_3 and hydrogen sulphide form $YbS_{1.48}$, and at 900°, they form a mixture of Yb_2S_3 and Yb_2O_2S. Pure Yb_2S_3 is prepared by heating Yb_2O_3 at 1300° in hydrogen sulphide to remove oxygen completely, and then by converting the lower sulphide formed to Yb_2S_3 at 1100° for 1 h. The sesquisulphide is also prepared from $YbCl_3$ and hydrogen sulphide at 1000° [18]. Yb_2O_2S is prepared by heating Yb_2O_3 with a 5% excess of Yb_2S_3 to 1350° under argon[22], or from Yb_2O_3 and dry hydrogen sulphide at 1000° [56]. It dissolves with difficulty in concentrated hydrochloric acid, but readily in aqua regia.

Lutetium. Only Lu_2O_2S has been described; it was obtained by Eick[29] by heating Lu_2O_3 with thioacetamide.

Actinide Sulphides and Oxysulphides

Actinium. Only Ac_2S_3 is known, prepared by heating the oxalate or oxide to 1400° in a graphite crucible, in a stream of hydrogen sulphide first passed through carbon disulphide [57].

Thorium. The compounds ThS, Th_2S_3, Th_4S_7 (or Th_7S_{12}), and ThOS are well known; they have promising refractory and semiconductor properties similar to those of the cerium compounds. ThS and Th_2S_3 are the most stable, the composition of the latter varying from $ThS_{1.22}$ to $ThS_{1.59}$ [40]; that of Th_7S_{12} varies from $ThS_{1.71}$ to $ThS_{1.76}$ [1,38]. Although the Th–S phase diagram has not been studied, the existence of these sulphides is indicated by preparative work, particularly that of Strotzer and Zumbusch[38]. Various products may be obtained, depending on the temperature, pressure, and proportions of the reagents. ThS and Th_2S_3 are prepared from stoichiometric proportions of the elements [40], and by thermal dissociation of higher sulphides or their interaction with a theoretical quantity of thorium hydride. Th_4S_7 is formed on dissociation of ThS_2 or the polysulphide, ThS_x [38]. ThS_2 is obtained by the action of hydrogen sulphide on the metal [63–65], the halides [66,67], or the hydride [41,42], from sulphur and thorium [38,63,64] or its carbide [65], by the action of carbon disulphide and hydrogen on ThO_2, [68] and by the treatment of mixed thorium and potassium chlorides with hydrogen sulphide [66,67]. ThO_2 may also be heated with carbon in a stream of hydrogen sulphide [69]. ThOS is obtained by treating ThO_2 with carbon disulphide [70], or the anhydrous chloride with hydrogen sulphide [71]. It is also formed as an impurity when ThS_2 is prepared in the presence of oxygen. At 600°–700° sulphur replaces the non-metal in thorium selenides and tellurides; these compounds also react with other sulphides [10], *e.g.*:

$$TiS_2 + ThTe_2 = ThS_2 + TiTe_2.$$

When heated in air or oxygen, thorium sulphides yield the oxide and sulphur dioxide. Below 300° chlorine converts them to $ThCl_4$ and sulphur dichloride. They are decomposed by concentrated inorganic acids, but not by boiling water or alkali solutions; they are oxidised by boiling hydrogen peroxide. ThS has the silvery lustre and conductivity of a metal, and is diamagnetic. Its dissociation pressure is less than 10^{-3} mm Hg at 2200°, and its microhardness[40] is $\sim$350 kg mm^{-2}. ThS forms a continuous series of solid solutions with CeS and US, for some of which lattice constants determined by Zachariasen[1] are given in Table 10. Th_2S_3 is very stable when heated in a vacuum, and melts between 1900° and 2000° without appreciable evaporation. It is diamagnetic, of microhardness[40] $\sim$250 kg mm^{-2}.

TABLE 10. Composition, %.

ThS	CeS	US	a, kX
33	67	—	5 725
50	50	—	5.709
67	33	—	5.701
50	—	50	5.587

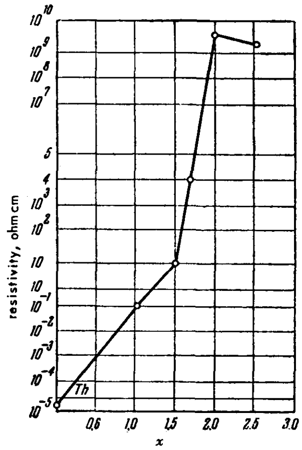

Fig. 8. Relation between resistivity of ThS_x and x.

TABLE 11. Electrical properties of thorium sulphides.

Formula	Resistivity, ohm cm	Temp. coeff. of thermo-e.m.f., mV deg^{-1}	Type of conductor
$ThS_{1,00}$	0.2	—	metallic
$ThS_{1,50}$	1.0	0.1	*P*-type semiconductor
$ThS_{1,70}$	25000	0.2	*P*-type semiconductor
$ThS_{2,00}$	10^7	—	semiconductor
$ThS_{2,50}$	$5 \cdot 10^6$	—	semiconductor

ThS_2, prepared as described above, varies in colour from yellow to black, probably because other sulphides are formed. Specimens, whose composition was checked by X-ray analysis, are purple or brown-violet[38,41,42], ThS_2 melts at 1904°, decomposing to lower sulphides.

In a study of the electrical properties of the sulphides, selenides, and tellurides of Ti, Zr, Hf, and Th, McTaggart[10] showed the sulphides of composition $ThS_{1.5}$, $ThS_{1.70}$, $ThS_{2.00}$, and $ThS_{2.50}$ to be semiconductors (Table 11, Fig. 8); he considers invalid the work of Eastman *et al.*[42], which showed the resistivity of all these compounds to be lower than 10^{-3}–10^{-4} ohm cm. The thorium sulphides are stable towards molten metals (Tables 12 and 13); like the selenides and tellurides, they resemble graphite and molybdenum sulphide in their lubricating power, and may be used as solid lubricants and as components of metal-ceramic bearings[10].

TABLE 12. Effect of molten metals on sintered ThS.

Metal	Temp., °C	Time, min	Atmosphere	Type of interaction
Ce	1500	15	vacuum	good ingot, firmly attached to crucible
Th	1325	6	»	ditto
Mg	900	5	»	good ingot, easily detached from crucible
Al	1500	10	»	ditto
Fe	1500	10	»	fine black film on ingot

TABLE 13. Effect of molten metals on Th_2S_3 and Th_4S_7.

Sulphide	Metal	Temp., °C	Time, min	Type of interaction
Th_2S_3	Ce	1500	15*	good ingot sticking firmly to crucible
Th_2S_3	Th	1500	15**	ditto
Th_2S_3	Th	1825	6	ingot easily detached from crucible, and showing fine efflorescence
Th_4S_7	U	1300	5	pure ingot, easily detached from crucible
Th_4S_7	U	1475	30	ditto
Th_4S_7	Ce	1500	12	good ingot, adhering to crucible
Th_4S_7	Ce	1500	15	ditto with fine layer of Th_4S_7 on ingot

* Porosity of crucible 20%.
** Porosity of crucible 5%.

Protactinium. Only PaOS is known, prepared by Elson, Fried, and Sellers[43] from hydrogen sulphide and $PaCl_5$.

Uranium. US, U_2S_3, U_3S_5, α-, β-, and γ-US_2, UOS_2, and UOS are known. US is obtained at 400°–500° from stoichiometric proportions of hydrogen sulphide and uranium powder, obtained by decomposition of the hydride[42]. Picon and Flahaut[45] prepared US, with the oxysulphide as an impurity, from UOS and aluminium at 1775°, excess aluminium and Al_2O_3 vaporising at 1500° in a vacuum. It dissolves in inorganic acids, but is inert towards acetic acid and ammonia and alkali solutions. It is converted to UOS in 48 h at 160°. U_2S_3 is formed on heating US_2 powder with aluminium in a graphite boat at 1325° for $1\frac{1}{2}$ h, in a vacuum[72]. Hot 50% acetic acid removes excess aluminium and Al_2S_3. U_2S_3 is also formed from stoichiometric quantities of uranium powder and hydrogen sulphide[42]. U_3S_5 is prepared by heating US_2 for 3 h at 1530° in a vacuum[72], and comprises most of the mixture obtained by heating US_2 under hydrogen for 2 h at 1530°. US_2, like US and U_2S_3, may be obtained from hydrogen sulphide and the powdered metal. Excess hydrogen sulphide reacts with UO_2 and carbon at 1200°–1300° to give UOS and steam at low temperature; carbon monoxide is evolved at higher temperatures, and the reaction is completed by a brief increase of temperature to 1400°–1500°.

Picon and Flahaut[47] report that α- and β-US_2 are stable above and below 1350° respectively; from U_3S_5 and dry hydrogen sulphide at 380° they obtained γ-US_2, which passes into the β form at 425°[48]. The three forms differ very little chemically, γ-US_2 being the most easily oxidised. U_2S_3, U_3S_5, and US_2 are also very similar chemically; they all react with inorganic acids, aqueous iodine, permanganate solution, and hydrogen peroxide[46], but not with aqueous solutions of strong alkalis or potassium dichromate. U_2S_3 and U_3S_5, unlike US_2, are not soluble in 50% acetic acid, even at the boil. The uranium sulphides are inert towards air over periods of several months, but are slowly converted to oxides at 300°. UOS is obtained by heating UO_2 or U_3O_8 with carbon in a stream of hydrogen sulphide[32]. On addition of ammonium sulphide to a solution containing the uranyl ion, the brown, relatively unstable UO_2S is precipitated in an impure state[73].

Neptunium. On treating NpO_2 at 1000° with a mixture of hydrogen sulphide and carbon disulphide, prepared by bubbling the former through carbon disulphide at 25°, NpOS is formed after a few hours and Np_2S_3 after 12 h[49]. The products were identified by X-ray analysis[1].

Plutonium. PuS, (Pu_2S_3–Pu_3S_4), and Pu_2O_2S are known. PuS was obtained by chance in an attempt to reduce PuF_3 with barium vapour in a barium sulphide crucible[50]. (Pu_2S_3–Pu_3S_4) was formed when dry plutonium "hydroxide" in a graphite crucible was heated slowly to 1340° under dry hydrogen sulphide[50] and maintained at 1340° for 2 h. Another specimen was made by heating $PuCl_3$ in a quartz crucible for 1 h at 900° in a stream of hydrogen sulphide. Pu_2O_2S was obtained by passing technical hydrogen sulphide, dried over phosphorus pentoxide, over a graphite crucible containing dry plutonium "hydroxide". The temperature was gradually raised to 1225°–1300° in 1 h and kept there for a further 30 min.

Americium. As with neptunium, Am_2S_3 and AmOS are formed from AmO_2, hydrogen sulphide, and carbon disulphide at 1500°[75].

APPLICATIONS

Although investigation of the rare-earth and actinide sulphides is incomplete, many possible technological uses are apparent. Thorium and cerium sulphides withstand fused salts and metals of high-melting point, such as uranium, cerium, thorium, titanium, and iron, and also relatively low-melting metals such as bismuth, tin, magnesium, and aluminium[77]. A method is described of preparing crucibles and other refractory vessels from these two sulphides, which are mixed in powder form with a 5% solution by volume of naphthalene in ether and moulded at a pressure 3.5–7 ton cm^{-2} before being sintered in vacuum furnaces[61]. Denser products are made by hot pressing of the powdered sulphides[40]. The refractories produced are very resistant to heat impact, but can only be used in a vacuum or an inert atmosphere[75].

The sesquisulphides in particular[10] combine semiconductor properties with a high melting point and low vapour pressure. The higher sulphides tend to lose sulphur at relatively moderate temperatures. The sulphides, especially those of cerium, lanthanum, and thorium, should be of use as thermistors and resistances, and also as thermoelectric generators on account of their high thermo-e.m.f. The sulphides which are semiconductors should also be investigated as possible heterogeneous catalysts. The monosulphides may be used in anti-emission screens on account of their high electronic work functions. The thorium sulphides are good solid lubricants. Further investigation and the increasing availability of these compounds will lead to their application in new fields, especially precision metallurgy and semiconductor technology, and to progress in the elucidation of their crystal and electronic structure.

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STEREOCHEMISTRY OF NUCLEOPHILIC ADDITION REACTIONS TO THE CARBONYL GROUP OF CYCLIC KETONES

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CONTENTS

INTRODUCTION

Stereochemical studies have undergone a qualitative change in the last 15–20 years, because of the development of conformational analysis. In addition to static stereochemistry, an ever increasing part is beginning to be played by studies on dynamic stereochemistry, in which a chemical reaction is investigated from the stereochemical viewpoint[1]. It is difficult to overestimate the importance of this movement in organic chemistry. In fact, the stereospecific synthesis of many compounds can be successfully achieved in practice only by using stereospecific reactions, and such syntheses are of particular importance in the chemistry of polymers and natural products, which have recently taken on an ever increasing economic significance. Conformational analysis has contributed to the successful study of the stereoselectivity of reactions and to the prediction of the possible results of a chemical process[2]. At present there exist a number of communications on the steric course of substitution and cleavage reactions at a saturated carbon atom, addition to a carbon–carbon double bond, etc.[1], but until recently, the stereochemistry of addition to the double bond of the carbonyl group, particularly in cyclic ketones, had received little attention. The original work and review articles in this field are devoted almost exclusively to the reduction of ketones to alcohols[3].

In the present review we have attempted to systematise the existing data on nucleophilic addition reactions (Ad_N) to the carbonyl group of cyclic ketones with a six-membered ring, free of additional distorting factors (*endo*- and *exo*-cyclic double bonds, oxide rings, bridge linkages, etc.).

This review embraces the literature on mono-, di-, tri-, tetra-, penta-, and hexa-substituted cyclohexanones, including polycyclic systems containing the keto-group in a six-membered ring. As reactions for comparison, we have selected chemical reduction under alkaline conditions, the acetylene and cyanohydrin syntheses, and the addition of organometallic reagents, particularly Grignard reactions.

1. MONOSUBSTITUTED CYCLOHEXANONES (see Table 1)*

Addition reactions to the carbonyl-group of monosubstituted cyclohexanones, particularly 2-methylcyclohexanone, have long been described, but the composition of the

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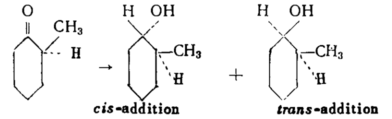
* The following symbols are used in the tables. The indices α and β, as in the steroid series, indicate the disposition of substituents above and below the plane of the diagram; 0 isomer not detected; + present in the mixture; *x* predominates in the mixture; *xx* greatly predominates in the mixture; a numeral with an asterisk * the yield (in %) based on the starting ketone; ! our suggested configuration; ? configuration (or content in the mixture) not established or doubtful; ?? configuration unknown; *a* and *e* conformation of the new substituent; substituent positions are indicated with reference to the carbonyl group.

TABLE 1. Stereosolubility of addition reactions to monosubstituted cyclohexanones.

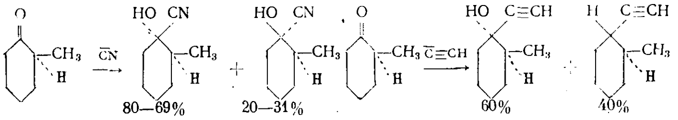
Existing substituent	Reagent	Entering substituent, R′	Content in product mixture, %		Reference
			cis-addition (R–R′)	*trans*-addition (R–R′)	
			Ortho-substitution		
CH_3	Na + ROH	H	*xx*, 98—99, 97—99, 88,72	?,2—1,3—1,12, 28	4,5,6 7,8
CH_3	$LiAlH_4$	H	82,70,69,64,60 60	18,30,31,36,40	9,10,11,12 8
CH_3	$NaBH_4$, CH_3OH	H	69	31	9
CH_3	$NaBH(CH_3O)_3$	H	70	30	9
CH_3	$NaBH_4$, pyridine	H	56	44	9
CH_3	$LiAlH_4$, $AlBr_3$	H	59—71	41—29	7,11
CH_3	KBH_4	H	41	59	8
CH_3	KCN	CN	80—75	20—25	13,14
CH_3	HCN	CN	69	31	14
CH_3	$HC\equiv CH$, KOH	$C\equiv CH$	60	40	13
CH_3	$HC\equiv CNa$, NH_3	$C\equiv CH$	51,34,23	49,66,77 (!)	15,16,17
CH_3	$HC\equiv CK$, t-C_4H_9OH	$C\equiv CH$	60	40(!)	18
CH_3	CH_3MgI	CH_3	25	75	19
C_2H_5	Na + ROH	H	*xx*	?	20,21
C_3H_7	Na + ROH	H	*xx*	?	20,22
iso-C_3H_7	$LiAlH_4$	H	69—57	31—43	11
iso-C_3H_7	$LiAlH_4$, $AlBr_3$	H	66—48	34—52	11
t-C_4H_9	Na + ROH	H	85,*xx*	15,?	11,20
t-C_4H_9	$LiAlH_4$	H	51	49	23
C_6H_{11}	Na + ROH	H	97,81	3,19	24,11
C_6H_{11}	$LiAlH_4$	H	71—68	29—32	11
C_6H_{11}	$LiAlH_4$, $AlBr_3$	H	57—13	43—87	11
C_6H_{11}	C_6H_5MgBr	C_6H_5	one isomer (?)		25
$C_6H_5CH_2$	$LiAlH_4$	H	*xx*	+	24,26
$C_6H_5CH_2$	KBH_4	H	*xx*	+	24
$C_6H_5CH_2$	$HC\equiv CNa$, NH_3	$C\equiv CH$	two isomers		27
C_6H_5	Na + ROH	H	100	0	24
C_6H_5	KCN	CN	44—46 (!)	+	28
			Para-substitution		
CH_3	Na + ROH	H	*xx*, 83	?,17	4,29,8
CH_3	$LiAlH_4$	H	81,79—81 75,84	19,21—19,25,16	12,30 8,10
CH_3	$NaBH_4$, CH_3OH	H	75	25	9
CH_3	$NaBH_4$, pyridine	H	60	40	9
CH_3	KBH_4	H	65	35	8
CH_3	$HC\equiv CNa$, NH_3	$C\equiv CH$	one isomer (??)		31
CH_3	C_6H_5MgBr	C_6H_5	one isomer (??)		32
CH_3O	$HC\equiv CK$, t-C_4H_9OH	$C\equiv CH$	one isomer (??)	27 60 did not agree after hydrogenation	33
CH_3O	C_2H_5MgBr	C_2H_5	one isomer (??)		33
iso-C_3H_7	Na + ROH	H	*xx*	+	29,34
iso-C_3H_7	$HC\equiv CNa$, NH_3	$C\equiv CH$	12 (?)	88 (?)	35
t-C_4H_9	Na + ROH	H	*xx*	+	29
t-C_4H_9	$LiAlH_4$	H	91—93	9—7	30
t-C_4H_9	$HC\equiv CNa$, NH_3	$C\equiv CH$	86	14	35
t-C_4H_9	C_2H_5MgBr	C_2H_5	27	73	36
C_6H_{11}	Na + ROH	H	55	45	8
C_6H_{11}	$LiAlH_4$	H	43	57	8
C_6H_{11}	KBH_4	H	50	50	5
			Meta-substitution		
CH_3	Na + ROH	H	?,20,22	*xx*.80,78	4,8,37
CH_3	$LiAlH_4$	H	6—7,8,11,15,13	94—93,92,89 85,87	37,9,8 30,10
CH_3	$LiAlH_4$, $AlBr_3$	H	6—7	94—93	11
CH_3	KBH_4	H	42	58	8
CH_3	KCN	CN	25	75	38
CH_3	$HC\equiv CNa$, NH_3	$C\equiv CH$	15—25 (??)	85—75	39
CH_3	$C_6H_5C\equiv CH$, KOH	$C_6H_5C\equiv C$	one isomer (??)	95—97*	42,43
CH_3	$C_6H_5C\equiv CMgBr$	$C_6H_5C\equiv C$			
CH_3	CH_3MgI	CH_3	60	40	38
t-C_4H_9	$LiAlH_4$	H	+	*xx*	40

resulting mixture of isomers has only rarely been determined.

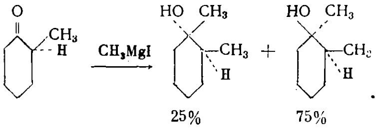
Thus in the reduction of 2-methylcyclohexanone with sodium and alcohol, Skita[4] separated only *trans*-2-methylcyclohexanol (*cis*-addition of hydrogen) from the reaction products, but he suggested that no method of reduction would give one isomer exclusively; the other would always be formed, even if in small amount. Later work has confirmed this in respect of 2-methylcyclohexanone; a number of workers[4-8] found that the reduction of 2-methylcyclohexanone with sodium and alcohol produces a mixture containing 99–72% of the *trans*- alcohol (*cis*-addition) and 1–25% of the *cis*-alcohol (*trans*-addition):



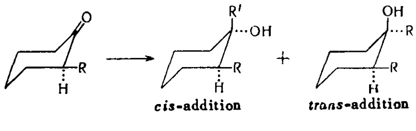
Reduction of this ketone with lithium aluminium hydride gives[8-12] from 60 to 82% of the *trans*-alcohol (*cis*-addition) and from 8 to 40% of the *cis*-alcohol (*trans*-addition). The predominant formation of the *trans*-alcohol is also found in the reduction of 2-methylcyclohexanone with sodium borohydride[9]. The addition of carbon-containing nucleophilic reagents to 2-methylcyclohexanone has also been much described, but apart from a few data on the acetylene synthesis, the stereochemistry of these reactions has not been studied at all until recently. The data on the acetylene synthesis[15-18] are so contradictory that no conclusions can be drawn. The recent study of the stereochemistry of the cyanohydrin, acetylene, and Grignard reactions of 2-methylcyclohexanone showed that a mixture of isomers is formed here also, *cis*-addition predominating in the cyanohydrin and acetylene syntheses. Thus the cyanohydrin synthesis produces a mixture containing, depending on the reaction conditions, from 80 to 69% of *cis*-1-cyano-2-methylcyclohexanol and from 20 to 31% of the *trans*-compound, while under the Nazarov–Favorskii conditions reaction with acetylene under pressure gives 60% of *cis*-1-ethynyl-2-methylcyclohexanol and 40% of the *trans*-compound[13]:



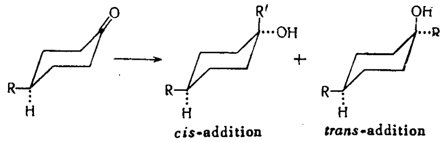
On the other hand, it has been shown[19] that the stereochemistry of the Grignard reaction is quite different, *trans*-1,2-dimethylcyclohexanol (*trans*-addition) predominating (75%) in the resulting mixture:



Comparison of data on the reduction of other 2-substituted cyclohexanones shows that reduction with sodium[11,20-22,24] or complex metal hydrides[11,23,24,26] also produces mainly the *trans*-alcohols with *cis*-configuration between the 2-substituent and the entering substituent (H):

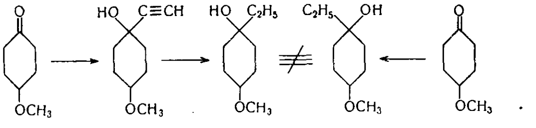


The position in respect of 4-substituted cyclohexanones is analogous, reduction of the ketones with sodium in alcohol[4,8,29,34] or with alkali metal hydrides[5,8-10,12,30] also producing predominantly the *trans*-alcohol with the *cis*-arrangement between the existing and the new (H) substituent:

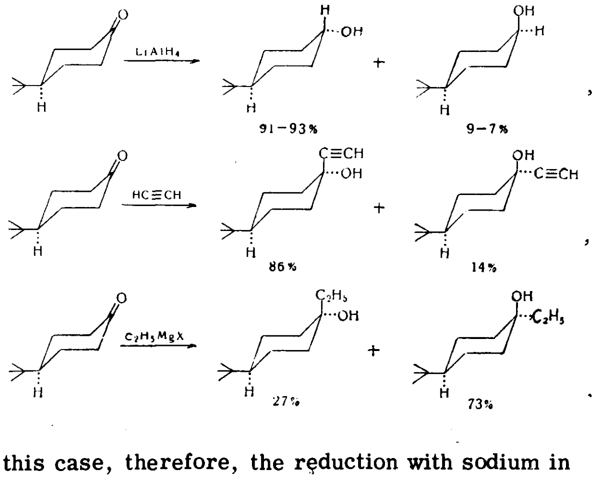


Information on the stereochemistry of the addition of carbon-containing substituents is very sparse in this series also.

Marvel's results[33] are interesting. By condensing 4-methoxycyclohexanone with acetylene in the presence of potassium t-butoxide he obtained, in low yield (27%), one isomer of 1-ethynyl-4-methoxycyclohexanol, which on hydrogenation gave 1-ethyl-4-methoxycyclohexanol. The reaction between the same ketone and ethylmagnesium bromide gave a different stereoisomer of 1-ethyl-4-methoxycyclohexanol in 63% yield. However, he did not establish the configurations of these compounds:

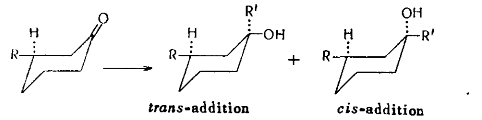


More is known about addition to 4-t-butylcyclohexanone. It has been shown[40] that this ketone exists only in one conformation, in which the t-butyl-group is in the equatorial position. Stork and White[29] show that when it is reduced with sodium in alcohol, it forms almost exclusively a product with an axial hydrogen atom at C_1, *i.e. trans*-4-t-butylcyclohexanol. The reduction of 4-t-butylcyclohexanone with lithium aluminium hydride produces, according to Elie and Ro[30], a mixture containing 91–93% of the same *trans*-alcohol. Moreover, Hennion[36] showed that condensation of this ketone with sodium acetylide in liquid ammonia gives a mixture of acetylenic alcohols in which 86% have the axial disposition of the ethynyl group. On the other hand, the Grignard reaction with ethylmagnesium bromide produces a mixture in which the tertiary alcohol with an equatorial ethyl group, *i.e. trans*-1-ethyl-4-t-butylcyclohexanol, predominates (73%)[36]:

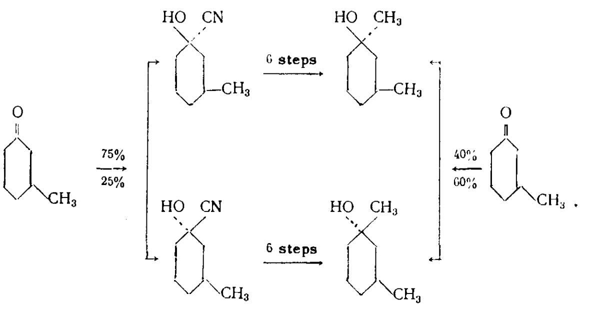


In this case, therefore, the reduction with sodium in alcohol or with lithium aluminium hydride, and the acetylene synthesis, take place predominantly in the same sense with respect to the double bond of the carbonyl group, while the Grignard reaction takes place predominantly in the opposite sense.

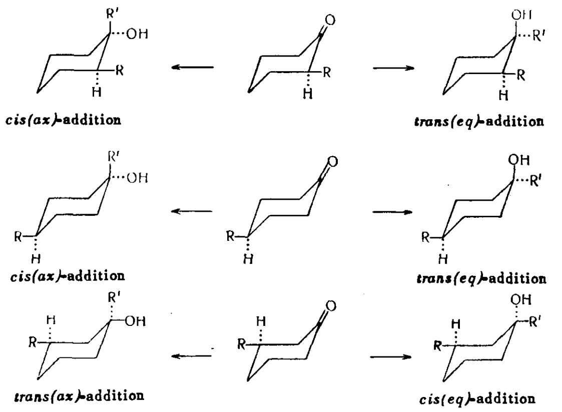
Goering and Serres[41] showed in 1952 that the configurations which had been given to the stereoisomeric 3-substituted cyclohexanols should in fact be reversed, and the stereochemical results obtained by the earlier workers on the reduction of *meta*-substituted cyclohexanones must also therefore be reversed. Taking this into account, it may be concluded that reduction both with sodium in alcohol and with complex metal hydrides produces in this case mainly the *cis*-alcohols (*trans*-addition):



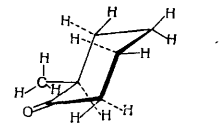
Iotsich[42] condensed 3-methylcyclohexanone with phenylethynylmagnesium bromide and obtained one of the two possible phenylacetylenic alcohols in 97% yield, while Bertond[43] condensed 3-methylcyclohexanone with phenylacetylene by the Favorskii method in the presence of potassium hydroxide and apparently obtained the same isomer, in 95% yield. It is interesting that 3-methylcyclohexanone also reacts with acetylenedimagnesium bromide to form only one glycol, in 93% yield[44]. Study of the stereochemistry of the cyanohydrin synthesis and the Grignard reaction of 3-methylcyclohexanone has shown that as with 2-methylcyclohexanone, both reactions have opposed spatial directivity[38]. In the cyanohydrin synthesis the resulting mixture consists of 75% of the *trans*-1-cyano-3-methylcyclohexanol (*trans*-addition) and 25% of the *cis*-compound. The Grignard reaction produces a mixture containing 60% of *cis*-1,3-dimethylcyclohexanol (*cis*-addition) and 40% of *trans*-1,3-dimethylcyclohexanol:



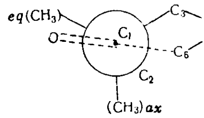
All addition reactions to the carbonyl group of monosubstituted cyclohexanones can be provisionally divided into two groups, of which the first comprises reactions (reduction with sodium and complex metal hydrides, the cyanohydrin and acetylene syntheses) which normally take place with a spatial directivity in one sense (predominantly *cis*-addition in the case of 2- and 4-substituents and *trans*-addition in the case of 3-substituents), and the second comprises the Grignard reaction, which normally shows the opposite spatial specificity (predominantly *trans*-addition with 2- and 4-substituted ketones and *cis*-addition with 3-substituted ketones). In deciding the spatial directivity of the reactions under review, it is of great importance to establish the conformation of the substituents in the starting ketone. Since the stereochemical course of reactions with t-butyl-substituted cyclohexanones, which have the substituent fixed in the equatorial position, fit into this scheme, it is clear that for reactions of the first group, the addition of the new substituent (H, CN, C⋮CH) takes place predominantly into the axial position. With the Grignard reaction, the new substituent enters predominantly in the equatorial position[38]:



In the case of other substituents of smaller volume than tertiary butyl, particularly in the *ortho*-position to the carbonyl group, there are two theoretical conformations with the cyclohexane ring in the "chair"-form, which differ as to whether the substituent is in the equatorial or axial position. Romers[45] studied the actual conformation of the 2-methylcyclohexanone molecule in detail by electron diffraction, and found that in the vapour phase this ketone exists in the "chair"-form, but without an axis of symmetry of the third order, because of distortion of the valency angle at C_1. At the same time, according to Romers' results, the valency angles at the other carbon atoms are still in the range 109.5° ± 2.5°, and the C–C and C–H bonds have length 1.54 ± 0.01 Å and 1.09 ± 0.02 Å respectively. The angle between the C–C bonds at C_1 is 117° ± 3°, and the angle between the C–C and C–O bonds is 121.5° ± 1.5°:



The methyl group occupies exclusively or almost exclusively the equatorial position, but distorted from the normal. Geometrical calculation shows that the angle between the projections of the methyl and carbonyl groups is 15° (105° with the methyl group in the axial position)[46]:



Thus an equatorial *ortho*-substituent occupies a more shielded position with respect to the carbonyl oxygen than the splayed position which occurs in the undeformed cyclohexane molecule. The Raman spectra of the methylcyclohexanones also show that the methyl group in the *ortho*-, *meta*-, and *para*-methylcyclohexanones is predominantly in the equatorial position. This is a further confirmation that *cis*-addition to *ortho*-substituted ketones takes place with axial entry of the substituent, and *trans*-addition with

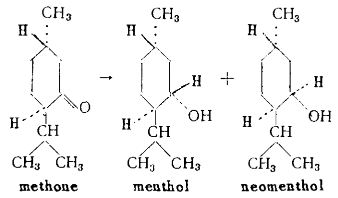
TABLE 2. Stereoselectivity of addition reactions to disubstituted cyclohexanones.

Ketone	Reagent	R′	Content in resulting mixture, %		Reference
			R′α-form	R′β-form	
	2,2-substitution				
2β-Methylcyclohexan-2-ol-1-one	Na + ROH	H	100*	0	47
2β-Ethylcyclohexan-2-ol-1-one	Na + ROH	H	70	30	47
	2,6-substitution				
2β, 6β-Dimethylcyclohexan-1-one	Na + ROH	H	100*	0	48
2β, 6β-Dimethylcyclohexan-1-one	Na in moist ether	H	*xx*	+	48
	2,5-substitution				
Menthone (2α, 5β)	$LiAlH_4$	H	71	29	12
Menthone	$NaBH_4$	H	49	51	9
2α-Methyl-5β-isopropylcyclohexan-1-one	$C_6H_5C{\equiv}CMgBr$	$C_6H_5C{\equiv}C$	one isomer (??)	did not agree after hydrogenation	39
2α-Methyl-5β-isopropylcyclohexan-1-one	$C_6H_5CH{=}CHMgBr$	$C_6H_5CH{=}CH$	one isomer (??)		
	2,3-substitution				
9β-*trans*-Decalone-1	Na + ROH	H	*xx*	0	49
3-Ethyleneketal-*dl*-18-nor-D-homo-18-androst-5-en-3, 17a-dione	$LiAlH_4$	H	*x*(17*a*)	+	50
9β-*trans*-Decalone-1	$HC{\equiv}CNa$, NH_3	$HC{\equiv}C$	66	33	51
9β-*cis*-Decalone-1	$LiAlH_4$	H	90	10	11
9β-*cis*-Decalone-1	$HC{\equiv}CNa$, NH_3	$HC{\equiv}C$	60*	0	51
	3,4-substitution				
9β-*trans*-Decalone-2	Na + ROH	H	99*	0	49
19-norandrostan-17β-ol-3-one	$NaBH_4$	H	85*(3*a*)	0	52
17α-Methyl-19-norandrostan-17β-ol-3-one	$NaBH_4$	H	95*(3*a*)	0	52
17α-Vinyl-19-norandrostan-17β-ol-3-one	$NaBH_4$	H	95*(3*a*)	0	52
17α-Ethyl-19-norandrostan-17β-ol-3-one	$NaBH_4$	H	67*(3*a*)	0	52
9β-*trans*-Decalone-2	$HC{\equiv}CK$ $t\text{-}C_5H_{11}OH$	$HC{\equiv}C$	one isomer	(??)	53
9β-*cis*-Decalone-2	Na + ROH	H	68	32	11
5β, 10β-Oestra-3, 17-dione	Na + ROH	H	0	+ (3*a*)	54
17α-Ethyl-5α, 10α-oestran-17β-ol-3-one	Na + ROH	H	0	+ (3*a*)	55
9β-*cis*-Decalone-2	$LiAlH_4$	H	90	10	11
5β, 10β-Oestra-3, 17-dione	$NaBH_4$	H	+ (3*e*)	0	54
17α-Methyl-5α, 10α-oestran-17β-ol-3-one	$NaBH_4$	H	+ (3*e*)	0	55

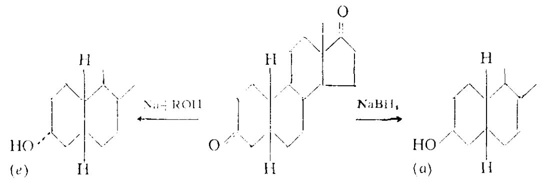
entry of the substituent in the equatorial position. No doubt the ketone can enter into reaction not only in the predominant conformation with an equatorial substituent, but also in the other conformation (with the substituent in the axial position), which may be a partial explanation of the incomplete spatial selectivity.

2. DISUBSTITUTED CYCLOHEXANONES (see Table 2)

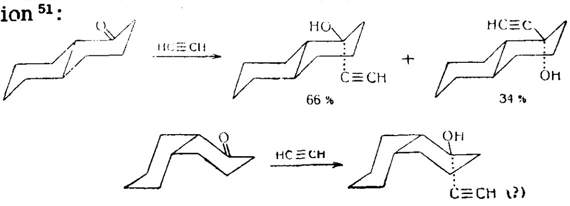
On passing to di- and tri-cyclic disubstituted ketones with more rigid rings, the conformational features of addition to the carbonyl double bond become much clearer. The stereochemistry of addition to such ketones with a cyclohexane ring retains in general features the same tendencies as in the case of monosubstituted cyclohexanones. On reduction with sodium and alcohol, these ketones also form mainly the alcohols in which the hydroxyl group is equatorial[11,47-49,54,55], and the same is found in reduction by means of lithium aluminium hydride[11,12,50]. In a number of cases, however, reduction with sodium borohydride leads predominantly to the formation of alcohols with an axial hydroxyl group (equatorial addition of hydrogen). Thus while Noyce and Denney[12] found that when menthone is reduced with lithium aluminium hydride menthol predominates (71%) in the reaction mixture, Dauben, Fonken, and Noyce[9] observed that neomenthol predominates (51%) in the mixture of alcohols obtained by reduction with sodium borohydride:



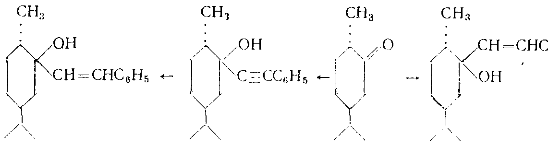
After reducing 5β,10β-oestra-3,17-dione [54] and 17α-methyl-5α,10α-oestran-17β-ol-3-one [55] with sodium in propanol, Rapala and Farkas obtained only products with an equatorial 3-hydroxy group, while by reducing the same ketones with sodium borohydride, they obtained only products with an axial hydroxyl group in the 3-position[55,54]:



The acetylene synthesis on 1-decalones shows interesting differences in the *cis*- and *trans*-compounds. While *trans*-1-decalone reacts with acetylene to form both stereoisomeric alcohols (the isomer with the axial ethynyl group predominating), *cis*-decalone produces only one isomer, apparently that with the ethynyl group in the axial position[51]:



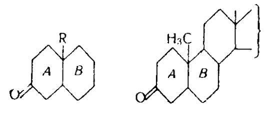
Rupe and Kambli[39] have shown that the condensation of *trans*-2-methylisopropylcyclohexanone with phenylethynylmagnesium bromide and styrylmagnesium bromide gives products with different spatial structures, but their configurations were not established:



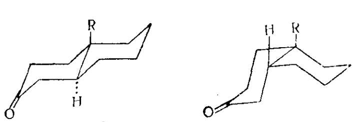
3. TRISUBSTITUTED CYCLOHEXANONES (see Tables 3 and 4)

As distinct from the case of mono- and di-substituted cyclohexanones, the stereochemical data on the reactions of tri- and more highly substituted cyclohexanones relate almost exclusively to rigid systems. This provides more definite results on the composition of the mixtures, particularly in the preparation of secondary alcohols, which isomerise in this case to a lesser extent. On the other hand, the great rigidity of these systems is associated with the appearance of additional factors which influence or might influence the stereoselectivity of the reactions. Because of this, it is considerably more difficult to separate the particular causes underlying the observed stereoselectivity.

Most data on the stereochemistry of addition to the carbonyl group of trisubstituted cyclohexanones relate to the 3,4,4-trisubstituted compounds: 10-substituted 2-decalones and 3-oxosteroids:

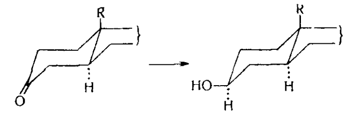


Both types of ketone belong to the angular-substituted decalin systems, and can exist with the rings A and B joined in the *trans*- and *cis*-positions, being thereby divided into two types:



trans-attachment *cis*-attachment

A definite similarity can be observed between the stereochemistry of addition to the carbonyl groups of 3,4,4-trisubstituted cyclohexanones and mono- and di-substituted cyclohexanones. Thus in the series under consideration, as before, reaction takes place, with a few exceptions, with entry of the hydrogen atom mainly in the axial position:



Cholestan-3-one has been the most studied in this series.

TABLE 3. **Stereoselectivity of addition reactions to 3, 4, 4-trisubstituted cyclohexanones.**

Ketone	Reagent	R′	Content in resulting mixture, %		Reference
			R′ α-form	R′ β-form	
10β-Methyl-*trans*-decalone-2	$LiAlH_4$	H	75*(*a*), 63(*a*)	?, 0	56,57
10β-Hydroxymethyl-*trans*-decalone-2 mesylate	$LiAlH_4$	H	>48* (*a*)	?	58
10β-Hydroxymethyl-*trans*-decalone-2 mesylate	$NaBH_4$	H	99* (*a*)	0	58
10β-Carboxy-*trans*-decalone-2	$NaBH_4NaOH$	H	69* (*a*)	0	58
10β-Carbethoxy-*trans*-decalone-2	$NaBH_4$	H	90* (*a*)	0	59
5β-Ethynyl-10β-methyl-5α-hydroxy-*trans*-decalone-2	$NaBH_4$	H	88* (*a*)	0	60
5β-Vinyl-10β-methyl-5α-hydroxy-*trans*-decalone-2	$NaBH_4$	H	83* (*a*)	0	60
5β-Ethyl-10β-methyl-5α-hydroxy-*trans*-decalone-2	$NaBH_4$	H	66* (*a*)	0	60
1-Methoxy-8-oxo-10aβ-methyl-4b, 5, 6, 6aα, 7, 8, 9, 10, 10a, 10b, 11, 12-dodecahydrochrysene	$LiAlH_4$	H	82* (*a*)	0	61
1-Methoxy-8-oxo-10aβ-methyl-4bα, 5, 6, 6aα, 7, 8, 9, 10, 10a, 10bα, 11, 12-dodecahydrochrysene	$LiAlH_4$	H	86* (*a*)	0	62
1-Methoxy-8-oxo-10aβ-methyl-5, 6, 6aα, 7, 8, 9, 10, 10a, 11, 12-decahydrochrysene	$LiAlH_4$	H	76* (*a*)	0	62
3, 6-Dioxoallocholanoic acid	Na+ROH	H	74* (3*a*)	0	63
2-Oxo-6α-hydroxycholanoic acid	Na+ROH	H	40* (*a*)	0	63
Allopregna-3, 11, 20-trione	$LiAlH_4$	H	75* (3*a*)	0	64
Allopregna-17α, 21-diol-3, 11, 20-trione 21-acetate	$LiAlH_4$	H	63* (3*a*)	0	65
Cholestan-3-one	$LiAlH_4$	H	96, 87, 88(*a*)	4, 13, 12(*e*)	66,67,68
14-Methylcholestan-3-one	$LiAlH_4$	H	+ (*a*)	0	69
5α, 22a-Spirostan-3, 6-dione	$LiAlH_4$	H	58* (3*a*)	0	70
Solanidan-3-one-18-al	$LiAlH_4$	H	+ (3*a*)	0	71
Androstan-3, 17-dione	$NaBH_4$ in CH_3OH	H	71* (3*a*)	0	72
Androstan-3, 17-dione	$NaBH_4$ in pyridine	H	93(3*a*)	7(3*e*)	72
Allopregna-3, 20-dione	$NaBH_4$	H	86, 76(3*a*)	14, 0	73,74
Allopregna-3, 11, 20-trione	$NaBH_4$	H	87(3*a*)	13	73
3-Oxoetianic acid methyl ester	$NaBH_4$	H	+ (*a*)	0	75
Cholestan-3-one	$NaBH_4$	H	86, 85(*a*)	14, 15(*e*)	67,68
Androstan-3-one	CH_3MgI	CH_3	42(*a*)	58(*e*)	76
Cholestan-3-one	CH_3MgI	CH_3	40, 43(*a*)	60, 57(*e*)	77,78
10β-Methyl-*cis*-decalone-2	Na+ROH	H	0	79* (*a*)	79
10β-Methyl-*cis*-decalone-2	$LiAlH_4$	H	100* (*e*)	0	79
5α-Ethynyl-10β-methyl-5β-hydroxy-*cis*-decalone-2	$NaBH_4$	H	57(*e*)	43(*a*)	60
10β-Hydroxymethyl-*cis*-decalone-2	$NaBH_4$	H	50(*e*)	0	59
10β-Hydroxymethyl-*cis*-decalone-2-**tosylate**	$NaBH_4$	H	19(*e*)	81(*a*)	56
1-Methoxy-8-oxo-10aβ-methyl-5, 6, 6aβ, 7, 8, 9, 10, 10a, 11, 12-decahydrochrysene	$LiAlH_4$	H	0	76* (*a*)	62
1-Methoxy-8-oxo-10aβ-methyl-4aβ, 5, 6, 6aβ, 7, 8, 9, 10, 10a, 10bβ, 11, 12-dodecahydrochrysene	$LiAlH_4$	H	0	62* (*a*)	62
3-Oxothiobillianic acid trimethyl ester	$NaBH_4$	H	0	50* (*a*)	80
Pregna-3, 16, 20-trione	Na+ROH	H	0	+ (*a*)	81
Testa-3, 17-dione 17-ethyleneketal	$LiAlH_4$	H	0	+ (*a*)	82
Pregna-3, 20-dione 20-ethyleneketal	$LiAlH_4$	H	0	82* (*a*)	82
3-Oxo-bisnorchol-7-enoic acid methyl ester	$LiAlH_4$	H	0	32* (*a*)	82
3-Oxobisnorcholanoic acid methyl ester	$LiAlH_4$	H	0	74* (*a*)	82
3, 11-Dioxobisnorcholanoic acid methyl ester	$LiAlH_4$	H	0	+ (3*a*)	82
Lithocholic acid	$LiAlH_4$	H	0	95* (*a*)	83
9α, 11α-Epoxy-3-oxolithocholanic acid methyl ester	$LiAlH_4$	H	0	80* (*a*)	84
Coprostan-3-one	$LiAlH_4$	H	4, 8, 7(*e*)	96, 92, 93(*a*)	66,67,68
Coproergost-22-en-3-one	$LiAlH_4$	H	0	+ (*a*)	82
22-Isospirostan-3-one	$LiAlH_4$	H	0	+ (*a*)	85
22a-Spirost-7-en-3-one	$LiAlH_4$	H	0	90* (*a*)	86
22-Isospirostan-7, 9(11)-dien-3-one	$LiAlH_4$	H	0	69* (*a*)	87
22-Isospirostan-3, 11-dione	$LiAlH_4$	H	0	63* (3*a*)	88
5β-Spirostan-3-on-27-oic acid	$LiAlH_4$	H	0	83* (*a*)	89
Testa-3, 17-dione	$NaBH_4$ in CH_3OH	H	20(3*e*)	80(3*a*)	72
Testa-3, 17-dione	$NaBH_4$ in pyridine	H	0	43* (3*a*)	72
Testan-17β-ol-3-one acetate	$NaBH_4$	H	17(3*e*)	83(3*a*)	72
Pregna-3, 20-dione	$NaBH_4$	H	15, ?	85, 63*(3*a*)	73,74
Pregnan-11α-ol-3, 20-dione acetate	$NaBH_4$	H	?	63*(3*a*)	74
Pregna-11β, 17α, 21-triol-3, 20-dione 21-acetate	$NaBH_4$	H	0	30* (3*a*)	73
Pregna-3, 11, 20-trione	$NaBH_4$ in C_2H_5OH	H	?	61* (3*a*)	74
Pregna-3, 11, 20-trione	$NaBH_4$ in pyridine	H	0	+, 82* (3*a*)	91,74
Pregnan-17α-ol-3, 11, 20-trione	$NaBH_4$	H	0, ?	78*, 63* (3*a*)	91,74
Coprostan-3-one	$NaBH_4$	H	17, 13(*e*)	83, 87(*a*)	67,68
3, 11-Dioxocholanoic acid	$NaBH_4$, NaOH	H	12(*e*)	88(*a*)	92
Digitoxigenone	$NaBH_4$	H	+	72(*a*)	93
Sarsasapogenone	CH_3MgI	CH_3	one isomer	(?) 100*	94

There are no data on the reduction of this ketone with sodium and alcohol, but its reduction with lithium aluminium hydride produces a mixture containing, according to various workers[66-68], from 96 to 88% of cholestan-3β-ol, while sodium borohydride shows a slightly reduced selectivity, producing 86–85% of the 3β-alcohol[67,68]. It is extremely interesting that methylmagnesium iodide reacts with this ketone to form predominantly (although the selectivity is small) 3β-methylcholestan-3α-ol (57–60%)[77,78], *i.e.* the product of equatorial addition of the methyl group:

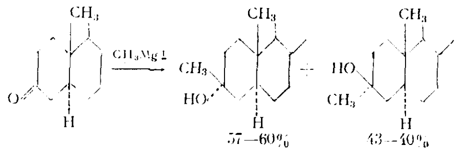
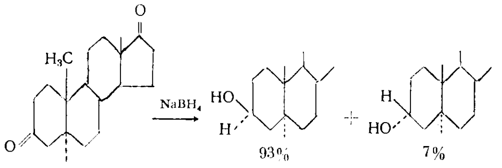
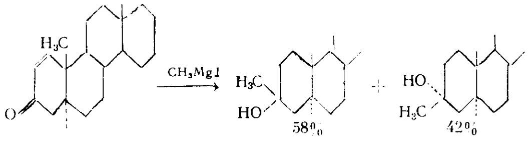


TABLE 4. **Stereoselectivity of addition reactions to various trisubstituted cyclohexanones.**

Ketone	Reagent	R′	Content in resulting mixture, %		Reference
			R′α-form	R′β-form	
	2,2,3-substitution				
Cholestan-1-one	Na+C_2H_5OH	H	64 (a)	36 (*e*)	95
Cholestan-1-one	Na+*n*-C_3H_7OH	H	91 (*a*)	9 (*e*)	96
D-Homotestan-3α-ol-11, 17a-dione acetate	$LiAlH_4$	H	+ (17a*a*)	0	97
Cholestan-1-one	$LiAlH_4$	H	35 (*a*)	65 (*e*)	96
D-Homotestan-3α-ol-11, 17a-dione acetate	$NaBH_4$	H	94 (17a*a*)	6 (17a*e*)	97
D-Homoepiandrostenone acetate	$NaBH_4$	H	85 * (17a*a*)	0	98
D-Homoandrost-5-en-3β-ol-17a-one	HC≡CH	C≡H	*x* (17a*a*)	+ (17a*e*)	99
D-Homotestan-3α-ol-11, 17a-dione	HC≡CK, t-C_4H_9OH	C≡H	86 (17a*a*)	14 (17a*e*)	100
D-Homotesta-3α, 11β-diol-17a-one acetate	HC≡CK, t-C_4H_9OH	C≡H	50 * (17a*a*)	0	100
D-Homotesta-3α, 11α-diol-17a-one 3, 11-diacetate	HC≡CK, t-C_4H_9OH	C≡H	85 * (17a*a*)	0	100
D-Homoandrosten-3-ol-17a-one	CH_3MgI	CH_3	0	90 * (17a*e*)	101
D-Homotestan-3α-ol-11, 17a-dione 3-acetate	CH_3MgI	CH_3	0	65 * (17a*e*)	100
	3,3,4-substitution				
Cholestan-2-one	Na+ROH	H	0	+ (*a*)	102
Cholestan-2-one	$LiAlH_4$	H	58 (*e*)	42 (*a*)	103
Cholestan-2-one	$NaBH_4$	H	82 (*e*)	18 (*a*)	103
	2,3,3-substitution				
Cholestan-4-one	Na+ROH	H	0	+ (*a*)	104
Cholestan-4-one	$LiAlH_4$	H	92 (*e*)	8 (*a*)	105
	3,4,5-substitution				
1α-Methyl-19-norandrostan-17β-ol-3-one	$NaBH_4$	H	70 * (3*a*)	0	52
	2,4,5-substitution				
2α-Hydroxy-*cis*-9β, 10β-decalone-3	$LiAlH_4$	H	27	73 (*e*)	106
2β-Hydroxy-*cis*-9β, 10β-decalone-3 acetate	$LiAlH_4$	H	30	70 (*e*)	106

A similar effect is observed with other ketones of this series. Thus androstan-3,17-dione, on reduction with sodium borohydride, provides androstan-3β,17-diol in 93% yield, the 3α-isomer being produced in a very small amount, while androstan-3-one, like cholestan-3-one, with methylmagnesium iodide, gives a mixture containing 58% of 3β-methylandrostan-3α-ol[76]:





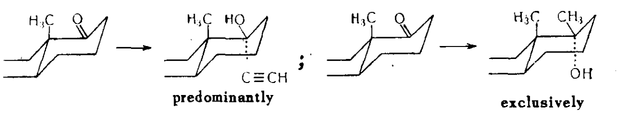
Such directivity has already been mentioned in respect of the monosubstituted cyclohexanones, where it was shown that the Grignard reaction takes place with stereoselectivity opposite to that found with reduction or the acetylene synthesis.

The steric course of the reduction of the ketones (axial addition of hydrogen) in the 3,4,4-trisubstituted cyclohexanones is also retained in respect of *cis*-fusion of rings A and B. The only exception is the reduction of 10β-methyl- and 10β-hydroxymethyl-*cis*-2-decalone with lithium aluminium hydride or sodium borohydride[50,79], where the results (predominantly equatorial addition of hydrogen) agree with those of the reduction of *cis*-2-decalones. These facts have not yet been explained. There are very few reliable data on the quantitative determination of the relative proportions of isomers in the products of addition to 3,4,4-trisubstituted cyclohexanones. Most workers give only the amount of the one isomer which they have separated, and the yield is sometimes less than 50% of the theoretical; no further information on the composition of the reaction product is usually given. However, a few results of the accurate separation of these mixtures (from cholestan-3-one[66-68,77,78], androstan-3-one[76], coprostan-3-one[66-68], testane-3,17-dione[72], and 3,11-dioxocholanoic acid[92]) show that the reduction of these ketones with lithium aluminium hydride is apparently somewhat more selective (87–96% of one isomer) than reduction with sodium borohydride (80–88% of the same isomer).

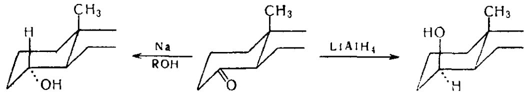
It is very interesting to compare the data on the stereochemistry of addition to 2,2,3-trisubstituted cyclohexanones. Representative of such ketones are the 1-oxosteroids and 17a-oxo-D-homosteroids. The reduction of cholestan-1-one with sodium and alcohol produces mainly alcohols with an equatorial hydroxyl group (64–91%)[95,96], and the same is found in the reduction of 17a-oxo-D-homosteroids with sodium borohydride (94%)[97]. However, according to Henbest's results[95], reduction of cholestan-1-one with lithium aluminium hydride gives predominantly cholestan-1α-ol with an axial hydroxyl group.

Studies by Dodson *et al.*[99] and Clinton *et al.*[100] have shown that the addition of acetylene to 17a-oxo-D-homosteroids proceeds mainly with the formation of an axial ethynyl group (86%). while the Grignard reagent adds exclusively in the equatorial position[100,101]. Exclusively axial addition apparently also occurs in the acetylene synthesis on 10β-methyl-6-methoxy-Δ^6-*cis*-1-octalone[107].

In this instance, therefore, the difference in the directivity of these two reactions is greater than with 4-t-butylcyclohexanone and the 3-oxosteroids:



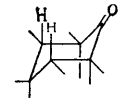
The 3,3,4- and 2,3,3-trisubstituted cyclohexanones such as cholestan-2-one and cholestan-4-one differ greatly in the directivity of their addition reactions. In both cases only reduction of the keto-group with sodium and alcohol produces alcohols with an equatorial hydroxyl group[102-104]; reduction with lithium aluminium hydride[103,105] or sodium borohydride[103] takes place mainly with addition of hydrogen in the equatorial position:



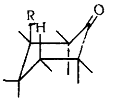
Such a sharp difference in the directivity of the reactions can only be due to the presence of the axial methyl group in the *meta*-position to the carbonyl group, which greatly hinders the approach of the reagent from one direction. However, this steric hindrance apparently does not affect the directivity in the case of sodium and alcohol, since only one isomer, with an equatorial hydroxyl group, has been obtained from the reduction products[102,104], although there are no quantitative data in the literature.

4. TETRASUBSTITUTED CYCLOHEXANONES (see Table 5)

In respect of the spatial specificity of addition reactions to the carbonyl group, the ketones of the tetrasubstituted cyclohexane series can be divided into two groups, the reactions of which correspond in general features with those already described. The first group comprises those compounds which do not contain other axial substituents, other than hydrogen atoms, in the *meta*-position to the carbonyl group, *i.e.* the tetrasubstituted cyclohexanones which are unsubstituted or monosubstituted in the 3- and 5-positions. The directivity of addition reactions to the carbonyl group of such ketones is in general features the same as in the case of mono-, di-, and tri-substituted cyclohexanones, other than the 2,3,3- and 3,3,4-trisubstituted cyclohexanones. The second group, which corresponds to these last compounds, includes the tetrasubstituted cyclohexanones which are geminally substituted in the 3- or 5-positions. A review of the available factual data confirms such a division:



First group
2,2,3,4-substitution
2,3,4,5-substitution
2,4,4,5-substitution
2,3,4,4-substitution



Second group
2,3,3,4-substitution
2,4,5,5-substitution
2,2,5,5-substitution

Thus ketones of the first group (2,3,4,5-, 2,4,4,5-, and 2,3,4,4-substitution) on reduction with sodium and alcohol or complex metal hydrides give predominantly, as a rule, alcohols with an equatorial hydroxyl group, the selectivity being apparently somewhat higher with lithium aluminium hydride[109-111,114-116,119] and reducing when using sodium borohydride[108,112,113].

A very interesting example, which is a connecting link between the first and second groups, is the sodium borohydride reduction of the methyl ester of 1β-hydroxy-3-oxoetianic acid (3,4,4,5-substitution), described by Schlegel and Tamm[121]. This compound contains an axial substituent in the *meta*-position to the carbonyl group — the

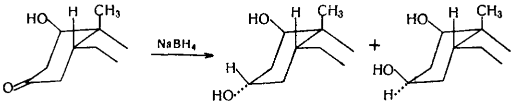
TABLE 5. Stereoselecticity of addition reactions to tetrasubstituted cyclohexanones.

Ketone	Reagent	R′	Content in resulting mixture, %		Reference
			R′α-form	R′β-form	
	2,2,3,4-substitution				
4,4-Dimethyl-19-norandrostan-17β-ol-3-one	$NaBH_4$	H	78 *(4*a*)	0	108
4,4,17α-Trimethyl-19-norandrostan-17β-ol-3-one	$NaBH_4$		80* (4*a*)	0	108
	2,2,4,5-substitution				
2,2,17α-Trimethyl-19-norandrostan-17β-ol-3-one	$NaBH_4$	H	90 * (*a*)	0	108
	2,4,4,5-substitution				
5α,22a-Spirostan-2α-ol-3-one acetate	$LiAlH_4$	H	81 * (*a*)	0	109
5α,22a-Spirostan-2β-ol-3-one acetate	$LiAlH_4$	H	58 * (*a*)	0	109
2α-Bromocholestan-3-one	$LiAlH_4$	H	87 * (*a*)	0	110
2α-Methylcholestan-3-one	$LiAlH_4$	H	87 * (*a*)	0	111
2α-Bromocholestan-3-one	$NaBH_4$	H	68,61 (*a*)	32,39	112, 113
2β-Methylcoprostanone	$LiAlH_4$	H	0	82 * (*a*)	111
	2,3,4,4-substitution				
α-Methylcholest-7-en-3-one	Na+ROH	H	83 * (*a*)	0	114
4α-Methylcholestan-3-one	$LiAlH_4$	H	87 * (*a*)	0	111
4α-Methylstigmastan-3-one	$LiAlH_4$	H	81 * (*a*)	0	115
4α-Methylcholest-7-en-3-one	$LiAlH_4$	H	85 *, 62 * (*a*)	0	114, 116
3-Oxo-5α,11α(H),4α,6β(H)-eudesman-6:13-olide	KBH_4	H	78 * (3*a*)	0	117
1α-(2′α-Hydroxyethyl)-7,7,10β-trimethyl-*trans*-decalone-2	CH_3MgI	CH_3	52 (2*a*?)	48 (2*e*?)	118
4β-Methylcoprostan-3-one	$LiAlH_4$	H	0	46 * (*a*)	111
3-Oxo-11α(H),4β,5β,6β(H)-eudesman-6:13-olide	KBH_4	H	0	76 * (3*a*)	117
6α-Hydroxy-3-oxo-4α(H),5β(H)-eudesmanoic acid	KBH_4. KOH	H	66 (3*e*)	0	117

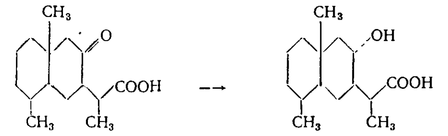
TABLE 5 (contd.)

Ketone	Reagent	R′	Content in resulting mixture, %		Reference
			R′α-form	R′β-form	
	2,3,4,5-substitution				
1-Methoxy-8β-hydroxy-11-oxo-10aβ-methyl-4bβ, 5, 6, 6aα, 7, 8, 9, 10, 10a, 10bβ, 11, 12-dodecahydrochrysene	$LiAlH_4$	H	0	83 * (11*a*)	119
	2,2,3,6-substitution				
1, 1, 6α, 10β-Tetramethyl-2β-hydroxy-*trans*-decalone-5 benzoate	$CH{\equiv}CNa$, NH_3	$C{\equiv}CH$	92 * (5*a*)	0	120
	3,4,4,5-substitution				
1β-Hydroxy-3-oxoetianic acid methyl ester	$NaBH_4$	H	50 (*a*)	50 (3*e*)	121
	2,3,3,4-substitution				
Friedelin	Na+ROH	H	0	75 *, 50 * (*a*)	122, 123
Friedelin	$LiAlH_4$	H	+	0	123
	2,4,5,5-substitution				
Cholestan-3β-ol-2-one tosylate	$NaBH_4$	H	0	90 * (*e*)	124
Cholestan-3β-ol-2-one acetate	$NaBH_4$	H	0	84 * (*e*)	124
7-Oxotetrahydroalantolic acid	Na+ROH	H	0	75* (7*a*)	125
7-Oxotetrahydroalantolic acid	$NaBH_4$	H	68 * (7*e*)	0	126
	2,2,5,5-substitution				
2, 2, 5, 5-Tetramethylcyclohexa-1, 3-dione	$LiAlH_4$	H	35 (α, β)	65 (β, β)	127

1β-hydroxy group — but a hydroxyl group has a smaller volume than a methyl group, and so screens one side of the carbonyl group to a substantially lesser extent than an axial methyl group. The reduction of the methyl ester of 1β-hydroxy-3-oxoetianic acid with sodium borohydride therefore produces a mixture of equal quantities of both isomers:



Tetrasubstituted ketones of the second group are reduced by all methods, except sodium and alcohol[122,123,125], to form mainly or exclusively alcohols with an axial hydroxyl group[123,124,126,127]. However, the examples of 7-oxotetrahydroalantolic acid, which by reduction with sodium and isopropanol gives the corresponding α-alcohol in 75% yield[125]



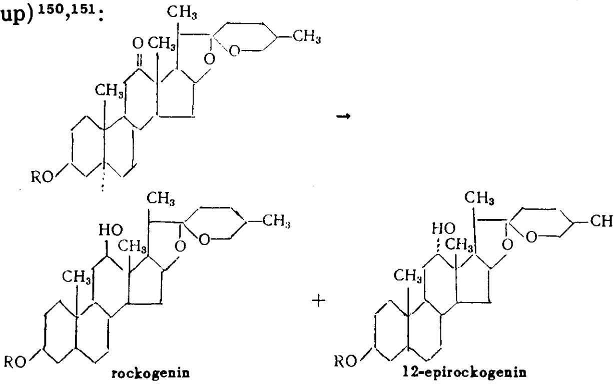
7-oxotetrahydroalantolic acid 7α-hydroxytetrahydroalantolic acid

and friedelin, which under the same conditions gives friedelan-3β-ol in 50–75% yield[122,123], show that reduction with sodium and alcohol takes place with the same stereoselectivity as in the case of less substituted ketones. This is possibly due to polar influence of the carboxyl group.

5. PENTASUBSTITUTED CYCLOHEXANONES (see Table 6)

The existing material on the stereochemistry of addition to the pentasubstituted ketones can be divided into nine groups of variously substituted cyclohexanes (2,2,3,4,4-, 2,2,4,4,5-, 2,3,4,4,5-. 2,2,3,4,5-, 2,2,3,6,6-, 2,2,4,5,6-, 2,3,3,4,5-, 2,3,3,6,6-, and 2,3,4,5,5-substitution). The first six of these do not possess the geminal substitution in the *meta*-position to the carbonyl group which exists in the last three. However, spatial hindrance exerts an effect in the pentasubstituted ketones, even when these do not possess large axial 3- or 5-substituents. While the 2,2,3,4,4-pentasubstituted ketones, mostly 4,4-dimethyl-3-oxotriterpenoids, are reduced by complex metal hydrides mainly to alcohols with equatorial hydroxyl[128-141], the 2,3,4,5-pentasubstituted ketones (7-oxosteroids)[103,147] and 2,2,3,4,5-pentasubstituted cyclohexanones (12-oxosteroids)[151,153] are converted by reduction with sodium borohydride predominantly into alcohols with an axial hydroxyl group. There are indications that even the reduction of 7-oxosteroids with sodium and alcohol (3β-hydroxyergost-22-en-7,11-dione)[144] and with lithium aluminium hydride (cholestan-3β-ol-7-one acetate)[103,146] leads predominantly to 7α-alcohols with an axial hydroxyl group.

The reduction of hecogenin with sodium and ethanol has produced only rockogenin[148] (12β-equatorial hydroxyl group, 57%), while with lithium aluminium hydride[149], both isomers are formed, and reduction of hecogenin acetate with lithium aluminium hydride produces 54–82% rockogenin and 18–46% 12-epirockogenin (12α-axial hydroxyl group)[150,151]:



rockogenin 12-epirockogenin

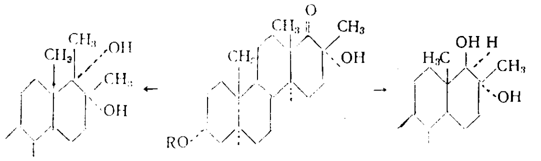
TABLE 6. Stereoselectivity of addition reactions to pentasubstituted cyclohexanones.

Ketone	Reagent	R′	Content in resulting mixture, %		Reference
			R′α-form	R′β-form	
2,2,3,4,4-substitution					
Elemadien-3-onic acid methyl ester	$LiAlH_4$	H	+ (*a*)	0	128
Masticadien-3-onic acid	$LiAlH_4$	H	+ (*a*)	0	129
Dihydromasticadien-3-onic acid methyl ester	$LiAlH_4$	H	+ (*a*)	0	129
Dihydroisomasticadien-3-onic acid	$LiAlH_4$	H	+ (*a*)	0	130
β-Amyren-3-one	$LiAlH_4$	H	55* (*a*)	0	131
Lupen-3-one	$LiAlH_4$	H	60* (*a*)	0	131
Taraxerone-3	$LiAlH_4$	H	+ (*a*)	0	132
20α, 21α-Epoxy-19α(H)-taraxastan-3-one	$LiAlH_4$	H	50* (*a*)	0	133
β-Boswellonic acid methyl ester	$LiAlH_4$	H	+ (*a*)	0	134
Betulonic lactone	$LiAlH_4$	H	85* (3*a*)	0	135
4, 4-Dimethylandrostan-17β-ol-3-one	$NaBH_4$	H	88* (*a*)	0	136
4, 4, 17α-Trimethylandrostan-17β-ol-3-one	$NaBH_4$	H	87* (*a*)	0	136
20-Isoeburico-7, 9(11)-dien-16β-ol-3-on-21-oic acid lactone	$NaBH_4$	H	76* (*a*)	0	137
Thurberogen-3-one	$NaBH_4$	H	60* (*a*)	0	138
Masticadien-3-onic acid	$NaBH_4$	H	+ (*a*)	0	129
Dihydromasticadien-3-onic acid	$NaBH_4$	H	+ (*a*)	0	129
Dioxoechinocystic acid methyl ester	$NaBH_4$	H	75* (3*a*)	0	139
Olean-12-en-3-on-28, 30-dioic acid dimethyl ester	$NaBH_4$	H	92* (*a*)	0	140
11-Desoxy-β-glycyrrhetinic acid methyl ester	$NaBH_4$	H	71* (*a*)	0	141
β-Boswellonic acid methyl ester	$NaBH_4$	H	+ (*a*)	0	134
2,2,4,4,5-substitution					
2, 2-Dimethylcholestan-3-one	$LiAlH_4$	H	85* (*a*)	0	111
2,3,4,4,5-substitution					
Cholestan-7-one	Na+ROH	H	+ (*a*)	0	142
Cholestan-3β-ol-7-one acetate	Na+ROH	H	78 (*a*)	22 (*e*)	143
3-Hydroxyergost-22-en-7, 11-dione	Na+ROH	H	45 (7*a*)	55 (7*e*)	144
Lanostan-3β-ol-7-one acetate	Na+ROH	H	70* (*a*)	0	145
Cholestan-7-one	$LiAlH_4$	H	67 (*a*)	33 (*e*)	142
Cholestan-3-ol-7-one acetate	$LiAlH_4$	H	50,43—35 (*a*)	50,57—65 (*e*)	146, 103
Lanostan-3β-ol-7-one acetate	$LiAlH_4$	H	70* (*a*)	0	145
Cholestan-3-ol-7-one acetate	$NaBH_4$	H	27 (*a*)	73 (*e*)	103
7-Oxocholanoic acid	$NaBH_4$	H	9 (*a*)	91 (*e*)	147
2,2,3,4,5-substitution					
Hecogenin	Na+ROH	H	57* (*a*)	0	148 148
Manogenin diacetate	Na+ROH	H	25* (*a*)	0	148
Mexogenin diacetate	Na+ROH	H	+ (*a*)	0	149
Hecogenin	$LiAlH_4$	H	+ (*a*)	+ (*e*)	150, 151
Hecogenin acetate	$LiAlH_4$	H	54,82 (*a*)	46,18 (*e*)	152
12-Oxo-13β-ursan-3β-ol acetate	$LiAlH_4$	H	90 (*a*)	10 (*e*)	153
Allopregna-3β, 17β-diol-12, 20-dione	$NaBH_4$	H	?	+ (*e*)	153
Allopregna-3β, 17α, 21-triol-12, 20-dione 21-acetate	$NaBH_4$	H	?	+ (*e*)	151
Hecogenin acetate	$NaBH_4$	H	+ (*a*)	*x* (*e*)	
2,2,3,6,6-substitution					
17β-Methyl-D-homotesta-3α, 17α-diol-11, 17a-dione diacetate	Na+ROH	H	17* (a*a*)	0	154
17β-Methyl-D-homotesta-3α, 17α-diol-11, 17a-dione diacetate	$LiAlH_4$	H	22* (17a*a*)	0	154
17β-Methyl-D-homotesta-3α, 17α-diol-11, 17a-dione acetate	CH_3MgI	CH_3	0	+17 (a*e*)	155
2,2,4,5,6-substitution					
2β, 4b-Dimethyl-2-allyl-7-ethylenedioxy-1, 2, 3, 4, 4aα, 4b, 5, 6, 7, 8, 10, 10aβ-dodecahydrophenanthren-4β-ol-1-one	$NaBH_4$	H	80* (*a*)	0	156
2β, 4b-Dimethyl-2-methallyl-7-ethylenedioxy-1, 2, 3, 4, 4aα, 5, 6, 7, 8, 10, 10aβ-dodecahydrophenanthren-1, 4-dione	$C_2H_5OC\equiv CMgBr$	$C\equiv COC_2H_5$	88 (1*a*)	12 (1*e*)	157
dl-Δ^8-4β-Hydroxy-2β-formyl-2α-(3′-hydroxypropyl)-4bβ, 7-dimethoxy-4aα, 10aβ-dodecahydrophenanthren-1-on-dilactol(4→2←3)-3-methyl ester	$C_2H_5OC\equiv CLi$	$C\equiv COC_2H_5$	68 (1*a*)	32 (1*e*)	158
dl-Δ^8-1-Oxo-4β-hydroxy-2α-(3′-dimethoxypropyl)-4bβ-methyl-7-ethylenedioxy-4aα, 10aβ-dodecahydrophenanthrene 2β-carboxylic acid	$C_2H_5OC\equiv CLi$	$C\equiv COC_2H_5$	89—63 (*a*)	11—37 (1*e*)	148
2,3,3,4,5-substitution					
2, 3-Secocholestan-6-on-2, 3-dioic acid	Na+ROH	H	0	90* (*a*)	159
Cholest-2-en-6-one	Na+ROH	H	0	+ (*a*)	159
Cholestan-6-one	Na+ROH	H	0	50* (*a*)	160
Cholestan-3α-ol-6-one	Na+ROH	H	0	93* (*a*)	161
Cholest-2-en-6-one	$LiAlH_4$	H	96 (*e*)	4 (*a*)	159
Cholestan-6-one	$LiAlH_4$	H	95 (*e*)	5 (*a*)	162
Cholestan-3α-ol-6-one	$LiAlH_4$	H	84* (*e*)	0	163
Cholestan-3β-ol-6-one	$LiAlH_4$	H	90* (*e*)	+	161
3α-Chlorocholestan-6-one	$LiAlH_4$	H	97*, 91* (*e*)	0	161, 164
3α-Bromocholestan-6-one	$LiAlH_4$	H	100* (*e*)	0	164
3α-Iodocholestan-6-one	$LiAlH_4$	H	100* (*e*)	0	164
6-Oxocholestan-3-acetic acid methyl ester	$LiAlH_4$	H	47* (*e*)	0	165
N-Benzyl-3-aminocholestan-6-one	$LiAlH_4$	H	75* (*e*)	0	166
5α, 22a-Spirostan-3, 6-dione	$LiAlH_4$	H	58* (6*e*)	+	70
2, 3-Secocholestan-6-on-2, 3-dioic acid dimethyl ester	$NaBH_4$	H	0	80* (*a*)	167
2, 3-Secocholestan-6-on-2, 3-dioic acid 2-methyl, 3-ethyl ester	$NaBH_4$	H	0	75* (*a*)	167
Androsta-3, 6, 17-trione 3-ethyleneketal	$NaBH_4$	H	56* (6*e*)	+	168
Cholestan-3β-ol-6-one 3-tosylate	$NaBH_4$	H	+ (*e*)	0	169
Androsta-3β, 17β-diol-6-one 3, 17-diacetate	CH_3MgJ	CH_3	+ (*e*)	0	170
Androstan-3β-ol-6. 17-dione 3-acetate	CH_3MgJ	CH_3	+ (6*e*)	0	170
17α, 20; 20, 21-Bis-methylenedioxy-3-ethylenedioxyallopregna-6, 11-dione	CH_3MgJ	CH_3	79* (6*e*)	0	171
Cholestan-6-one	CH_3MgI	CH_3	60* (*e*)	0	172
Cholestan-3β-ol-6-one	C_2H_5MgJ	C_2H_5	92* (*e*)	0	173, 174
5α, 25D-Spirostan-3β-ol-6-one 3-acetate	CH_3MgI	CH_3	+ (*e*)	0	175
2,3,3,6,6-substitution					
19-Oxo-18-iso-β-amyranol	$LiAlH_4$	H	+ (*e*)	0	176
19-Oxo-18-iso-β-amyranolic acid	$LiAlH_4$	H	+ (*e*)	0	177

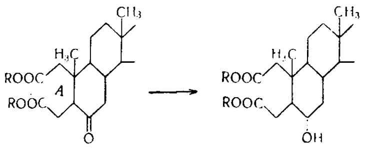
TABLE 6 (contd.)

Ketone	Reagent	R′	Content in resulting mixture, %		Reference
			R′α-form	R′β-form	
	2,3,4,5,5-substitution				
Testan-3α-ol-11, 17-dione	N+ROH	H	0	99* (11*a*)	178
D-Homotesta-3α, 17aβ-diol-11-one	N+ROH	H	0	+ (*a*)	97
dl-Pregn-5-en-3, 11, 16, 20-tetrone 3-ethyleneketal	N+ROH	H	0	16* (11*a*)	179
Ergost-22-en-3β-ol-11-one acetate	Na+C_2H_5OH	H	0	66* (*a*)	180
Ergost-22-en-3β-ol-11-one acetate	Na+*n*-C_3H_7OH	H	0	100* (*a*)	181
11-Oxotigogenin acetate	Na+ROH	H	0	87* (*a*)	182
Adrenosterone	$LiAlH_4$	H	62* (11*e*)	0	183
Androst-5-en-3, 11, 17-trione 3, 17-bisethyleneketal	$LiAlH_4$	H	83* (*e*)	0	184
Androsta-3, 5-dien-3-ol-11, 17-dione 3-benzoate	$LiAlH_4$	H	64* (11*e*)	0	184
Testan-3α-ol-11, 17-dione cyanohydrin acetate	$LiAlH_4$	H	+ (11*e*)	0	185
D-Homotestan-3α-ol-11, 17a-dione acetate	$LiAlH_4$	H	+ (11*e*)	0	97
17, 20; 20, 21-Bis-methylenedioxy-A-norpregna-2, 5-diol-11-on-2-oic acid	$LiAlH_4$	H	68* (*e*)	32 (*a*)	186
Pregna-3α, 20α-diol-11-one diacetate	$LiAlH_4$	H	83* (*e*)	0	187
Pregna-3α, 17α, 20β, 21-tetrol-11-one 20, 21-acetonide	$LiAlH_4$	H	53* (*e*)	0	188
17α, 20β-Epoxypregna-3α, 20α-diol-11-one diacetate	$LiAlH_4$	H	90 (*e*)	10 (*a*)	189
Pregnan-3α-ol-11, 20-dione acetate 20-ethyleneketal	$LiAlH_4$	H	92* (11*e*)	0	190
Allopregnan-3β-ol-11, 20-dione acetate 20-hemithioketal	$LiAlH_4$	H	88* (11*e*)	0	191
Pregna-3α, 17α-diol-11, 20-dione 20-ethyleneketal	$LiAlH_4$	H	76 (11*e*)	24 (11*a*)	192
Allopregna-3, 11, 20-trione	$LiAlH_4$	H	75* (11*e*)	0	64
Pregn-5-en-17α-ol-3, 11, 20-trione 3-ethyleneketal	$LiAlH_4$	H	79 (11*e*)	21 (11*a*)	193
4-Chloropregnan-17α-ol-3, 11, 20-trione 3, 20-bis-ethyleneketal	$LiAlH_4$	H	90* (11*e*)	+ (11*a*)	192
Pregn-4-en-3, 11, 20-trione 3, 20-bis-ethyleneketal	$LiAlH_4$	H	94 (11*e*)	6 (11*a*)	194
Allopregna-17α, 21-diol-3, 11, 20-trione 21-acetate	$LiAlH_4$	H	63* (11*e*)	0	65
Pregn-5-en-17α, 21-diol-3, 11, 20-trione 3, 20-bis-ethyleneketal	$LiAlH_4$	H	88 (*e*)	12 (*a*)	195
Cortisone 3, 20-bis-ethyleneketal	$LiAlH_4$	H	90 (*e*)	10 (*a*)	196
Pregna-1, 4-dien-17α, 21-diol-3, 11, 20-trione 3, 20-bis-semicarbazone 21-acetate	$LiAlH_4$	H	90* (11*e*)	0	197
16-Isopropoxypregna-5, 16-dien-3, 11, 20-trione 3-ethyleneketal	$LiAlH_4$	H	41* (11*e*)	0	179
11-Oxolanost-24-enol acetate	$LiAlH_4$	H	+ (*e*)	0	198
Lanostan-3β-ol-11-one acetate	$LiAlH_4$	H	93* (*e*)	0	199
Lanostan-3β-ol-7, 11-dione acetate	$LiAlH_4$	H	100* (11*e*)	0	199
Ergost-22-en-3β-ol-11-one acetate	$LiAlH_4$	H	90* (*e*)	0	180, 181
22-Isospirostan-3, 11-dione	$LiAlH_4$	H	63* (11*e*)	0	200
11-Oxotigogenin acetate	$LiAlH_4$	H	75* (*e*)	+	182
Pregn-5-en-17α, 21-diol-3, 11, 20-trione 3, 20-bis-semicarbazone	KBH_4	H	99* (11*e*)	0	201
Pregna-1, 4-dien-17α, 21-diol-3, 11, 20-trione 3, 20-bis-semicarbazone	KBH_4	H	85* (11*e*)	0	202
7-Methylpregn-4-en-17α, 21-diol-3, 11, 20-trione 3, 20-bis-semicarbazone 21-acetate	KBH_4	H	54* (11*e*)	0	203
3α-Hydroxy-11-oxoetianic acid acetate	$NaBH_4$+NaOH	H	74* (*e*)	0	204
3, 11-Dioxoetianic acid 3-ethyleneketal	$NaBH_4$+NaOH	H	90* (*e*)	0	205
Pregnan-3α-ol-11, 20-dione	$NaBH_4$	H	85* (11*e*)	0	206
Pregnan-3α-ol-11, 20-dione 20-ethyleneketal	$NaBH_4$	H	87* (11*e*)	0	207
Pregna-3α, 17α-diol-11, 20-dione 20-ethyleneketal	$NaBH_4$	H	100* (11*e*)	0	207
Pregna-3α, 17α-diol-11, 20-dione	$NaBH_4$	H	74 (11*e*)	0	208
3-Diethoxy-20-cyanopregn-17-en-21-ol-11-one	$NaBH_4$	H	+ (*e*)	0	209
Pregna-3, 11, 20-trione 3, 20-bis-ethyleneketal	$NaBH_4$	H	91* (11*e*)	0	207
Pregnan-17α-ol-3, 11, 20-trione 3, 20-bis-ethyleneketal	$NaBH_4$	H	96* (11*e*)	0	207
20-Isopropoxypregna-5, 17(20)-dien-3, 11, 16-trione 3-ethyleneketal	$NaBH_4$	H	50* (11*e*)	0	179
5α-Pregna-17α, 21-diol-3, 11, 20-trione 3, 20-bis-ethyleneketal	$NaBH_4$	H	67* (11*e*)	0	210
3α-Hydroxy-11-oxocholanoic acid	$NaBH_4$+NaOH	H	80* (*e*)	0	92
3β-Hydroxyergostan-11-one	$NaBH_4$	H	84* (*e*)	0	210
5β-Pregnan-3α-ol-11, 20-dione 20-ethyleneketal	CH_3Li	CH_3	50* (11*e*)	0	211
5β-Pregna-3, 11, 20-trione 3, 20-bis-ethyleneketal	CH_3Li	CH_3	65* (11*e*)	0	211
5α-Pregna-3, 11, 20-trione 3, 20-bis-ethyleneketal	CH_3Li	CH_3	82* (11*e*)	0	211
18-Benzylidene-14-iso-17-isoallopregnan-3β-ol-11, 20-dione	$LiAlH_4$	H	75* (11*e*)	0	212
9β-Ergostan-3β-ol-11-one acetate	$LiAlH_4$	H	0	+ (11*a*)	213

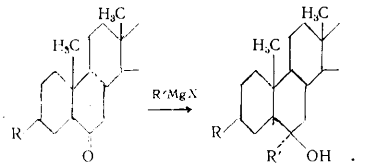
The sodium borohydride reduction of hecogenin acetate produces 12-epirockogenin in greater amount[151]. The reduction of 17β-methyl-D-homoetiocholan-3α,17α-diol-11,17α-dione with sodium in isopropanol or with lithium aluminium hydride gives the 17aβ-alcohol, possessing an equatorial hydroxyl group, in low yield[154]. On the other hand, the action of methylmagnesium iodide on 17β-methyl-D-homoetiocholan-3α,17α-diol-11,17a-dione acetate produces only 17β,17aβ-dimethyl-D-homoetiocholan-3α,17α,17aα-triol-11-one acetate, which is formed by addition of the methyl group in the equatorial position[155]:



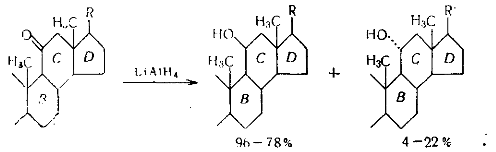
The literature on the stereochemistry of addition to the carbonyl group of 6-oxosteroids (2,3,3,4,5-substitution) indicates considerable steric hindrance. Here, as would be expected from the presence of the axial methyl group in the *meta*-position, only with sodium and alcohol does reduction of the carbonyl group take place predominantly with addition of hydrogen in the axial position[159–161]. Reduction with lithium aluminium hydride[159–166] or particularly with sodium borohydride[167–169] produces the 6β-alcohol with an axial hydroxyl group as the predominant product. The esters of 2,3-secocholestane-6-one-2,3-dioic acid are exceptions[167]; this is apparently due to the loss of rigidity of ring A and the possible polar influence of the acid side chains:



The Grignard reaction on 6-oxosteroids leads exclusively to 6α-methyl-6β-hydroxy-compounds[170-175].



The considerable literature on the stereochemistry of addition reactions to 2,3,4,5,5-pentasubstituted ketones with a cyclohexane ring relate only to 11-oxosteroids. The data can be collated into a few rules which can be deduced from the published material. 11-Oxosteroids with an axial methyl group in the *meta*-position show considerable steric hindrance to the approach of a reactant from the direction of this group, so that only reduction with sodium and alcohol produces 11α-hydroxysteroids formed by the axial addition of hydrogen[97,178-182]. In all the other cases described in the literature, the reactions take place predominantly with addition of the substituent in the equatorial position. It was earlier thought[188] that all these reactions are strictly stereospecific, forming 11β-hydroxy-compounds exclusively, but the studies of Bernstein *et al.*[195,196], Brooks *et al.*[182], Poos[193], and several others[189,192,194] showed that when 11-oxosteroids are reduced with lithium aluminium hydride a small quantity of the 11α-hydroxysteroid (4–22%) is formed in addition to the main product, 11β-hydroxysteroid:



There is nothing in the literature on the formation of 11α-hydroxy-compounds by the reduction of 11-oxosteroids with sodium or potassium borohydride.

Fonken[211] has shown that 11-oxosteroids condense with methyllithium to form, as would be expected, 11α-methyl-11β-hydroxy-compounds. Interesting results have been obtained in the lithium aluminium hydride reduction of 11-oxo-compounds in which the B and C or C and D rings are *cis*-fused. Thus the reduction of 18-benzylidene-14-iso-17-isoallopregnan-3β-ol-11,20-dione with lithium aluminium hydride gave 18-benzylidene-14-iso-17-isoallopregnan-3β,11β,20-triol in 75% yield[212], while from the reduction products of 9β-ergosten-3β-ol-11-one acetate only 9β-ergosten-3β,11α-diol, which has an equatorial hydroxyl group that can be acetylated, was obtained[213]. The same product is obtained in the reduction of this steroid with lithium and methanol in liquid ammonia[213].

6. HEXASUBSTITUTED CYCLOHEXANONES (see Table 7)

The compounds of this type for which the literature contains data on the stereochemistry of addition to the carbonyl group either carry halogen or oxygen as a substituent, or are 6-oxo-3,5-cyclosteroids. The existing material shows that for compounds of the first class, the spatial directivity of the reactions is greatly dependent on the conformational position of the non-alkyl substituent *ortho* to the carbonyl group. Thus 6-bromocholestan-3β-ol-7-one acetate, in which the bromine atom has the axial conformation (6β-configuration) is reduced by lithium aluminium hydride to form only the 7β-hydroxy-compound[110] (axial addition of hydrogen), while the ketone with equatorial bromine (6α-configuration) is reduced to a mixture of the two epimers, containing 56% of the 7α-hydroxy- and only 14% of the 7β-hydroxy-steroid[110]:

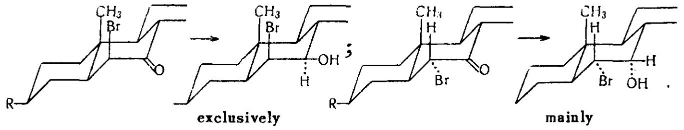
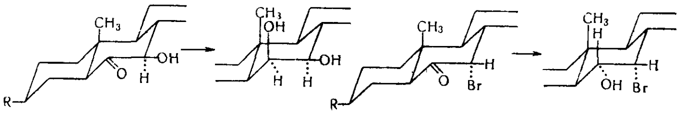


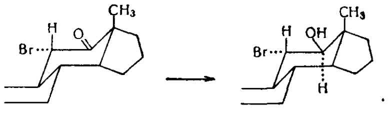
TABLE 7. Stereoselectivity of addition reactions to hexasubstituted cyclohexanones.

Ketone	Reagent	R′	Content in resulting mixture, %		Reference
			R′α-form	R′β-form	
	2,3,4,4,5,6-substitution				
6β-Bromocholestan-3β-ol-7-one acetate	LiAlH₄	H	60*(*a*)	0	110
6α-Bromocholestan-3β-ol-7-one acetate	LiAlH₄	H	44(*a*)	56(*e*)	110
	2,3,4,5,6,6-substitution				
23a-Bromo-5α, 25D-spirostan-3β, 11β-diol-12-one 3-acetate	LiAlH₄	H	+ (*a*)	+ (*e*)	214
23a-Bromo-5α, 25D-spirostan-3β, 11β-diol-12-one 3, 11-diacetate	LiAlH₄	H	46*(*a*)	0	214
11α, 23ξ-Dibromo-5α, 22a-spirostan-3β-ol-12-one acetate	NaBH₄+NaHCO₃	H	72 (*a*)	28(*e*)	215
	2,2,3,3,4,5-substitution				
Cholestan-5-ol-6-one	Na+ROH	H	0	+ (*a*)	105
Cholesta-3β, 5α-diol-6-one	Na+ROH	H	0	60* (*a*)	216
3, 5-Cyclocholestan-6-one	Na+ROH	H	0	40* (*a*)	162
Cholestan-5α-ol-6-one	LiAlH₄	H	+ (*e*)	0	105
Cholesta-3β, 5α-diol-6-one	LiAlH₄	H	82* (*e*)	0	216
Cholesta-3β, 5α-diol-6-one acetate	LiAlH₄	H	60* (*e*)	0	217
3, 5-Cycloandrostan-6-one	LiAlH₄	H	80* (*e*)	0	218
3, 5-Cycloandrosta-6, 17-dione	LiAlH₄	H	90* (*e*)	0	218
3, 5-Cyclocholestan-6-one	LiAlH₄	H	86*.0.13 (*e*)	0.78*.77 (*a*)	218, 219. 162
5-Bromocholestan-3β-ol-6-one acetate	NaBH₄	H	+ (*e*)	+ (*a*)	220
3, 5-Cyclocholestan-6-one	CH₃MgJ	CH₃	96* (*e*)	0	221
	2,2,3,4,5,5-substitution				
Pregna-5α, 9α, 17α,21-tetrol-3, 11, 20-trione 3, 20-bis-ethyleneketal	LiAlH₄	H	68 (11*e*)	+	222
17, 20; 20, 21-Bis-methylenedioxy-3-ethylenedioxy-9α-methylpregn-5-en-11-one	LiAlH₄	H	+ (*e*)	0	223
3α, 9α-Dihydroxy-11-oxocholanoic acid	NaBH₄+NaOH	H	78* (*e*)	0	92
3β, 9α-Dihydroxy-11-oxocholanoic acid methyl ester acetate	NaBH₄	H	98 (*e*)	0	92
	2,3,3,4,5,6-substitution				
3α, 7β-Dihydroxy-6-oxoallocholanoic acid	NaBH₄	H	90(*e*)	0	224
7α-Bromocholestan-3β-ol-6-one acetate	NaBH₄	H	47 (*e*)	53 (*a*)	220
7α-Bromocholestan-6-one	NaBH₄	H	44 (*e*)	56 (*a*)	225
	2,3,4,5,5,6-substitution				
22-Isoallospirostan-3β, 12β-diol-11-one	LiAlH₄	H	94* (*e*)	0	226
5α, 22a-Spirostan-3β, 12β-diol-11-one 3-acetate 12-tosylate	LiAlH₄	H	40* (*e*)	0	227
12α-Bromo-11-dehydrocortisone acetate	LiBH₄	H	+ (*e*)	0	228
Pregn-4-en-21-ol-3, 11, 20-trione 3, 20-bis-semicarbazone 21-acetate	LiBH₄	H	91* (*e*)	0	229
	2,3,3,4,4,5-substitution				
11-Oxo-oleanolic acid methyl ester acetate	LiAlH₄	H	+ (*e*)	0	230

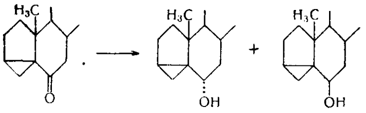
An analogous effect is found with 7-substituted 6-oxo-steroids. For example, 3α,7β-dihydroxy-6-oxoallocholanoic acid is reduced by sodium borohydride to form only the 6β-hydroxy-isomer with an axial hydroxyl group[224], while 7α-bromocholestan-3β-ol-6-one acetate is reduced by the same reagent to a mixture containing 53% of the 6α-hydroxy- and 47% of the 6β-hydroxy-compound[220], *i.e.* the addition of hydrogen takes place also from the direction screened by the angular methyl group:



An interesting effect is found in the reduction of 11α,23ξ-dibromo-5α,22α-spirostan-3β-ol-12-one acetate, with an equatorial bromine atom, by means of sodium borohydride[215]. While the sodium borohydride reduction of 12-oxo-compounds leads mainly to the formation of products of addition of hydrogen in the equatorial position[151,153], the introduction of the 11α-bromine atom directs this reaction towards predominantly axial entry of hydrogen[215]:



In its general features, the reduction of 6-oxo-3,5-cyclosteroids obeys the same rules as in the case of ketones with an axial *meta*-substituent. Reduction of 3,5-cyclocholestan-6-one with sodium and alcohol produced only the 6α-alcohol with an equatorial hydroxyl group[162]. Reduction with lithium aluminium hydride gives the 6β-alcohols with axial hydroxyl in dominant amount[162,218,219]:

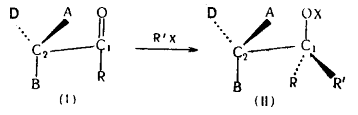


However, the existing literature on this subject are somewhat contradictory. Thus Wagner, Wolff and Wallis[218] show that the lithium aluminium hydride reduction of 3,5-cyclocholestan-6-one produces only 3,5-cyclocholestan-6β-ol (in 86% yield), while in the same reaction, Shoppee and Summers[162] and Kosower and Winstein[219] obtained 3,5 cyclocholestan-6α-ol in considerably predominant amount.

7. ATTEMPTED GENERALISATION OF THE RESULTS ON THE STEREOCHEMISTRY OF NUCLEOPHILIC ADDITION TO THE CARBONYL GROUP

Tiffeneau[231] suggested that addition to a carbonyl group in ketones with an asymmetric carbon atom adjacent to the keto group takes place under the influence of this asymmetric centre. This theory found its widest development in the so-called "Cram rule", deduced by Cram and Abd El Hafez[232] from a study of the stereochemistry of addition to optically active ketones and aldehydes. Although Cram himself related this rule only to aliphatic compounds, later workers attempted to apply it to cyclic ketones.

According to the Cram rule, addition of a nucleophilic reagent to a ketone (or aldehyde) takes place from the less screened side of the carbonyl double bond in conformation (I), where this bond lies between substituents A and D of smallest volume (A < D < B) attached to the adjacent asymmetric centre:

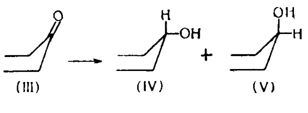


It is thus assumed that in the initial conformation the oxygen atom occupies a position between the smallest substituents on C_2 (A and D), and the substituent on C_1 (R) occupies a shielded position with respect to the largest substituent on C_2 (B). However, the conformation which exists in *ortho*-substituted ketones with a six-membered ring is nearer that in which the carbonyl oxygen and the equatorial *ortho*-substituent are in the shielded position with respect to one another, since the angle of projection between them is 15°.[46] Existing data show that the Cram rule cannot apparently be applied to the cyclohexane series. According to this rule, which was deduced from the Grignard reaction and reduction with lithium aluminium hydride, the addition to 2-methylcyclohexanone of the methyl group in the first case and hydrogen in the second must take place from the same direction. In practice, however, these two reactions show opposite selectivity[13,18]. Moreover, the selective course of nucleophilic addition reactions depend, according to the Cram rule, on the presence of an asymmetric centre adjacent to the carbonyl group[232], but in the cyclohexane series even ketones without asymmetric centres, such as 4-t-butylcyclohexanone, show a spatial selectivity in these reactions[29,30,36].

Other attempts at generalisation in the literature relate exclusively to the reduction of cyclic ketones.

In 1919 Skita[233] considered that the reduction of cyclic ketones with sodium and alcohol always gives *trans*-alcohols as the main product (*cis*-addition of hydrogen). This was developed by Vavon[234], who, on the basis of a number of examples, proposed the rule that *trans*-alcohols are predominantly formed when cyclic ketones are reduced in alkaline medium, and by Hückel[235], who extended Skita's suggestion to include the reduction of oximes. However, after the actual configuration of 3-substituted cyclohexanols had been proved[41], it became clear that 3-substituted cyclohexanones are reduced by sodium and alcohol to form not the *trans*-, but the *cis*-alcohols (*trans*-addition of hydrogen).

Finally, in 1953 Barton[236] formulated a rule for the stereoselectivity in the ionic reduction of ketones (with sodium and alcohol, complex metal hydrides, etc.), according to which such reduction of ketones not sterically hindered (III) produces as the main product the thermodynamically more stable isomer with an equatorial hydroxyl group (IV):



Barton was led to his rule from the fact that the composition of the mixture of alcohols (IV) and (V) formed in such a reduction is close to that of the mixture obtained when either of the stereoisomers (IV) or (V) is isomerised under the action of alkaline reducing agents. It was considered that the composition of the equilibrium mixture depends only on the relative thermodynamic stability of the two isomers (IV) and (V). The equilibrium position in this case is independent of the method by which it is attained. However, Hückel[11] recently showed that the composition of the equilibrium mixture of the alcohols (IV) and (V) is different when different isomerising agents are used (sodium, lithium aluminium hydride, sodium borohydride, etc.). On the other hand, Hückel and Naab[237] and later Doering and Aschner[238] showed that the isomerisation of secondary alcohols from one form into the other under the action of alkaline agents is an oxidation-reduction process in which the ketone (III) is an intermediate. The equilibrium in such processes will only depend on the relative thermodynamic stabilities of the components (or more correctly, on the energies of activation) only with symmetrical (ideally dynamically homologous) systems[239]. The systems under consideration are clearly not of this type, and therefore the composition of the equilibrium mixtures obtained in the reduction of the ketones is not determined by the relative thermodynamic stabilities of the isomers (IV) and (V), but primarily by the kinetics of the competing reactions (III) → (IV) and (III) → (V). This agrees completely with Hückel's deduction[239] that "the quantitative relationship between the components in competing reactions is determined primarily not by their thermodynamic stabilities, but mainly by the relative rates of the reactions taking place in the various possible directions".

The suggestion that the equilibrium depends on the kinetics of the reduction reactions finds confirmation in the following facts: (1) the use of different reducing agents gives mixtures of alcohols of different composition[11]; (2) the addition of aluminium bromide to the lithium aluminium hydride can completely change the directivity of the reduction,[11], because of attack by the larger ion $AlBr_3H^-$ instead of AlH_4^-; (3) increasing the temperature of the lithium aluminium hydride reduction from -60° to +35° increases the quantity of the conformationally less stable isomer with the axial hydroxyl group[11]; and (4) reduction of lanostan-3,11-dione[181] and cholesta-3β,5α-diol-6-one[216] with sodium and alcohol produces the alcohols with an equatorial hydroxyl group (11α, 6α), while reduction with lithium aluminium hydride gives the alcohols with axial hydroxyl (11β, 6β), which are not isomerised to the former alcohols by the action of sodium. Quite recently, Beckett, Harper, Balon, and Watts[240] also apparently came to the conclusion that the stereochemistry of the reduction of tropinone depends primarily on kinetic and not thermodynamic factors.

In 1956 Dauben, Fonken, and Noyce[9] put forward the suggestion that the stereoselectivity of the reduction of cyclic ketones with complex metal hydrides is determined by two factors, the first, which they called "steric approach control", comprising screening of one or other side of the molecule, and the second ("product development control") comprising the energetic effect, which depends on the relative stabilities of the resultant reaction products. The reduction of menthone with lithium aluminium hydride, which gives predominantly axial addition of hydrogen with the formation of the more stable equatorial hydroxyl group, they attributed to the influence of the second factor, and the reduction with sodium borohydride, which leads mainly to equatorial addition of hydrogen, to screening of the carbonyl bond by the 2-isopropyl group and to the larger size of sodium borohydride as compared with lithium aluminium hydride. However, the radius of the boron ion (B^{3+} = 0.2 Å) is less than that of the aluminium ion (Al^{3+} = 0.57 Å)[241,242], so that only the solvated ion $BH(OR)_3^-$ can have a larger volume, and this is confirmed by the identity in the stereoselectivity in reduction with sodium borohydride in methanol and with the complex $NaBH(OCH_3)_3$. The steric hindrance in the ketone molecule is ascribed by Dauben, Fonken, and Noyce[9] to the presence of axial alkyl groups in the *meta*-position to the carbonyl group. The influence of the second factor, in their opinion, is shown by the complex hydride ion so orientating itself in the reaction mixture that when it decomposes, the product is the more stable alcohol isomer with the equatorial hydroxyl group. Here again, therefore, the relative thermodynamic stabilities of the end products are largely responsible for the stereoselectivity of the reaction. The existence of steric hindrance because of axial *meta*-substituents is well known[1,243]. It is also known that an axial substituent in the cyclohexane ring enters into steric reaction even with axial hydrogen atoms in the *meta*-position. According to Angial and Mills[244], the distance between the 1a- and 3a-hydrogen atoms in the undistorted chair form of cyclohexane is 2.51 Å, which is only slightly greater than the sum of the van der Waals' radii for two hydrogen atoms (2.34 – 2.4 Å)[241,242]. When the hydrogen is replaced by any other axial substituent, the sum of the van der Waals' radii for this substituent and the axial hydrogen atom becomes greater than 2.51 Å, causing strong mutual repulsion. Thus for an axial hydroxyl group, with a van der Waals' radius for oxygen of 1.36 – 1.4 Å[241], this sum becomes 2.6 Å. The cyano- and ethynyl-groups are linear, and their axis is approximately parallel to the axial carbon–hydrogen bond, so that any reaction between these substituents and *meta*-hydrogen atoms will depend only on the van der Waals' radius of triply-bonded carbon (1.7 – 1.8 Å)[241], and the sum of the two van der Waals' radii (1a, 3a) will be 2.9 Å. The methyl group, being branched, has large dimensions in the 1a–carbon–3a–hydrogen direction (2.05 Å)[241,242]. Even these rough calculations show: (1) that not only axial carbon-containing *meta*-substituents, but even axial *meta*-hydrogen atoms, cause spatial screening of one side of the carbonyl group, and (2) that this screening effect increases with increasing size of the entering substituent.

The steric hindrance therefore depends on the number and size of the axial substituents (including hydrogen atoms) in the *meta*-position to the keto-group, and on the size of the entering substituent (or attacking complex).

The experimental material given above shows that with increase in the size of the entering substituent (from hydrogen to methyl) with the same ketone, or with increased steric hindrance in the ketone (for the same reaction), there is an increase in the yield of isomer formed by entry of the substituent in the equatorial position. This can only be due to the influence of the steric hindrance factor. On the other hand, decreasing the size of the attacking agent and the number and size of the axial *meta*-substituents in the ketone molecule leads to the formation of an increased quantity of the isomer formed by axial addition. This cannot be explained by a simple comparison of the relative thermodynamic stabilities of the two isomers, as follows from the Barton rule[236].

In fact, in the reduction of ketones of low steric hindrance, when the entering substituent (H) is small in comparison to the hydroxyl group, the secondary alcohol with the equatorial hydroxyl group which is the main product is conformationally more stable, as is seen by calculation and from experiments[1,242] independent of alkaline isomerisation. However, the isomer which is the main product in the cyanohydrin and acetylene syntheses has in the axial position a cyano- or ethynyl-group, which have a greater effective volume than the hydroxyl group. Comparison of the van der Waals' radii and the generalised Auwers-Skita rule[1,242] both show that an axial cyano- or ethynyl-group in combination with an equatorial hydroxyl group is apparently conformationally less favourable than the reverse. Some attempts can be made to explain these facts. The Arrhenius equation for the velocity constant of a reaction, $K = \alpha e^{-q/RT}$, contains two terms, of which one ($e^{-q/RT}$) depends on the energy of activation, and the other (the frequency factor α) is related to non-thermodynamic quantities: the frequency of collisions, the size of the molecules, the size of the "sensitive region", and other steric factors.

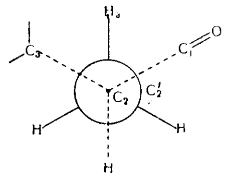
According to Hückel[239], all organic reactions can be divided into two groups: (1) reactions whose rates depend mainly on differences in the energies of activation, and (2) reactions whose rates are mainly determined by the frequency factor.

The high velocity of reactions in which the carbonyl group takes part indicates its comparatively low energy of activation (10–13 kcal mole^{-1}), and the considerable complexity of molecules of cyclic ketones must inevitably lead to a small frequency factor. It can thus be assumed that these reactions belong to the second group.

The stereoselectivity of nucleophilic addition to the carbonyl group of cyclic six-membered ketones is apparently therefore determined by two opposing factors: one which directs the entering substituent into the axial position, and one which depends on steric hindrance and directs the substituent into the equatorial position.

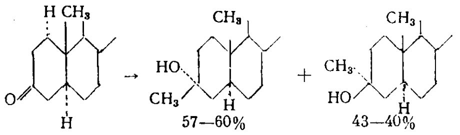
It seems probable that the first factor is determined mainly by the orientation taken up by the charged nucleophilic (anion) attacking agent under the influence of polar forces, and not the thermodynamic stability of the end products. This orientation is closely bound up with the actual mechanism of the nucleophilic reaction, and may be due to the difference in the electrostatic fields originating from the upper and lower ends of the carbonyl double bond, produced, for example, by the non-compensated dipole moments of the carbon–hydrogen bonds.

In comparing the stereochemical data on the nucleophilic addition, the Grignard reaction with 2-methylcyclohexanone[19] is clearly more stereoselective than the reaction with 3-methylcyclohexanone[38], the first producing 75% equatorial addition, and the second only 60%. A molecular model of 2-methylcyclohexanone shows that a methyl group in the equatorial position will be most stable when the hydrogen atoms are in angular positions with respect to the substituents at C_2.

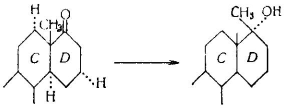


In this case the hydrogen atom H will be the same distance from the carbon atom C_1 as the axial *meta*-hydrogen atoms, *i.e.* it will act as a third axial *meta*-hydrogen atom, causing additional steric hindrance. The existence of considerable steric hindrance in 2-methylcyclohexanone in comparison with 3-methylcyclohexanone is additional confirmation that these ketones enter into these reactions predominantly in the conformation with an equatorial methyl group. In fact, if with the methyl group in this position there is more hindrance with 2-methylcyclohexanone, there would be considerably more screening of one side of the molecule with an axial methyl group in the case of 3-methylcyclohexanone.

It is very interesting to compare the stereochemistry of the Grignard reaction in the cyclohexane and steroid series. 3-Oxosteroids, which like 3-methylcyclohexanone possess two axial *meta*-hydrogen atoms, react with methylmagnesium iodide to form a mixture containing 57–60% of the product of equatorial addition of the methyl group[76–78].



However, 17a-oxo-D-homosteroids, which have three axial *meta*-hydrogen atoms in a rigid system (at C_{12}, C_{14}, and C_{16}), form only the equatorial addition product[100,101]:



and Clinton, Christiansen, Neumann, and Laskowski[100] explained this as being due to these hydrogen atoms. The difference in the stereoselectivity of the reactions of 17a-oxo-D-homosteroids (with a rigid skeleton) and 2-methylcyclohexanone shows that the latter clearly reacts partly in the conformation with an axial methyl group.

We have attempted to systematise the existing data on the stereochemistry of these nucleophilic addition reactions from the point of view of increasing steric hindrance in the ketone molecule, using average compositions of the mixtures formed from variously substituted ketones with the cyclohexane ring (Table 8). The steric hindrance is considered as being due to hydrogen atoms and methyl groups in the *meta*-position to the carbonyl group in the ring or in a side chain, and possessing, in the most stable conformation, an axial disposition.

TABLE 8. Content in the mixture (%) of the isomer with axial disposition of the entering substituent.

Reagent	Hindering axial groups and disposition of substituents				
	2H 3-, 4-, 3, 4, 4	3H 2-; 2,2-; 2,5-; 2, 3-, 2,2,3-2,3, 4,4-; 2,3,4,4,5-; 2,2,3,4,5	1CH₃ 1H 3,3,4-	1CH₃, 2H 2,3,3-; 2,3 3,4,5-; 2,2,3,3,4,5	2CH₃ 1—2H 2,3,4,4,5-;2,3, 4,5,5,6-, 2,3,3, 4,4,5
Na in alcohol	78	80	main product	main product	main product
HCN	75	73	?	?	?
HC≡CH and KOH	86	73	?	?	?
$LiAlH_4$	82	61	42	23	14
$NaBH_4$	77	55	18	low ?	0
CH_3MgI	38	26	?	0	0

Table 8 shows that increasing the number and size of the axial substituents in the *meta*-position to the keto-group causes a regular increase in the quantity of isomer formed by equatorial entry of the substituent.

It cannot at present be stated definitely whether the volume of the incoming substituent or the size of the attacking complex as a whole plays a large part in the stereoselectivity of the reaction.

Summarising what has been set out above, despite the limited quantity of material, it appears that the spatial directivity of nucleophilic addition reactions (which may be the result of definite orientations of molecules in the reaction mass) depends on two factors — polar orientation (polar factor) and steric hindrance (steric factor).

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LIGNIN

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CONTENTS

I. INTRODUCTION

The study of the structure of natural lignin and the conditions under which it is formed in the plant cell, and also the search for methods of utilising the enormous amount of lignin wastes from the modern paper and hydrolytic industries, are tasks of great scientific and economic importance.

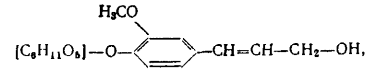
Lignin constitutes about 30% of the plant resources which are annually renewed on a hugh scale on the earth. It is the most important natural aromatic polymer, and is thus potentially a rich source of phenolic products, which are widely used in modern industrial organic synthesis.

During the past decade a great deal of research has been done on the chemistry and the biogenesis of lignin, which to a large extent enables us to understand and to explain the structure of this interesting natural polymer.

II. PATHWAYS OF LIGNIN BIOSYNTHESIS IN PLANTS

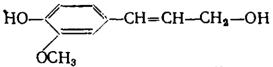
Study of plant evolution shows that lignin has a protective function, since the start of biosynthesis of lignin in plants is associated with the transition to life on land. Botanists consider that lignin first appeared in the Pteridophyta. No lignin is present in algae, liverworts, or mosses. It is contained in small amounts in horsetails, and definitely occurs in ferns[1].

The process of lignification and lignin formation in the plant cell must be regarded as part of normal metabolism. Manskaya[1] showed that cambium and wood of the new annual layer of pine contain β-glucosidase and the oxidising enzymes peroxidase and polyphenol-oxidase. Coniferin (a glucoside)



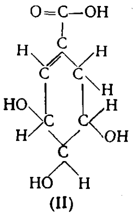
found in the cambium of conifers, serves as a substrate for oxidising enzymes. Under the action of the β-glucosidase it is split into glucose and coniferyl alcohol, the latter of which, by being oxidised and reduced, can serve as an intermediate link in the chain of reactions accompanying respiration of the cells. When the living cells die off in the course of lignification, the oxidising processes begin to predominate over the reducing processes, and the oxidation products are deposited in the form of lignin. Thus on Manskaya's hypothesis the formation of lignin is directly associated with breakdown of the respiratory apparatus in plant cells. When the cell wall, and in particular the region of the middle lamella, where the main amount of lignin is found, lignifies, the life of the cell and the activity of the enzymes cease.

The biosynthesis of lignin in plants has been investigated in detail during recent years by several workers[2-6]. A method which proved to be fruitful was to compare the principles underlying the synthesis of amino-acids by bacteria and of lignin monomers by the plant cell. Many protein amino-acids, *e.g.* phenylalanine and tyrosine, contain benzene nuclei. The experimental results now available show that coniferyl alcohol (I) (or its glucoside coniferin) is formed in the plant *via* the same intermediate stages as occur in the biosynthesis of phenylalanine or tyrosine in micro-organisms:



(I)

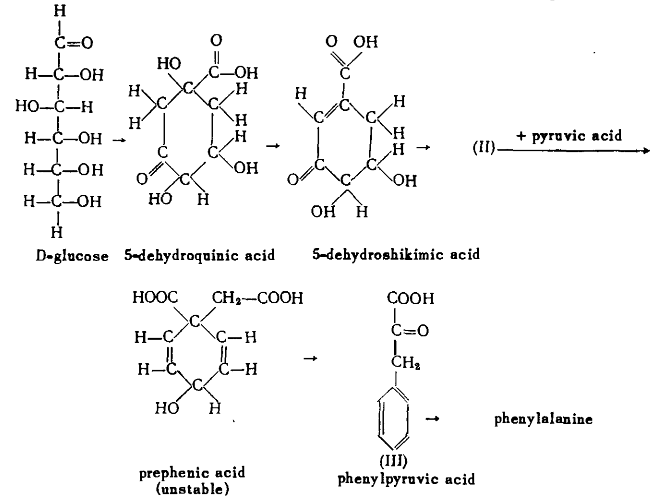
A protracted study of the metabolism of some mutants of *Aerobacter aerogenes* and *Escherichia coli* using radioactively labelled starting materials clarified the biosynthetic pathways of aromatic and in particular phenylpropane derivatives, which include phenylalanine and tyrosine as well as the lignin monomer, coniferyl alcohol[7,8]. It was shown that, starting from glucose, bacteria synthesise aromatic amino-acids in several stages. The organism first converts the glucose molecule through intermediate steps into the cyclic compound shikimic acid (II), a substance which is widely distributed in the vegetable kingdom[9]:



(II)

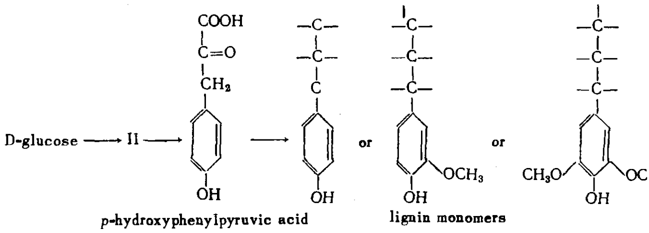
This latter compound, after a series of changes, passes into the aromatic compound hydroxyphenylpyruvic acid[10] and then into an aromatic precursor of proteins.

The biosynthesis of aromatic substances by bacteria can be represented schematically by the following stages[11]:

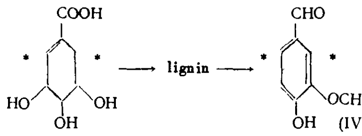


As can be seen from the scheme, the glucose molecule (the main product of photosynthesis) is converted into the cyclic compound 5-dehydroquinic acid[12], and then into 5-dehydroshikimic acid[13] and shikimic acid. This last acid can condense with pyruvic acid to form the unstable prephenic acid[14], which splits off carbon dioxide and water to yield (III). Phenylalanine can be formed from (III) by transamination[15].

The synthesis of aromatic lignin monomers by plants resembles the bacterial synthesis and is represented by the following sequence[11]:



The possibility of accomplishing such a stepwise aromatisation of shikimic acid has been demonstrated by the work of American biochemists[16-18]. Shikimic acid labelled in the 2,6-positions was introduced artificially through the leaves into the growing sugar cane. After six days of such feeding, the plant was cut, the lignin was separated, and from it vanillin (IV) was obtained by the usual methods. The cyclohexene ring of shikimic acid was shown[18] to pass directly into the aromatic nucleus of lignin, the radioactive carbon tracer (^{14}C) occupying the 2,6-positions in the vanillin:



(IV)

According to investigations by Brown and Neish[19], precursors in the formation of lignin can be also phenylalanine, cinnamic acid, and especially 4-hydroxy-3-methoxycinnamic (ferulic) acid, which is detected chromatographically in aqueous extracts of straw and wheat[20].

To obtain confirmation of these hypotheses, Freudenberg[21] introduced radioactively labelled ferulic acid or penylalanine into the wood of a young spruce. Structural lignin was obtained by treating the radioactive region of the branches with alcohol in the presence of hydrochloric acid (by ethanolysis). After radioactively labelled phenylalanine had been introduced, it was possible to isolate from the wood of the spruce active lignin and also active coniferin[22]. These results show that plants possess all the enzymes which are necessary to convert an aromatic amino-acid into a ring-substituted carbinol. The hydroxylation of the nucleus, partial methylation of the phenolic hydroxyl, and reduction of the terminal carboxyl group, evidently occur at the same time as aromatisation, and are catalysed by enzymes of the phenolase type[23,24] or methyl-transferase[25]. The order in which the hydroxylation, methylation, and reduction reactions occur has not yet been confirmed experimentally.

When L-coniferin, obtained from L-glucose and radioactive coniferyl alcohol, was used, no radioactive lignin was obtained[26], which is perhaps explained by the absence of the enzyme L-glucosidase in plant tissue.

Freudenberg showed the presence of cellular β-glucosidase by using the synthetic glucoside indican, which is split by the β-glucosidase present in wood tissue into glucose and indoxyl. The latter is oxidised to indigo by the action of air. Application of indican to a wood section gave a blue coloration due to indigo[27].

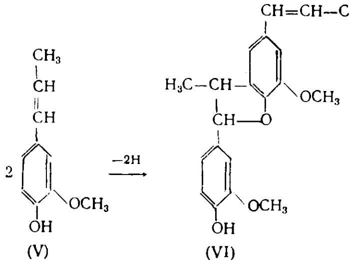
According to Freudenberg, coniferyl alcohol — coniferin aglucone — originates from an acid possessing a C_6-C_3 grouping, the precursors of which are shikimic and prephenic acids. During the period of growth, the cambium and the neighbouring cells contain a large amount of coniferin[28]. It diffuses into the newly formed cells, and is there hydrolysed by β-glucosidase into glucose and coniferyl alcohol. The latter, coming into contact with laccase and peroxidase, is transformed into lignin[27].

Thus lignin formation involves both enzyme systems, the presence of which in the lignification zone can be detected by means of colour reactions[29,30].

III. ARTIFICIAL PREPARATION OF LIGNIN BY ENZYMIC DEHYDROGENATION OF CONIFERYL ALCOHOL

Study of the course of the biochemical synthesis of lignin in plants *in vivo* proceeded in parallel with intensive investigation of the intermediate products formed by enzymic oxidation of coniferyl alcohol *in vitro*. The genetic relationship of coniferin to lignin was first suggested by Tiemann as early as 1875 [31], and later this idea was fruitfully applied by Klason[32].

The possibility of obtaining a product similar in properties to lignin by enzymic oxidation of aromatic monomers was pointed out by Erdtman[33]. He showed that the substance obtained by Cousin in 1908 [34] by the oxidation of isoeugenol (V) with fungal oxidases was the phenylcoumaran derivative (VI) having the structure suggested for lignin:



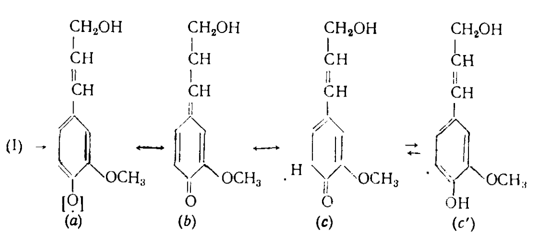
(V) (VI)

Study of this oxidising enzymic reaction made clear the principle underlying the formation of lignin, which on Erdtman's hypothesis[33] was to be regarded as a product of the dehydrogenation of guaiacylpropane derivatives having an oxidised side-chain.

During the past decade Freudenberg and his collaborators have studied the possibility of preparing lignin *in vitro*. When air is passed through a dilute (< 0.5%) aqueous solution of coniferyl alcohol in the presence of fungal laccase at 20° and pH 5.5–6.5, a brownish-grey deposit is formed. Up to 80–90% of the coniferyl alcohol is used up in this process. The fungal laccase can be replaced by cambium laccase, horseradish peroxidase, or dilute solutions of hydrogen peroxide[35]. The time required for the formation of lignin varies from a few minutes to many hours depending on the concentration of the enzymes. Some of the products of low molecular weight can be extracted from the precipitate with butanol, and the residue ("dehydropolymer") represents a biosynthetic lignin formed by enzymic dehydrogenation of coniferyl alcohol.

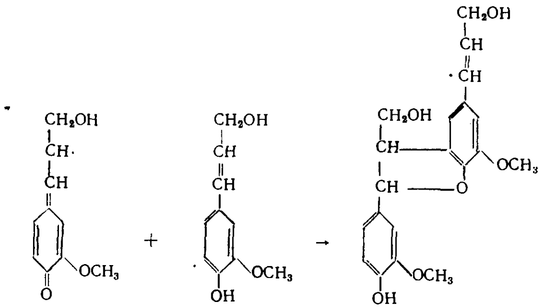
Physical and chemical studies of biosynthetic and natural lignin preparations suggested that they were quite similar[36-40]. Investigations with labelled coniferyl alcohol *in vitro* and *in vivo* confirmed that coniferyl alcohol is utilised in the biosynthesis of lignin[20,41-43]. The preparation of dimeric products by the enzymic dehydrogenation of coniferyl alcohol *in vitro* and their chromatographic detection in the cambial sap must be regarded as the most important result[44]. Study of the structure of the dimeric products makes it possible to judge the nature of the bonds between the phenylpropane monomers in lignin. It must be stressed, however, that it is impossible to apply with complete success conclusions derived from *in vitro* experiments to processes occurring in the living cell[45]. It is still true that "no natural compound has been structurally elucidated by following its biosynthesis, nor is it likely that this will be accomplished, especially in so complex a group of ill defined compounds as the lignins"[45].

The "oxidase" system (mainly laccase)[46-48] takes part in the enzymic dehydrogenation of coniferyl alcohol and the formation of lignin dehydropolymer. According to Freudenberg[49], the formation of lignin in spruce wood begins with the dehydrogenation of coniferyl alcohol, and the radical which is formed (*a*) can be represented in several mesomeric and tautomeric forms (*b*), (*c*), (*c'*):



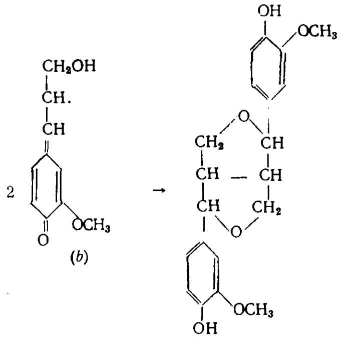
As a result of spontaneous dimerisation, these mesomeric radicals are stabilised, forming dimeric intermediate products, the secondary structural units of lignin. Four of them, the structures of which have been elucidated, form about 80% of all these products. It has proved possible to isolate the following intermediates[26,29,49-51]:

A. Dehydrodiconiferyl alcohol (VII), corresponding to about 20% of the initial coniferyl alcohol. Its formation can be explained by condensation of the tautomeric radical (c') with a quinomethane of the type of (b), the phenolic hydroxyl groups undergoing ring-closure with formation of a benzenoid structure:



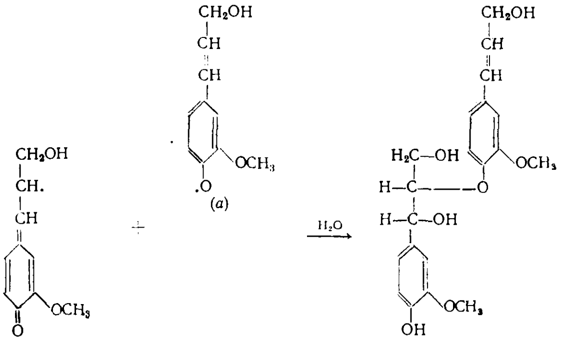
(b) (c') (VII)

B. DL-Pinoresinol (VIII), corresponding to 20% of the initial coniferyl alcohol. It is formed from two quinomethyl radicals (b):



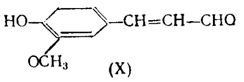
(b) (VIII)

C. The β-ether of guaiacylglycerol and coniferyl alcohol (IX), corresponding to 30% or more of the initial coniferyl alcohol. It is formed from (b) and (a) with subsequent addition of water:



(b) (IX)

D. Coniferaldehyde (X) (1% yield)

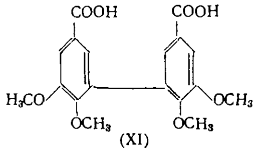


(X)

E. Dehydrodiconiferyl aldehyde, 4%.

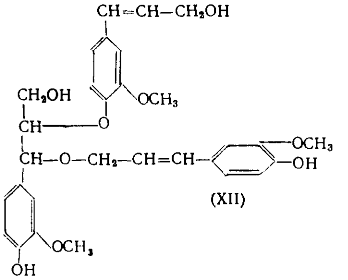
F. Aldehyde corresponding to (IX), 3%.

G. Dehydrodipinoresinol, a crystalline diphenyl derivative formed from two molecules of (VIII) with the elimination of two hydrogen atoms, 4%. Dehydrodiveratric acid (XI) can be obtained from this, after methylation and oxidation; the link between the two molecules is thus in the 5,5'-positions[27].



(XI)

H. A diether formed by two molecules of coniferyl alcohol with guaiacylglycerol (XII), 5%.

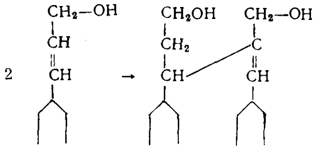


(XII)

I. A diether formed by coniferyl alcohol (β) and dehydrodiconiferyl alcohol (γ) with α-guaiacylglycerol, analogous to (XII).

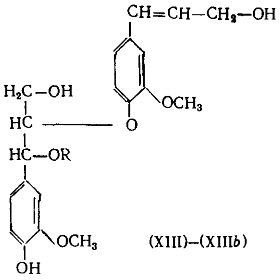
The maximum yield of each substance occurs at different stages in the formation of lignin[27], and it is therefore unallowable to add up the above percentages. The continued action of enzymes leads to the occurrence of further dehydrogenation and condensation processes, with the formation of polymeric lignin[49]. The initial radical, dehydrogenated coniferyl alcohol, is optically inactive. Therefore all dimeric intermediate products are also inactive, as are both native and biosynthetic lignins.

The above forms of combination between different radicals do not exhaust the variety of possible links. Some time ago it was shown spectrophotometrically[52] that diphenyl links probably occur in dehydropolymers and in native lignin. It is possible that $\alpha-\beta$ bonds are formed between two side-chains, and these may arise as a result of dimerisation of coniferyl alcohol or of a coniferaldehyde group[50]:



The possibility of links between $\alpha-\alpha'$ carbon atoms is likewise not excluded[53,54]. No direct proof of the existence of quinomethyl radicals is yet available. This is evidently due to their short life. Spectrophotometric measurements have shown that their half-life under the experimental conditions was about 60 sec.

If the enzymic dehydrogenation of coniferyl alcohol is carried out in water containing 30% of methanol, the methyl ether (XIIIa) is formed. In the presence of much sorbitol or of a sugar, an adduct is formed between the dimeric structural unit and the polyhydroxy compound (XIII*b*):

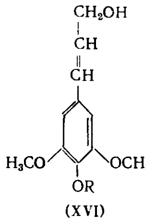

(XIII)–(XIII*b*)

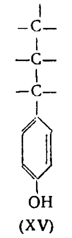
where for (XIII) R = H, for (XIII*a*) R = CH_3, and for (XIII*b*) R = $C_{12}H_{21}O_{10}$.

Direct spectrophotometric measurements[55], colour reactions, and the formation of the methyl ether and the adduct with the sugar (XIII*b*) may serve as a basis for accepting the existence, even if for only a short period, of quinomethyl radicals during the enzymic dehydrogenation of coniferyl alcohol. The formation of a chemical bond with a sugar molecule is important also for an understanding of the nature of the possible links between the aromatic units in lignin and carbohydrates.

The enzymic dehydrogenation of coniferyl alcohol does not lead to its quantitative conversion into biosynthetic lignin. This is explained by the fact that the lignin itself undergoes degradation as a result of the action of the laccase or peroxidase enzymes[35]. This process is probably similar to the humification of lignin and phenolic substrates in the soil. It should also be noted that wood-degrading fungi contain, predominantly in the mycelia, laccase and peroxidase, the enzymic action of which leads to the breakdown of lignin[27]. Consequently, both the formation and the decomposition of lignin can evidently be caused by the same enzymes.

Although coniferyl alcohol may be regarded as the original structural unit for lignin from conifer wood (spruce), the lignin from deciduous species contains also sinapyl alcohol (XIV), while the lignin of annual plants contains *p*-hydroxyphenol residues (XV):


(XVI)


(XV)

where for (XIV) R = H and for (XVI) R = $C_6H_{11}O_5$.

Sinapyl alcohol, which is found in the wood of deciduous trees in the form of the glucoside syringin (XVI), does not form lignin. The action of laccase and peroxidase on sinapyl alcohol leads solely to the formation of an 80–90% yield of syringoresinol (the 5,5'-dimethoxy derivative of pinoresinol)[35,56].

Freudenberg believes that in this case intermediates containing phenyl ether links, *e.g.* as in (VII) or (IX), cannot be formed owing to steric hindrance[27]. This to some extent explains the experiments *in vitro*, because the lignin of deciduous wood necessarily includes coniferyl alcohol, apart from sinapyl alcohol, as a structural unit.

Study of the degradation products of lignins obtained from different kinds of plants has shown that each of them is built up from monomers of several types in varying proportions. Therefore the term "lignin" refers not to a single compound but to a group of closely related products[11]. The great variety of combinations arising among the separate structural units leads to the formation, not of an individual substance of definite constitution, lignin, but to a group of "lignin substances"[57].

Gymnosperm lignin (spruce, pine, etc.) is, according to Freudenberg, a dehydropolymer of coniferyl alcohol. The lignin of angiosperms (beech, etc.) is formed by the dehydropolymerisation of coniferyl and sinapyl alcohols. Monocotyledonous plants (bamboo, etc.) contain also a substantial amount of *p*-hydroxyphenyl structural units[58].

IV. ISOLATION OF LIGNIN AND LIGNIN–CARBOHYDRATE BONDS

The separation of unchanged natural lignin ("protolignin") from plant tissue has unfortunately not yet been achieved. All existing methods require the application of chemical, mechanical, or fermentation procedures to the plant tissue for the separation. However, Brauns has shown[59,60] that is is possible to remove 2–3% of the total amount of lignin by extracting wood with cold ethanol. It was found that after numerous reprecipitations the preparation behaved in many respects as protolignin, exhibited typical lignin reactions, and gave derivatives identical with those obtained directly from wood. Chromatographic analysis of the products of hydrolysis of native beech lignin (according to Brauns) showed that it contains no combined carbohydrates[61]. However, it differs substantially from the main part of the lignin, *e.g.* in the content of free phenolic hydroxyls. By extracting spruce wood with cold acetone or alcohol, it is possible to obtain substances of low molecular weight of the type of lignans, to which the soluble lignin obtained by Brauns[37] evidently belongs. Therefore the lignin isolated by Brauns' method can hardly be considered any longer to be representative of the lignin in wood[62].

The task of isolating natural lignin from wood touches directly on the problem of lignin–carbohydrate bonds, the discovery of the nature of which has been the aim of numerous investigations, summarised in the work of Merewther, Lindgren, and others[63-66]. The insolubility of lignin in tissues can be explained in three ways: it is chemically combined with some component of the cell wall, it has a high molecular weight and therefore has a low solubility, or it is "encrusted" with carbohydrates to such an extent that it cannot be extracted by organic solvents.

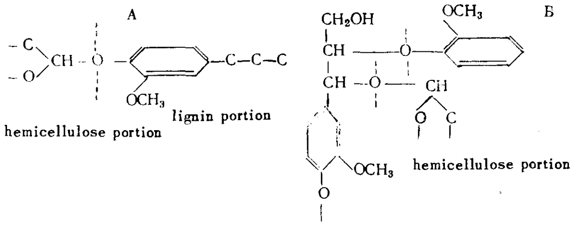
The "encrustation" theory was shown to be untenable by the work of Brauns and Seiler[67], who ground up finely divided wood meal with water to such an extent that part of it passed into colloidal solution, from which the wood was separated in the form of a fine powder. It could be completely dissolved by cuprammonium hydroxide solution, and reprecipitated with acid. Nevertheless, lignin could not be extracted from such wood powder, either with ethanol or with dioxan. Brauns' lack of success can be explained by the swelling of the wood in water and the possible formation of additional hydrogen bonds between carbohydrates and lignin.

The second possible cause is also improbable, since lignin can be partly extracted from wood by ethanol in the presence of very small amounts of hydrochloric acid, which are insufficient to bring about the depolymerisation of lignin.

The most probable cause is the presence of hydrolysable lignin–carbohydrate bonds in wood. Heating wood with water, chlorination, ethanolysis, acetylation, and boiling with sulphite and sulphate led to the separation of compounds containing no free carbohydrates but liberating lignin and sugar on hydrolysis. Since such products were separated under greatly varying conditions, it can be assumed that part of the wood exists in the form of a lignin–carbohydrate complex[68-71]. Xylan has been frequently identified as the principal carbohydrate linked with the lignin[72].

According to the results of Aaltio and Roshier[73], wood contains two lignin–carbohydrate complexes, one in the middle lamella, where the greatest amount of lignin is concentrated, and the other (with a very different ratio of lignin to hemicellulose) in the secondary wall.

Considerable scientific and technological interest attaches to the nature of the bonds existing between the lignin and the carbohydrate components of vegetable tissue. Among the many types which have been suggested, the following are selected as the most probable — (A) phenyl β-glucosides and (B) benzyl ethers:



Phenyl β-glucoside structures (A) are abundant in woody tissue (coniferin), and such links are evidently very probable for some of the lignin–carbohydrate complexes.

Study of the ultra-violet absorption of fractions of acetylxylolignin showed the presence of phenyl glucoside bonds in the lignin of wheat straw[74]. As with all glucoside structures, phenyl β-glucosides are hydrolysed by acids. It was shown also that such links, in contrast to alkyl glucosides, are relatively easily broken also by alkalis[71,75]. The possibility of the existence of phenyl β-glucoside links was shown also with a model substance[76].

It is quite probable that some lignin–carbohydrate links are also benzyl ethers (B). In contrast to ordinary ethers, the oxygen bonds here are more difficult to break down with acid[77]. The presence of benzyl ether groups in lignin has now been proved by numerous experiments. The reactive alcoholic hydroxyl attached to the α carbon atom of the propane side-chain of the structural unit of lignin may be the position for the formation of a chemical bond with carbohydrates in the biosynthesis of lignin. This is convincingly shown by the later papers of Freudenberg (see XIII*b*)[55].

Thus there now exists hardly any doubt as to the presence in wood (and in other plant tissue) of a lignin–hemicellulose complex. The chemical nature of the lignin–carbohydrate bonds varies. The most probable are phenyl β-glucoside structures and benzyl ethers.

During recent years attempts have been made to isolate lignin from wood without the use of acid or alkaline catalysts. An interesting method was suggested by Asplund[77a], treatment of the wood with steam at 170°–180° for $1-1\frac{1}{2}$ min. In this case softening of the middle lamella is accompanied by breakdown of the bonds and liberation of the lignin. No data are yet available as to the nature of the resulting preparation; it can merely be assumed that lignin which has been subjected to such a strong, though short-lived, thermal treatment will differ from the natural, native lignin.

Experimental work has shown that high yields of lignin can be extracted from well ground wood by neutral solvents. Recently this has been most successfully accomplished by Björkman[78] and by Pew[79]. The latter ground the wood in a dry state, and observed that the carbohydrates themselves underwent strong cleavage during the grinding. In order to shorten this process, Björkman ground the wood in the form of a suspension in toluene. The resulting wood meal did not swell and proved to be less soluble in alkali than Pew's material.

Wood ground by Björkman's method is extracted first with aqueous dioxan and then either with an aqueous solution of acetic acid or with dimethylformamide. Both fractions contain about half of the lignin present in the wood. The dioxan-soluble lignin contained only a few per cent of carbohydrates (mainly hemicelluloses). The first fraction was termed by Björkman "milled wood lignin" and represents about 30% of the wood lignin. The second fraction, obtained from the dimethylformamide extract, was termed the "lignin–carbohydrate complex"; it contained about one part of lignin associated with 3–4 parts of carbohydrates. Electrophoretic studies[65] have shown that this "complex" consists of two fractions with different mobilities, a pure hemicellulose fraction and a lignin–hemicellulose fraction, in which the weight ratio of the two components is approximately 1 : 1.

Björkman's lignin cannot be regarded in any way as wood protolignin, since mechanical treatment can produce breakdown of the chemical links between the parts of the lignin complex. However, the use of comparatively mild conditions to separate the product in quite a good yield led to the acceptance of this preparation as the most suitable material for studying the structure of lignin.

During the past 10–12 years biochemical methods have also been used to separate lignin[80,81]. In the enzymic breakdown of wood by the so-called "brown rot" fungus, the latter destroys the cellulose and other carbohydrates, setting free the lignin, which becomes accessible for extraction with neutral solvents.

On the basis of his biochemical investigations, Nord[81] concludes that lignin is not combined with other components of wood. This contradicts the now proven facts of the existence of lignin–hemicellulose complexes in wood. Biochemical lignin, obtained by the fermentative action of "brown rot" fungi, can hardly be identical with natural lignin. As Freudenberg[27] has shown, wood-degrading fungi contain, predominantly in the mycelium, laccase and peroxidase, the enzymic action of which leads to rupture of the links between carbohydrates and lignin and also to destruction of the latter.

An investigation made not long ago of the properties of lignin obtained by Schubert and Nord's[81] enzymic degradation of spruce wood with the fungus *Lenzites saepiaria* showed that it differed sharply from natural lignin (especially with respect to the methoxyl content). Therefore the native character of enzymically separated lignin is now denied[82].

Other methods for extracting lignin in the presence of catalysts (acid or alkaline) lead to its interaction with the solvent used for extraction[83]. It has been proved that an alkoxyl group adds on to lignin when it is obtained by extraction with ethanol in the presence of hydrochloric acid[84], a phenolic group during extraction with phenol[85], and a mercaptoacetic acid group in mercaptoacetyl lignin[86].

The alkoxy groups in the lignin derivatives obtained by condensation of the corresponding alcohol with lignin can be split off again by means of acid[87]. However, this requires the use of severe methods, which may change the nature of the lignin.

A new method for preparing ethanol-lignin[88] consists in treating spruce wood meal with a mixture of alcohol and chloroform (1 : 4) in the presence of 0.2 *N* hydrochloric acid at 60°. In this way it is possible to separate 80% of the lignin in the wood, 20% of it being converted into an ether-soluble oil.

A good yield of lignin can be obtained by the action on wood of benzyl alcohol containing 1 – 2% of hydrochloric acid[89]. In view of the fact that benzyloxy groups are comparatively readily cleaved forming toluene on reduction with hydrogen in the presence of palladium under mild conditions, Brauns[90] proposed this method for obtaining lignin free from benzyl radicals. To what extent it would be possible to remove benzyloxy groups without changing the lignin is difficult to assess. If this could be fully achieved, then it would be possible to obtain in this way a product closely similar to natural lignin. Hydrolytic methods of splitting carbohydrate – lignin bonds, which make it possible to obtain different lignin preparations (Willstätter's hydrochloric-acid lignin[91], "cuprammonium lignin"[92], or "periodate lignin"[93]), result in a marked change in the properties (*e.g.* the lignin loses its solubility in organic solvents). At the present time these methods, and the products obtained by means of them, cannot be regarded as entirely suitable for studying the structure of lignin.

V. ANALYTICAL DATA[44]

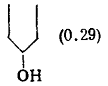
As already pointed out, the lignin isolated by Björkman[78] is closely similar in properties and structure to natural lignin. Therefore the analytical data cited below are based on Björkman's lignin obtained from conifer species (spruce) or on "guaiacyl lignin"[94].

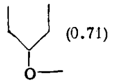
Elementary analysis of the Björkman lignin shows that it contains 63.84% C, 6.04% H, 29.68% O, and 15.75% OCH_3.[78] If account is taken of the fact that this lignin contains 1.9% of a sugar, then the appropriate correction (it being assumed for simplicity that the sugar consists of equal proportions of hexosans and pentosans) yields the following calculated formula for the phenylpropane or C_9 unit:

$$C_9H_{8.83}O_{2.37}(OCH_3)_{0.96} \quad (M = 184.7).$$

It can be seen from this formula that 0.96 OCH_3 group is associated with 2.37 oxygen atoms, or one methoxy group with 2.43 oxygen atoms. The distribution of oxygen not combined as methoxyl is of considerable interest for an understanding of the nature of the functional groups present in the phenylpropane structural unit of lignin.

Of the 2.37 oxygen atoms present in the C_9 monomer, one may be the phenolic oxygen of the guaiacyl nucleus. According to the data of Swedish investigators, however, only 0.29 oxygen atom occurs in the form of a free phenolic hydroxyl[95,96]. Hence the difference, 0.71 oxygen atom, must be present in blocked phenolic groups, evidently as the oxygen of alkyl aryl ethers:





The difference between the total oxygen and the oxygen forming part of phenolic hydroxyls (2.37 - 1 = 1.37 atoms) occurs as aliphatic hydroxyls, and as carbonyl and ether groups.

Acetylation of lignin shows the presence of 1.15 hydroxy groups[78], of which 0.29 represents phenolic hydroxyl. Hence the difference, 0.86, represents aliphatic hydroxy groups (primary, secondary, or tertiary).

The content of carbonyl groups in Björkman's lignin was determined volumetrically using potassium borohydride[97], which gave 0.41 – 0.48 carbonyl group for every methoxy group. Investigations recently carried out with model carbonyl compounds similar in structure to lignin have shown that the hydroxylamine method gives results which are too low, whereas use of borohydride yields values which are close to the theoretical content of carbonyl groups in the products investigated[97].

If the content of carbonyl groups in lignin is taken as 0.41 (this value requires verification), the remaining aliphatic oxygen (0.51 - 0.41 = 0.10) can be ascribed to alkyl–alkyl ether bridges, since carboxy groups and diphenyl ether links have not been found in spruce lignin.

On the basis of this oxygen balance, the formula for Björkman lignin can be written as $C_9H_{7.68}$(phenolic OH)$_{0.29}$ · . (aliphatic OH)$_{0.86}$(carbonyl O)$_{0.41}$(alkyl aryl ether O)$_{0.71}$ · . (dialkyl ether O)$_{0.10}$(OCH_3)$_{0.96}$.

The molecular weight of the Björkman "milled wood lignin" is about 11 000, which corresponds roughly with 60 phenylpropane units.

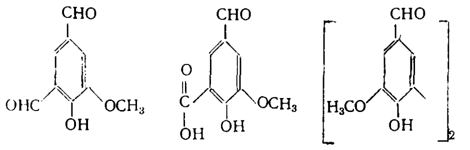
VI. THE STRUCTURE OF LIGNIN

The phenylpropane structural unit of lignin substances (guaiacylopropane unit for spruce lignin) possesses an aromatic nucleus which has been methoxylated and hydroxylated, as well as a propane side-chain carrying various oxygen-containing functional groups.

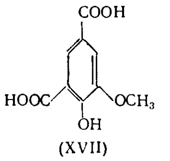
Consideration of the structure of wood lignin can suitably start from an account of the principles underlying substitution in aromatic nuclei and of the ways in which they can condense together. The methods of hydrolytic cleavage utilised to study many plant polymers (*e.g.* cellulose, starch) are unsuitable for application to lignin. The most valuable have proved to be oxidative cleavage in alkaline medium, cleavage by hydrogenation, and also cleavage with metallic sodium or potassium in liquid ammonia[98,99].

1. Oxidative degradation with alkali and nitrobenzene[100-102]. By this method, vanillin is obtained from spruce lignin, and mixtures of vanillin and syringaldehyde from deciduous lignin. Lignin from straw[103] yields also *p*-hydroxybenzaldehyde on oxidation, this compound being formed in small quantities from lignins of hard woods and soft woods too[104,105].

Spruce lignin has been found[106] to contain also derivatives of vanillin substituted in the *ortho* position relative to the phenolic hydroxyl:

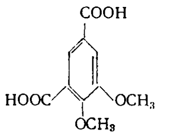


Oxidation of ligninsulphonates obtained by boiling aspen wood with sulphite leads to the separation[107] of appreciable amounts of 5-carboxyvanillic acid (XVII):



(XVII)

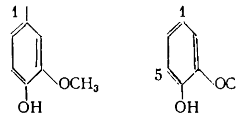
2. Oxidative cleavage of wood meal or of isolated lignin with permanganate, after preliminary methylation with diazomethane, involves the formation of veratric and isohemipinic (XVIII) acids in yields of 4.9% and 0.9% respectively based on the lignin:



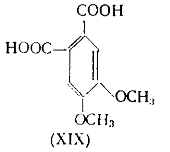
(XVIII)

If lignin is first heated with 70% caustic potash at 170°, then methylated with dimethyl sulphate, and finally oxidised with permanganate, the yield of isohemipinic acid can be approximately doubled[108,110,111].

Experimental data on the nitrobenzene and permanganate oxidation indicate the existence in natural lignin of guaiacyl radicals substituted in the 1- and 1,5-positions:



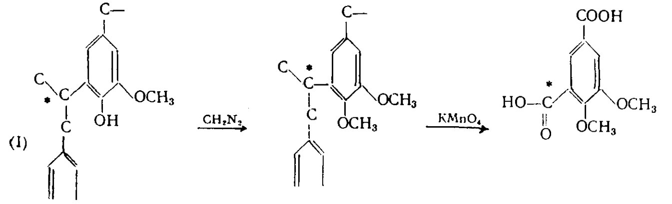
Richtzenhain[109] separated 1.3% of metahemipinic acid (XIX), in addition to isohemipinic acid, by the permanganate oxidation of isolated methylated "alcohol-lignin".

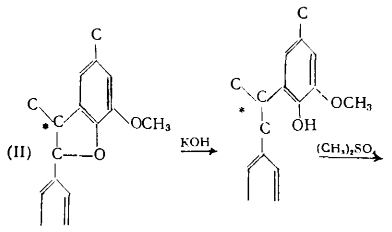


(XIX)

However, he was unable to prove the presence of metahemipinic acid in protolignin by oxidation of wood meal[112]. This acid evidently originates in condensation processes occurring in the lignin macromolecule during its separation with alcohol in the presence of acid catalysts.

The formation of isohemipinic acid can be explained by the presence of *ortho*-substituted phenolic nuclei [see scheme (I) below].

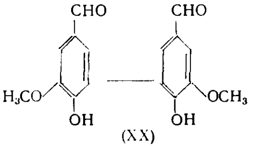




The increase in the yield of veratric and isohemipinic acids after severe alkali treatment of lignin (before methylation and permanganate oxidation) can be explained either by the presence of etherified phenolic hydroxyls, which are hydrolysed by the action of alkali, or by the existence of a structure similar to that occurring in dehydrodiconiferyl alcohol. Scheme (II) shows that the action of strong caustic alkali can cause rupture of the oxygen link and formation of the product capable of yielding additional isohemipinic acid.

Freudenberg[113] synthesised artificial lignin from coniferyl alcohol labelled in the β-position of the side-chain with radioactive carbon (indicated by an asterisk in the scheme). In both cases of permanganate oxidation (*i.e.* with and without alkali treatment) the resulting isohemipinic acid was radioactive. It is thus proved that the β carbon atom is linked to the nucleus of the neighbouring guaiacyl unit.

In the above two condensation schemes, the aromatic structural units are linked *via* the side-chain. Special interest attaches to condensation with the formation of a diphenyl structure. Pew[114] was able some time ago to isolate dehydrodivanillin (XX) from lignin after oxidation with nitrobenzene and alkali. Under the conditions used, numerous model substances not containing diphenyl links were unable to form such a product.

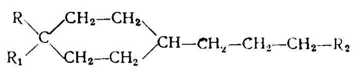


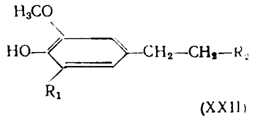
(XX)

The yield of XX was several per cent, so that it can be concluded that diphenyl links of this type are quite abundant in lignin.

The presence of diphenyl structures in natural lignin is supported also by spectrochemical investigations[52]. Thus aromatic nuclei can be linked either by means of an ether bond or by C–C bonds. Leopold[115] suggested that these two types of bonds occur in roughly equal proportions in the lignin molecule. Later investigations show that the number of units linked by C–C bonds ("condensed units") is evidently less and constitutes 30–40%[44] of the total number of links.

3. Hydrogenolysis of lignin preparations. This leads to the production of considerable quantities of derivatives of propylcyclohexane and of substituted phenols (XXI), (XXII) [116-120].


(XXI)


(XXII)

1. $R = R_1 = R_2 = H$	1. $R_1 = H$; $R_2 = OH$
2. $R = H$; $R_1 = OH$; $R_2 = OH$	2. $R_1 = OCH_3$; $R_2 = H$
3. $R_1 = R_2 = H$; $R = OH$, etc.	3. $R_1 = OCH_3$; $R_2 = OH$

Identification of the products of hydrogenation and hydrogenolysis showed the presence of one free or etherified hydroxyl group in the γ- and β-positions of the side-chain of the phenylpropane structural unit of lignin[121].

The hydrogenation of sulphate lignin under pressure demonstrated[122] that water-soluble and ether-soluble phenolic compounds predominate among the reaction products, cyclohexanol, catechol, and guaiacol being isolated in addition to other aromatic substances. Results of the hydrogenation of lignin, yielding up to 50% of cyclohexylpropane derivatives, show that a great proportion of lignin is composed of phenylpropane derivatives, since there can be no doubt that the cyclohexyl ring is formed by hydrogenation of benzene nuclei.

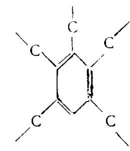
4. An important contribution to the uncovering of the aromatic structure of lignin was made by Shorygina and her collaborators. By treating cuprammonium lignin with metallic sodium in liquid ammonia at -33° nine times, they were able[123,124] to separate dihydroeugenol from the fraction of low molecular weight, and from aspen lignin they also separated 1-(4-hydroxy-3,5-dimethoxyphenyl)propane[125].

Extraction with ether of the acid portion of the decomposition products of lignin yielded hydrated eugenol, *i.e.* 1-(4-hydroxy-3-methoxyphenyl)propan-2-ol. In the case of cuprammonium lignin, a total of about 28% of monomeric aromatic substances was obtained[126].

The formation of dihydroeugenol (as a result of hydrogenation of phenols) was confirmed also by the cleavage of spruce wood with metallic sodium under the same conditions[125]. Chromatographic analysis of the phenols obtained[127] showed that their composition was quite complicated. In addition to the previously observed dihydroeugenol and 1-(4-hydroxy-3-methoxyphenyl)propan-2-ol, the cleavage products contained 1-(4-hydroxy-3-methoxyphenyl)propan-1(and 3)-ols.

The *p*-hydroxybenzyl alcohol grouping, which is extremely important for an understanding of many of the reactions of native lignin (see below), is usually detected by indirect methods. Employment of the decomposition of lignin with sodium enabled Shorygina and her collaborators for the first time to demonstrate the presence of this group directly. The possibility of a far reaching cleavage of lignin with metallic sodium into monomers shows that the aromatic components are linked to one another mainly by C–O–C bonds, which, of course, does not exclude the presence of a certain number of C–C bonds between the main units in lignin isolated from wood[128]. The cleavage of the phenyl ether bonds of lignin by the action of alkali metals in liquid ammonia was confirmed also by Freudenberg's work[129].

Kratzl[98] included, among the criteria which he suggested for distinguishing lignin from other substances in wood, its ability to yield benzenepolycarboxylic acids on oxidation with permanganate[130]. Although the yield of such polycarboxylic acids (especially of the pentacarboxylic acid) obtained from native lignin is low (0.14% according to Cabott's data)[131], the possibility of obtaining them is an argument in support of the existence in protolignin of a small number of systems of the type (XXIII):


(XXIII)

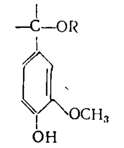
As a result of condensation processes occurring during alkaline or acid treatment of lignin preparations, the yield of polycarboxylic acids obtained during oxidation with alkaline permanganate is sharply increased[131,132].

VII. REACTIVE GROUPS IN LIGNIN

Among the reactive groups in lignin, the three carbon atoms of the propane side-chain, which can carry various functional groups, are usually included. These are responsible for the majority of the typical reactions of lignin—sulphonation by sulphite solution at different pH values, alkylation by alcohol, and reaction with mercaptoacetic acid[44]. The phenolic hydroxy (free or etherified) situated *para* to the propane side-chain is also an important reactive group of lignin, governing many properties of native and technical lignins (*e.g.* the ability to dissolve in alkalis, form salts, etc.).

During recent years there has been considerable interest in the determination of the content of phenolic hydroxyl groups in lignin. Their amount forms one of the criteria of identity between artificial lignin preparations and native lignin[133]. Several different methods for determining phenolic hydroxyls in lignin have been published[134-137]. Among the suggested methods the most important is the spectrochemical method, which has been developed and thoroughly investigated by Aulin-Erdtmann[138]. The spectra of phenols undergo bathochromic shifts when they are measured in the ionised condition, *i.e.* in an alkaline medium. If the shift for an appropriate model is compared with the spectrum of lignin, an estimate can be obtained of the number of free phenolic hydroxyls in the preparation under investigation. The content of phenolic groups fluctuates depending on the lignin preparation tested and on the method of determination. Therefore the number of phenolic hydroxyls per phenylpropane unit indicated above (0.29 OH/OCH_3) must be regarded as approximate. The complexity of the lignin molecule and steric factors result in several cases in some of the phenolic hydroxyls not being recorded, even by an optical method[133]. The three-carbon propane side-chain of the aromatic structural unit of lignin is a most important functional group, and it is mainly by means of this group that the phenylpropane units are linked together. The propane side-chain is also the location of the most important reactions, the most characteristic of lignin. The α carbon atom of the propane chain is especially important.

Lignin contains several types of functional groups with different reactivities with respect to sulphonation. However, the hydroxylated α carbon atom (benzyl atom), in either the free or the etherified form (XXIV), is evidently responsible for sulphonation and for reaction with methanol and hydrochloric acid and with mercaptoacetic acid[139].

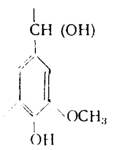

(XXIV)

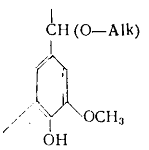
1. R = H; 2. R = alkyl

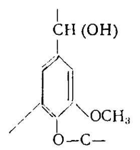
The main reaction in the sulphite process for obtaining cellulose is based on the conversion of lignin into water-soluble ligninsulphonic acid. The process by which wood is delignified during boiling with sulphite is still not very clear[140]; according to Hägglund[141], it occurs in two stages: in the first stage, lignin is sulphonated in the solid state without dissolution, and in the second stage the action of hydrogen ions produces hydrolytic liberation of ligninsulphonic acids and their passage into solution with further sulphonation to a content of about 0.5 SO_3H group per methoxyl. Hägglund's hypothesis of a two-stage sulphonation of lignin was confirmed by boiling periodate lignin[142] with bisulphite.

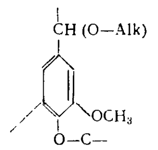
From an investigation of numerous model substances, Lindgren[143,144] worked out a very probable picture of the sulphonation of the various groups which are evidently present in lignin. He imagined four possible structural variants having different reactivities with respect to sulphonation.

Rapid sulphonation of lignin, which is observed even in neutral sulphite solution, occurs at the expense of the phenolic benzyl alcohol A and its ethers B, the aliphatic hydroxyl or ether group being replaced by SO_3H.


A


B

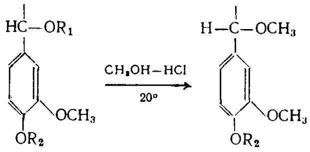

C


D

A grouping which reacts slowly in neutral medium but quite rapidly with acid sulphite solution is represented by C, *i.e.* guaiacylcarbinols etherified at the phenolic hydroxyls. Structural elements which react only with acid sulphite solutions (group D) are guaiacylcarbinols etherified both at the phenolic and at the alcoholic hydroxyls. It is quite possible, however, that some of the sulpho groups are combined also with other carbon atoms (not only with the benzyl carbons) of the lignin complex.

It is very significant that during sulphite treatment (as during mild alkylation) no additional formation of free phenolic hydroxyls is observed[95,96,138]. This means that the α carbon atom is linked either to a free hydroxyl or, if it is etherified, to an alkyl but not an aryl radical.

The presence of benzyl alcohol and benzyl ether groups was shown also by the reaction with alcohol in the presence of small amounts of mineral acid. By the action of 0.5% methanolic hydrochloric acid on Brauns' lignin at room temperature, up to 50% of methoxyl (based on its original content in the lignin) can be introduced[145]. Methylation for 72 h enabled up to an additional 70% of methoxyl to be introduced into Björkman's lignin.

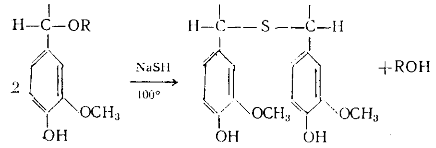


where R_1 = H or C – alkyl; R_2 = H or C – alkyl.

Brauns[89] put forward the hypothesis that such alkylation leads to acetalisation of the carbonyl group or that an existing acetal group is transalkylated. If, however, all the carbonyl groups in lignin are reduced with sodium tetrahydroborate, and the lignin is then again treated with methyl alcohol in the presence of hydrochloric acid, it is methylated just as before reduction. In view of the absence of carboxyl groups in native lignin, the only process which remains probable is alkylation of the benzyl group. Examination of the reaction with methanol in the presence of hydrochloric acid of numerous model substances of the type of benzyl alcohol or benzyl ethers showed that the alcohol or ether groups were replaced by methoxyl, the rate of reaction being different for each class and depending on the nature of the radicals in the side-chain[145].

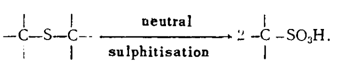
The presence of a benzyl alcohol or an alkyl benzyl ether group in lignin received additional support from a study of sulphide formation in model substances and in lignin during the boiling of cellulose with sulphate[146-148].

It was shown that *p*-hydroxybenzyl alcohol and *p*-hydroxybenzyl ether react with a neutral solution of sodium hydrogen sulphide at 100° to form the corresponding dibenzyl sulphide[146,147].



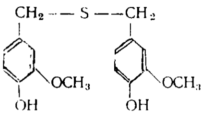
Sulphide formation occurs under similar mild conditions also with Brauns' and Björkman's lignins[149,150].

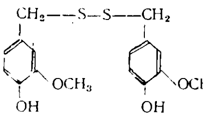
Neutral sulphite treatment of thiolignin preparations and model sulphides results in the formation of ligninsulphonic acids containing the whole of the sulphur in the form of sulphonic acid groups which can be titrated potentiometrically. The number of such groups corresponds exactly with the quantity to be expected if such sulphite treatment converts one sulphide group into two sulphonic acid groups:

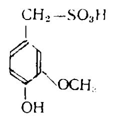


$$-\overset{|}{\underset{|}{C}}-S-\overset{|}{\underset{|}{C}}- \xrightarrow[\text{sulphitisation}]{\text{neutral}} 2\ -\overset{|}{\underset{|}{C}}-SO_3H.$$

Thus under conditions of the neutral sulphite treatment of thiolignin there is a complete replacement of sulphide groups by sulphonic acid groups[148]. A similar exchange has been shown in model experiments. For example, divanillyl sulphide (XXV) and divanillyl disulphide (XXVI) on neutral sulphite treatment are rapidly converted into vanillylsulphonic acid (XXVII) in good yield.


(XXV)


(XXVI)


(XXVII)

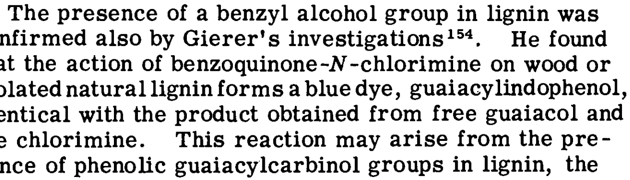
Etherification of the phenolic hydroxyl group completely blocks reaction with sulphite under mild conditions.

If thiolignin preparations are heated with a mixture of acids (HI, HCl, and H_3PO_2)[151], they give up a large part of their combined sulphur in the form of H_2S, which can be determined iodometrically. This cleavage reaction is to some extent specific to *p*-hydroxy- and *p*-alkoxy-benzyl sulphide and disulphide[152]. An analogous cleavage is observed also with ligninsulphonic acids.

On the basis of the above there are sufficient grounds for accepting the hypothesis[153] that the reactions of sulphonation and sulphide formation occur to a considerable extent at the same reactive groups in lignin.

The presence of a benzyl alcohol group in lignin was confirmed also by Gierer's investigations[154]. He found that the action of benzoquinone-*N*-chlorimine on wood or isolated natural lignin forms a blue dye, guaiacylindophenol, identical with the product obtained from free guaiacol and the chlorimine. This reaction may arise from the presence of phenolic guaiacylcarbinol groups in lignin, the alcoholic substituent being split off as aldehyde under the conditions of the coupling reaction (in faintly alkaline solution) with the formation of the corresponding indophenol[155].

By treatment of spruce lignin it was possible to isolate "guaiacylindophenol" (XXVIII), and aspen lignin yielded in addition "syringylindophenol" (XXIX)[154].

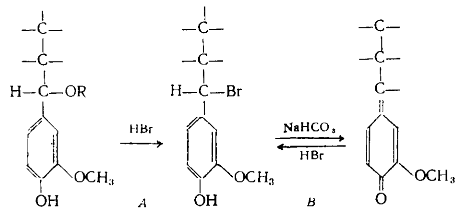


(XXVIII) (XXIX)

where for (XXVIII) R = H, and for (XXIX) R = OCH_3.

The reaction does not take place in the absence of phenolic and alcoholic hydroxyl in the free state. Quantitative measurements showed that in Brauns' lignin approximately every seventh, and in Björkman's lignin every fourteenth, phenylpropane unit has the guaiacylcarbinol structure[154].

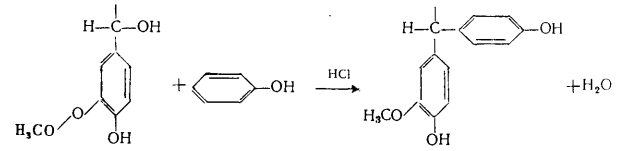
Apart from the colour reaction with the quinoneimine, other reactions were found which demonstrated the presence in lignin of *p*-hydroxybenzyl alcohol and *p*-hydroxybenzyl ether groups. It has been known for a comparatively long time[156] that both *p*-hydroxybenzyl alcohol and *p*-hydroxybenzyl ether are very readily converted by the action of HBr into *p*-hydroxybenzyl bromide (reaction *A*), which reacts in ethereal or chloroform solution with an aqueous solution of sodium bicarbonate to form a *p*-quinomethane (reaction *B*):



The occurrence of quinomethane reactions (*A* and *B*) in solution is readily observed from the change in the absorption curve. Adler and Stenemur[157] worked out a technique for carrying out "quinomethane" reactions with various model substances for lignin, and showed that a dioxan–chloroform solution of Brauns' lignin, which originally had a single maximum in the absorption curve, gave a new maximum after reactions *A* and *B*.

Shorygina's discovery by chromatography[127] of the "benzyl alcohol" group, the indophenol and quinomethane reaction, and also the results of studies on the model reactions of sulphonation, sulphide formation, and alkylation with methanol containing hydrogen chloride — all these important investigations demonstrate convincingly the presence of *p*-hydroxybenzyl alcohol (or ether) groups in native lignin.

The condensation of lignin with phenol in the presence of a small amount of hydrochloric acid may also to some extent be adduced as evidence of the presence of a benzyl carbon atom. Reaction between lignin and phenol leads to the formation of phenol-lignin, the phenol reacting with hydroxyls in the lignin situated *para* or *ortho* to the phenolic hydroxyl[158,159].

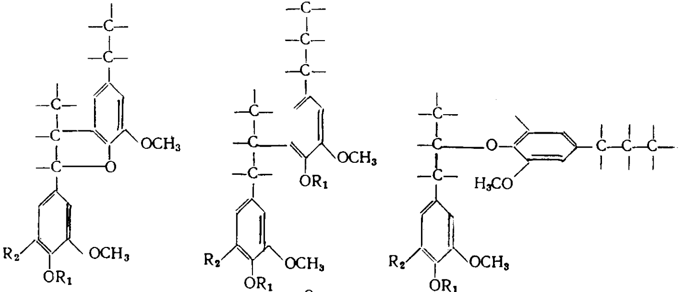


(XXX)

The formation of a diphenylmethane structure (XXX) was confirmed experimentally not long ago[160]. As Ziegler[155] has shown, benzoquinone-*N*-chloroimine splits off the carbinol group from *p*-hydroxybenzyl alcohol, and removes the methylene bridge from *p*-hydroxydiphenylmethane. Therefore compounds having the diphenylmethane structure (XXX) may be expected to yield two indophenols — (1) a derivative of phenol itself and (2) a "guaiacylindophenol" of the type of (XXVIII). After reaction of Brauns' and Björkman's lignins with 2,6-xylenol and subsequent treatment with the quinonechlorimine in faintly alkaline solution, it was possible to separate and identify both indophenols by means of paper chromatography[160].

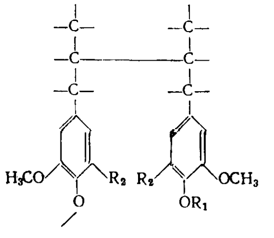
No quantitative assessment of the reaction between phenol and the "benzyl group" in lignin has yet been made. It is quite probable that the condensation of phenol with hydroxy groups occurs also at the β or γ carbon atoms of the propane side-chain. The possibility of condensation with glycol groups in the side-chain[158] is not excluded, although the proportion of these in the lignin macromolecule appears to be small[161].

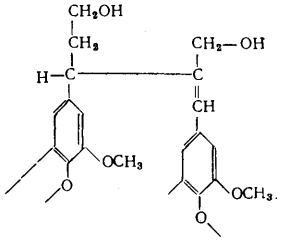
In the main dimeric products (VII)–(IX) and (XII), obtained by Freudenberg in the enzymic dehydrogenation of coniferyl alcohol and the formation of "biochemical lignin", the links between the guaiacyl(or syringyl)propane units necessarily involve the β carbon atom of the side-chain. Study of the dehydrogenation of coniferyl alcohol and of several model compounds[77,162,163] suggests the existence of the following types of bonds involving the β C atom in lignin:



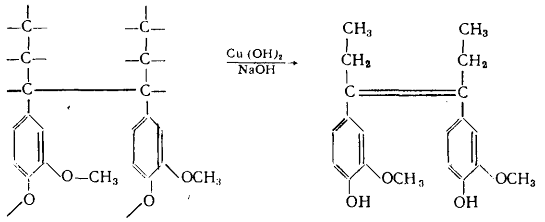
A. phenylcoumaran B. β-aryl C. β-aryl ether

Apart from these three main types there is the possibility of the existence of bonds between β–β' and α–β carbon atoms. Formation of the latter was shown recently in the dimerisation of cinnamyl alcohol[164].


β—β'

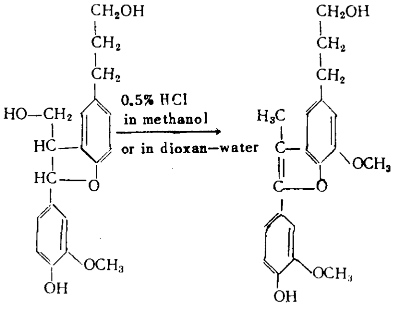

α—β

Pearl and Beuer[53] suggested the existence also of α–α' carbon bonds in lignin, since oxidation of ligninsulphonic acids with alkaline copper hydroxide leads to the formation of a small quantity of stilbene derivatives:



The phenylcoumaran structure (A) was considered in the early 1930's to be characteristic of lignin[33],[34] and investigated in detail in connection with the sulphite reaction[165], but has now been shown to be present in comparatively small proportions in the lignin molecule. Dehydrodiconiferyl alcohol, having the phenylcoumaran structure, is formed in amounts up to 20% of the original coniferyl alcohol during the biosynthesis of lignin. Adler[166] employed a spectrophotometric method to determine the abundance of the phenylcoumaran structure.

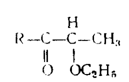
The action of $CH_3OH-HCl$ or of HCl in aqueous dioxan on dihydrodehydrodiconiferyl alcohol or its methyl ether was found to convert the saturated phenylcoumaran system into the unsaturated phenylcoumarone system:

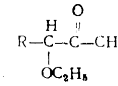


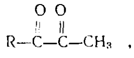
Phenylcoumaran has a typical guaiacylpropane absorption spectrum with a maximum at about 282 mμ. The phenylcoumarone obtained exhibits both a sharp increase in absorption and a bathochromic shift at the maximum to about 310 mμ. Björkman's lignin treated with a $CH_3OH-HCl$ mixture for 24 h showed an increase in absorption. It was found by comparison with the phenylcoumarone maximum obtained on models that lignin does not contain more than 5–7% of the phenylcoumaran structure[154]. Freudenberg, employing acetolytic ring cleavage (acetic anhydride–acetic acid–perchloric acid), also came to the conclusion that native lignin contains comparatively few phenylcoumaran rings.

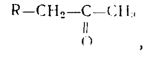
The possibility of the existence of both phenylcoumaran (type A) and β-aryl (type B) structures is demonstrated by the formation of isohemipinic acid, as noted previously in the section concerned with the oxidative cleavage of native lignin with potassium permanganate. The β-aryl ether structure (type C) is of considerable interest and importance for an understanding of the nature of the links between the individual monomers. In the biosynthesis of lignin Freudenberg separated from among the dimeric products of guaiacylglycerol β-coniferyl ether, having a structure of the β-aryl ether type, with a yield of more than 30%.

Investigations carried out in the 1940's by Hibbert and his coworkers[167–171] showed that treatment of wood meal (or lignin preparations separated under mild conditions) with ethanol in the presence of HCl results in the formation, together with ethanol-lignin, of four ketones:


$R{-}\underset{\overset{\|}{O}}{C}{-}\overset{H}{\underset{\overset{|}{OC_2H_5}}{C}}{-}CH_3$,
(XXXI)

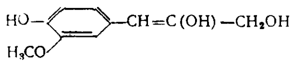

$R{-}\overset{H}{\underset{\overset{|}{OC_2H_5}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}CH_3$,
(XXXII)

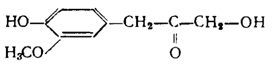

$R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}CH_3$,
(XXXIII)


$R{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3$,
(XXXIV)

where R = 4-hydroxy-3-methoxyphenyl for conifer lignin or R = 4-hydroxy-3,5-dimethoxyphenyl for lignin from deciduous species.

Hibbert considered that native conifer lignin is formed from the extremely reactive β-hydroxyconiferyl alcohol (XXXV), which is the enolic form of the keto-alcohol (XXXVI).


(XXXV)

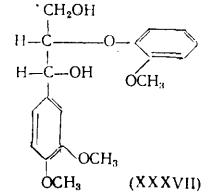

(XXXVI)

The extremely reactive side-chains of the propylphenol units of lignin undergo intramolecular rearrangements[172] according to the scheme:

$$R{-}CH_2{-}CO{-}CH_2OH \rightleftarrows R{-}CH{=}C(OH){-}CH_2OH \rightleftarrows$$
$$\rightleftarrows R{-}CH(OH){-}C(OH){=}CH_2 \rightleftarrows R{-}CH(OH){-}CO{-}CH_3 \rightleftarrows$$
$$\rightleftarrows R{-}C(OH){=}C(OH){-}CH_3 \rightleftarrows R{-}CO{-}CH(OH){-}CH_3,$$

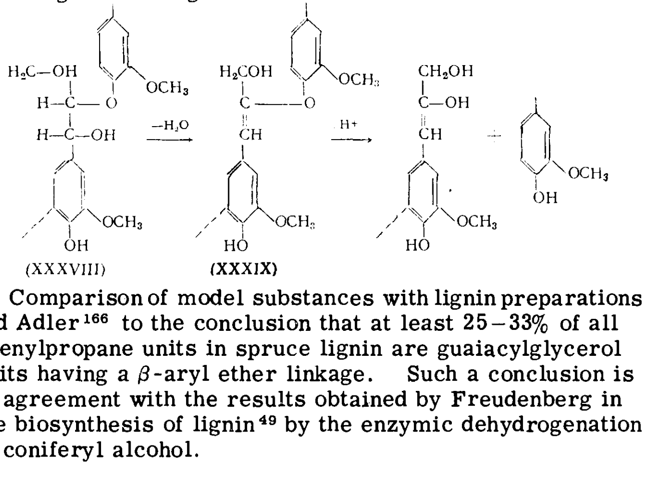
where R = 4-hydroxy-3-methoxy(or 3,5-dimethoxy)phenyl. As a result of such allylic and keto-enol transitions, etherification with ethanol in the presence of HCl may give rise to the compounds (XXXI) and (XXXII), and disproportionation of R.CH(OH).CO.CH_3 may yield (XXXIII) and (XXXIV).

Adler[166] studied veratrylglycerol β-guaiacyl ether (XXXVII) as a model substance containing a β-aryl ether structure:


(XXXVII)

This product on treatment with sulphite solutions or with cold methanol in the presence of HCl was converted into sulphonic acid derivatives or gave a methyl ether at the α carbon atom. But the most important fact was that, like lignin, it gave Hibbert ketones on ethanolysis. The products obtained by the ethanolysis of lignin by Hibbert's method (see above) are characterised by a considerable content of $\equiv C(CH_3)$ groups. On heating the model substance (XXXVII) with 0.2 *N* hydrogen chloride in aqueous dioxan (1 : 9) (acidolysis), guaiacol was liberated, *i.e.* the proportion of free phenolic hydroxyls increased, and the reaction products formed were shown chromatographically to include ketones also containing $\equiv C(CH_3)$ groups.

In order to determine the abundance of the β-aryl ether structure in lignin, Adler[166] compared the behaviour of the model substance (XXXVII) and lignin preparations in acid hydrolysis. Two preparations were used, dioxan–hydrochloric acid lignin[173] and Björkman's lignin[78]. In both cases acid hydrolysis gave an ether-soluble oily fraction containing monomeric "Hibbert ketones" in addition to a solid substance insoluble both in water and in ether. The solid substances were characterised by an increased content of free phenolic hydroxyls and $\geqslant C(CH_3)$ groups. Adler supposes that the guaiacylglycerol β-aryl ether structures (XXXVIII) in lignin undergo acid hydrolysis. Apparently dehydration occurs first, leading to the enol aryl ether (XXXIX), which is sensitive to acid hydrolysis. This reaction exposes a new phenolic hydroxyl in addition to the hydroxyconiferyl alcohol. The latter undergoes Hibbert rearrangements to give monomeric ketones.

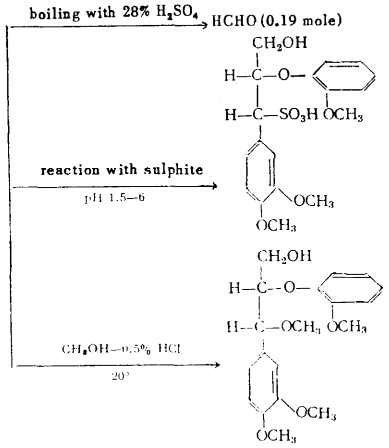


(XXXVIII) (XXXIX)

Comparison of model substances with lignin preparations led Adler[166] to the conclusion that at least 25–33% of all phenylpropane units in spruce lignin are guaiacylglycerol units having a β-aryl ether linkage. Such a conclusion is in agreement with the results obtained by Freudenberg in the biosynthesis of lignin[49] by the enzymic dehydrogenation of coniferyl alcohol.

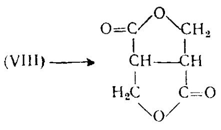
The synthetic model substance, veratrylglycerol β-guaiacyl ether (XXXVII), proposed by Adler, behaves like lignin in three important reactions:

(XXXVII)



According to this scheme, the compound (XXXVII) yields formaldehyde on being boiled with 28% H_2SO_4, is sulphonated by acid sulphite solutions, and forms a methyl ether with CH_3OH and HCl. In contrast to lignin, however, this product does not react with sodium hydrosulphide under mild conditions[146-150]. This fact again shows that the use of model substances to ascertain the structure of lignin, and the conclusions thus obtained, can have only a relative value, since no single model can reproduce the whole variety of properties which Nature has piled into the lignin macromolecule.

To determine the presence in native lignin of a lignan structure, *i.e.* of bonds between the β carbon atoms of the propane side-chains [this structure is represented by pinoresinol (VIII) among the dimeric products of biosynthesis], Erdtman's cleavage reaction[175] was employed[174]. If pinoresinol is methylated, brominated, and then oxidised, the dilactone of bishydroxymethylsuccinic acid should be obtained.



However, it has not yet proved possible to separate this lactone from native lignin.

Structures of lignan type are apparently present in lignin, since natural lignans are akin to lignin in many respects. Freudenberg found up to 20% of pinoresinol among the dimeric products of biosynthesis. Its content in wood protolignin requires more exact determination.

The third (γ) carbon atom of the propane side-chain displays its properties in the reactions of hydrogenation, ethanolysis, and of hot concentrated mineral acid. The cyclohexylpropanols obtained by the hydrogenation of lignin preparations contain a primary alcoholic hydroxyl attached to the γ carbon atom[116-120]; during ethanolysis $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-CH_3$ groups are formed. On treatment with sulphuric acid, formaldehyde is obtained as a result of secondary reactions, although not in a quantitative yield[174,176].

In order to prove that the formaldehyde was formed from the γ carbon atom, Freudenberg[177] synthesised biolignin from coniferyl alcohol having a labelled terminal carbon, and showed that the resulting product was radioactive and was, in fact, formed from the γ carbon atom. It can thus be supposed that the γ carbon atoms of the propane side-chain are either free or bear an oxygen-containing functional group, *i.e.* are linked to hydroxyl groups which are freed by chemical treatment (possibly etherified alkyls or aryls). Lindgren and Mikawa[178] were able to detect by means of a colour reaction the presence of a small proportion of cinnamyl alcohol structural groups in spruce lignin.

The great activity of the cinnamyl alcohol structure makes it unlikely that it is present in lignin which has been isolated, even if native lignin contains it. Therefore the colour reactions were carried out on wood sections about 20 μ thick which had been extracted. After the colour reaction had been obtained (treatment with a solution of toluene-*p*-sulphonyl chloride in pyridine, followed by careful rinsing and treatment with a solution of *p*-nitrosodimethylaniline and potassium cyanide in aqueous alcohol), the light absorption of these sections was measured on a Beckman spectrophotometer.

A double bond conjugated to the nucleus (*i.e.* the structure of the side-chain in coniferyl alcohol and coniferyl and sinapyl aldehydes) is a structural element of lignin which appears to be present in small amount. A small quantity (1%) of coniferyl aldehyde was found by Freudenberg[49] among the dimeric products of biosynthesis.

Native lignin from spruce wood gives a red colour with phloroglucinol (the Wiesner reaction). Adler[179,180] explains it by the reaction of the latter with coniferyl aldehyde, which he was the first to separate (in small yield) from wood. These conclusions were confirmed also by Kratzl[181] and Pew[182]. The proportion of coniferyl aldehyde groups in lignin is very low, about 0.1%[183], *i.e.* one for every 35 phenylpropane units (in Brauns' lignin) or for every 40–60 units in ligninsulphonic acid[179,180].

Although the structure of the phenylpropane units in lignin, and to a considerable extent the way in which they are linked, have become clear, the character of the side-chain requires further investigation in many respects.

In view of fresh work on the determination of carbonyl groups in lignin by the tetrahydroborate method[97], according to which every two phenylpropane structural units are accompanied by almost one carbonyl group (0.41–0.48 CO/OCH_3), it is necessary to re-examine both the distribution of oxygen in the side-chain and existing ideas about the structure of the latter. Therefore the "problem of the side-chains" is one of the most important in the chemistry of lignin[184]. The constitution of the side-chains of lignin is obscure and is difficult to determine because of their tendency to undergo rearrangements and changes in the positions of the substituents depending on the method employed to isolate the lignin. Following the work of Gierer[97], however, great attention has been paid to the role of carbonyl groups in the side-chain, and in future investigations the model substances will probably include the carbonyl group as an essential part of their propane side-chain. Therefore the schematic structures for lignin published[44] during recent years, in which the propane side-chains are practically devoid of carbonyl groups (as followed from earlier investigations) are inaccurate.

During recent years numerous studies have been made of the physical properties of the lignin macromolecule[185]. The molecular weights of soluble lignin and lignin derivatives have been investigated by various methods[186,187]. The values obtained varied within the limits 300–14 000. The molecular size is probably affected by hydrolytic degradation during the isolation of the lignin and by condensation into larger molecules. For lignins which are soluble in organic solvents the molecular weights vary within the limits 800–10 000. A high molecular weight is found for ligninsulphonic acids (20 000–100 000), which is explained by condensation processes occurring (owing to the acidity of the medium) during the initial stage of sulphonation.

Results obtained from diffusion measurements show that lignin exists as a tangled spiral[188]. An X-ray investigation carried out by Becherer[189] refuted Jodl's view[190] of a crystallite structure for lignin: it is a typical amorphous substance having a three-dimensional structure.

Fundamental investigation of the colloidal nature and lyophilic properties of lignin were carried out by Odintsov[191]. On the basis of a large amount of experimental data he discovered the laws governing the swelling of the plant cell in different media and the part played by lignin in these processes, which are important for an understanding of the mechanism of the hydrolysis of wood.

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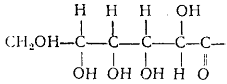
This review of the most important papers published during the past twelve years on the nature, structure, and properties of lignin enables some preliminary conclusions and generalisations. These conclusions, of course, do not pretend to cover exhaustively the extensive and varied results, which are sometimes contradictory and controversial. But it must be emphasised that the aromatic nature of the main part of the lignin "polymolecule"* is not open to doubt.

Aromatic structural units exist in native lignin and are formed as a result of complex oxidation–reduction processes occurring in the living plant cell and involving the multifunctional enzymic system demonstrated by numerous investigators.

Fresh light was thrown on the complex problems of the assimilation of carbon dioxide by the living cell, with the formation of carbohydrates and the further conversion of the latter into aromatic products, by the elucidation of the role of phosphorus compounds of sedoheptulose (XL) in the photochemical conversion of carbon dioxide into carbohydrates in living plants[192].



$$CH_2OH-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\underset{O}{\overset{}{\underset{\Vert}{C}}}-CH_2-OH$$

(XL)

Sedoheptulose 1,7-diphosphate undergoes cyclisation under the influence of enzymes with subsequent conversion into aromatic monomers of lignin, as had been shown schematically earlier (see the biosynthesis of aromatic substances by bacteria).

It is difficult to say anything about the order of priority in which carbohydrates and cyclohexene precursors of lignin are formed, but there is no doubt about their genetic relationship, and the chemical links between the lignin which is formed and the carbohydrates in the plant cell are obvious.

In the course of phylogenetic evolution plants have acquired strength and rigidity, in which lignin has played an essential part. Cotton fibres, consisting of pure cellulose, differ fundamentally from wood fibres, the cell walls of which are lignified. Electron microscopy has shown that in these cells plaits of cellulose are embedded in an amorphous mass of lignin and hemicellulose, one of the most frequently observed substances of this group being xylan[192].

The presence of a lignin–hemicellulose complex in wood has been proved, and, it seems, can be used to explain the difficulty of isolating native aromatic lignin unchanged from plant tissue.

Lignin is not uniformly distributed in the plant cell. Preparations separated by the Björkman method from spruce wood contain some fractions which differ not only in their content of carbohydrate residues but apparently also in the degree of condensation of the aromatic lignin itself which forms part of the complex. This is proved by the fact that ligninsulphonic acids differing in molecular weight are obtained, and is due to the lignification of the cell itself taking place gradually, over a period of time.

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* By "polymolecule" Freudenberg meant a molecule formed by the repetitition, not necessarily regular, of a monomer unit.

The links between the lignin and the carbohydrates are not all of the same type. Apart from the readily hydrolysable phenyl β-glucoside and the more difficultly cleaved benzyl ether links, it is possible that stable C – C bonds exist between lignin and carbohydrates. An indirect proof of this can be found in the work of Kratzl and coworkers[193] showing that methanol introduced into lignin can form some stable C – C bonds in addition to benzyl alcohol groups.

Freudenberg's extremely convincing and effective investigations on the biosynthesis of lignin based on coniferyl alcohol have revealed important regularities underlying the condensation of aromatic monomers. In his latest work, published not long ago[194], he obtained a new class of carbohydrate compounds, ethers of sugars of lignin structural units, by enzymic dehydrogenation of coniferyl alcohol in the presence of sugars. Previously Siegel[195] had adduced data on the participation of cellulose in the oxidative polymerisation of eugenol during the formation of lignin from it. The above work shows that the formation of lignin from aromatic monomers in the plant cell necessarily involves carbohydrates, which were ignored in Freudenberg's previous investigations. In the light of Freudenberg's latest experimental results[194], the conclusions of Traynard[196], that the carbohydrate components forming part of the lignin molecule are not linked by the polyose chain, appear quite probable.

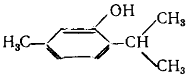
Coniferyl alcohol is by no means the only substance to be regarded as an aromatic monomer in the formation of lignin materials. Lignins have been obtained based on other phenylpropane monomers — ferulic acid, cinnamic acid, and eugenol.

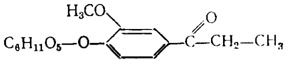
The possibility of obtaining coniferin from phenylalanine[22] is an important argument in support of the probable similarity of the starting materials involved in the formation of protein and the walls of the living plant cell. The presence of a small quantity of nitrogen in the composition of lignin can now be explained by the possible participation of phenylalanine or tyrosine in the biosynthesis of coniferin and then of lignin in the cell.

The formation of lignin materials based on phenylpropane monomers not containing methoxyls (cinnamic acid, phenylalanine) indicates that methoxylation is evidently the last stage in the formation of the aromatic precursors of lignin.

Non-methoxylated aromatic nuclei have been detected even in "finished" lignin. Thus Smith[197] isolated from aspen lignin 6.9% of hydroxybenzoic acid, combined, in his opinion, by means of ester links with aliphatic hydroxyls of the side-chain of the lignin molecule. In view of the great reactivity of the hydroxyl group attached to an α carbon atom, it is quite probable that not only carbohydrate residues (adducts with sugar, prepared by Freudenberg, or coniferyl alcohol radicals) but also aromatic monomers can be linked to it.

The enzymic system for the lignification of plants is by no means universal, but is strictly specific. When labelled vanillin is introduced into growing tissue, no radioactive lignin is formed. Thus vanillin is not assimilated in the biosynthesis of lignin. It is characteristic that all labelled aromatic monomers tested as precursors of lignin by introduction (implantation) in growing tissue which gave the corresponding lignin preparations had a propane side-chain. However, not every phenylpropane unit can be assimilated in biosynthesis. When delignified tissue from spruce bark is grown on thymol (XLI) or on propionylguaiacylglucose (XLII), the colour reaction with phloroglucinol characteristic of lignin is not observed; if the same tissues are then cultured on media containing coniferin, the test is shown distinctly[198].


(XLI)


(XLII)

Biochemical investigations of lignification should lead to accurate definition of the enzymic systems involved with a delimitation of their functions.

The order of the bonds between the aromatic precursors of lignin is not uniform. This is explained by the presence of highly reactive functional side groups and positions in the phenolic nucleus possessing great potentialities for condensation. In contrast to other natural and synthetic polymers, the lignin "polymolecule" possesses an irregular structure[49]. However, this irregularity is not equivalent to chaos or randomness in the principles underlying the condensation of the monomers. Lignin, like other natural polymers, has its own structural order. It is more complicated and more difficult to discern.

The principle of the simulation of lignin reactions, which has found wide application in the chemistry of lignin during the past 12 – 15 years, and has revealed many peculiarities of lignin, is nevertheless of limited value. A critical approach is necessary in attempting to use analogy to transfer to lignin the results from the models.

The lignin "polymolecule", isolated by Björkman's method, possesses a molecular weight of 11 000 – 12 000. Its colloidal properties and steric factors considerably restrict the applicability of the usual methods, even including optical methods, for determining the functional groups (*e.g.* phenolic hydroxyls, carbonyls). All this requires the development of new methods and reactions specific to the main structural units.

Future work on the chemistry of lignin will probably involve, as the main problem, the elucidation of the nature of the non-aromatic groups, in particular of the propane side-chain. Its lability and tendency to undergo rearrangement are responsible for the variety of oxygen-containing functional groups attached to the carbon atoms of the side-chains. Intramolecular changes in them were shown by the investigations of Hibbert[167–171] (see above). According to Hibbert's scheme, oxygen may be present in the side-chain in the form of carbonyl or of alcoholic or enolic hydroxyls. To postulate any one definite structure for the propane side-chain, seems to be unjustified, since that would be contrary to its extraordinary variability.

It is quite reasonable to assume that the considerable divergences in the analytical data (in the determination of carbonyl groups, phenolic and enolic groups) have their origin in the nature of the propane side-chains, which change depending on the experimental conditions.

It is important to note that the three carbon atoms of the side-chain are the location of the majority of the condensation processes leading to the formation of the lignin "polymolecule", the irregularity of the structure of which is to a considerable extent explained by the nature of the side-chains. They are the points of formation not only of ether links but also of carbon – carbon bonds between the chains and with aryl radicals (α – α′-, α – β-, β-aryl bonds, etc.).

The side-chains are responsible also for additional condensation processes occurring in the lignin "polymolecule" during many technically important methods of processing wood (in the hydrolysis of wood, in the cellulose–paper industry).

The presence and the proportion of double bonds in the side-chains have not yet been completely ascertained. Measurement of the nuclear magnetic resonance in artificial lignin preparations has not been able to show the presence of double bonds. Wacek considers that their content is below 0.1 per phenylpropane unit[62].

The aromatic framework of lignin is built up from three benzene nuclei which are hydroxylated and methoxylated to differing extents (4-hydroxy-, 4-hydroxy-3-methoxy-, and 4-hydroxy-3,5-dimethoxy-phenyl nuclei). They occur in different proportions, but the guaiacyl (4-hydroxy-3-methoxy) grouping predominates, especially in the lignin of conifer wood.

As a result of the orienting influence of the phenolic hydroxyl, the aromatic nuclei in lignins are reactive mainly at the 5- and to some extent at the 6-positions. The formation of biphenyl structures and addition to a β carbon atom of a side-chain of a neighbouring unit both occur at the 5-position of the nucleus. The phenolic hydroxyls govern the formation of phenyl ether and glucoside links.

On the basis of the investigations of Freudenberg and Adler, it may be assumed that the predominant form of the linkage of phenylpropane units in native lignin is the β-aryl ether link, as in guaiacylglycerol β-coniferyl ether (IX).

At the present time there are still insufficient grounds for representing the lignin "polymolecule" in terms of the ordinary symbolism of organic chemistry, but individual details, fragments of the overall picture, still with many blank patches, are being accumulated. In view of the great progress made in the study of lignin during recent years, it seems likely that the elucidation of its structure is approaching its final solution.

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Industry

DIFFERENTIAL CAPACITY AND STRUCTURE OF THE ELECTRICAL DOUBLE LAYER AT THE MERCURY/ELECTROLYTE INTERFACE

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CONTENTS

1. INTRODUCTION

It is well known that an electrical double layer appears at the interface between two phases, one of which contains ions or polar molecules; it is formed because the electrochemical potentials in the two phases (*e.g.* metal and solution) are unequal. In general, one needs to consider the difference in chemical potential for the ions in the metal and in the solution, the influence of any external electric field, and also the specific adsorption of ions or polar molecules on the metal surface.

If any of the components of a system comprising an electrode immersed in an electrolyte is present in both phases at finite concentrations, an electrochemical reaction may be made to proceed in either direction by an externally applied potential. It is usually assumed that equilibrium in the electrical double layer is not thereby disturbed, and that the passage of current through the electrode/solution interface affects the double layer structure only in so far as it alters the surface concentration of ions. Levich has discussed[1,2] the non-equilibrium double layer. Equilibrium in the electrical double layer is maintained also when a low-amplitude alternating current is passed through the electrode, provided the frequency is not too high. However, the impedance measured by an alternating current is found[3-8] to be a complex quantity when an electrochemical reaction is proceeding at the metal surface, and there is no easy method of applying such measurements to the problem of establishing the structure of the double layer. Therefore, in studies of the double layer structure in the presence of various inorganic and organic materials, it is usual to employ an ideally polarisable electrode, *i.e.* an electrode such that the passage of ions through the interphase boundary is either thermodynamically impossible or very strongly retarded by a high energy of activation. A system consisting of mercury and a deoxygenated solution of a capillary-inactive electrolyte (*e.g.* KCl) approximates to an electrode of this type over a certain range of potential. This paper is concerned, on the whole, with electrodes which are similar in properties to the ideally polarisable electrode.

The ideally polarisable electrode is the site of an electrostatic equilibrium between two phases and is therefore electrically equivalent to a leakage-free capacitor. The thermodynamic considerations connecting the interfacial tension (σ) between a metal and a solution with the charge (ϵ) and potential (φ) of the electrode, and with the surface density and the activity of ions and molecules in the dissolved state (Γ_i and a_i respectively), are applicable to the ideally polarisable electrode. The thermodynamic treatment of this electrode leads to the basic equation of electrocapillarity, which may be expressed in the following form at constant temperature and pressure:

$$d\sigma = -\varepsilon d\varphi - \sum_i RT\ \Gamma_i\ d\ln a_i, \tag{1}$$

where R is the gas constant and T the absolute temperature. This equation was first derived by Frumkin[9] on the assumption that potential-determining ions were present in solution; the derivation is strict and is equally applicable to electrodes which are not ideally polarisable (*e.g.* thallium amalgam[10,11]). However, Frumkin's argument met with criticism as regards the ideally polarisable electrode, as it did not correspond to physical reality. Numerous alternative derivations of the electrocapillarity equation have since been put forward[12-14], but they all lead to the same result. A detailed study of the thermodynamics of adsorption at the electrode/solution interface has recently been carried out by Parsons[15].

The basic electrocapillarity equation leads to some important conclusions on the adsorbability of ions and neutral molecules at an electrode surface. In particular, Lippman's equation, which relates the differential capacity of the electrical double layer (C) to the surface tension, follows directly from Eqn. (1) when the solution composition constant is:

$$C = \frac{d\varepsilon}{d\varphi} = -\frac{d^2\sigma}{d\varphi^2}. \tag{2}$$

There are two main methods of studying the electrical double layer at an ideally polarisable electrode: the electrocapillarity curve method, developed by Gouy[16-18] and by Frumkin[19], and the method based on measurements of differential capacity. Although the earliest direct measurements of double layer capacity were carried out as long ago as 1870 by Varley[20], all the measurements reported up to 1935 gave differential capacity values several times smaller[21-26] than those calculated on the basis of Eqn. (2) using the second differential of the electrocapillarity curve. This inconsistency was resolved in 1935 by Proskurnin and Frumkin[27], who showed that the double layer capacity was extremely sensitive to traces of organic impurities and that reliable values for differential capacities could be obtained only if the experiments were conducted under the most stringent conditions of cleanliness (such as careful purification of all reagents to remove organic impurities and the use of apparatus containing no rubber tubing or bungs or greased joints).

When comparing the relative merits of the electrocapillary curves and the differential capacity curves it should be remembered that the capacity is more sensitive to changes in the double layer structure than is the surface tension. Thus, differential capacity curves are sensitive to the minutest traces of surface-active substances in solution. The capacity at φ = -0.7 V (normal calomel electrode) is lowered by $\sim 4\ \mu$F cm^{-2} for 3 N KCl when n-butyl alcohol is added to the 6×10^{-3} M level[28], but the surface tension is changed[29] by no more than 0.7 dyne cm^{-1} (these quantities can be measured with a precision of $\sim 1\%$ and $\sim 10\%$ respectively). On the other hand, the information on the electrical double layer which the differential capacity curves can provide is less complete than that derived from electrocapillarity measurements. In practice, the evaluation of surface charge and ionic adsorption from differential capacity data involves integration constants which need to be determined independently, as will be shown below. Electrocapillarity measurements are particularly suitable in this respect. If follows that the two methods (differential capacity and electrocapillary curves) must in general be considered as complementing each other in double layer studies. With solid electrodes, which do not permit direct electrocapillarity measurements, only the differential capacity method is available. Numerous recent papers deal with measurements of the differential capacity of solid electrodes[30-46], but this work suffers from experimental difficulties inherent in the preparation of clean, smooth, and reproducible surfaces, and therefore lacks precision. This is the reason for the choice of the mercury electrode in studying the structure of the double layer. We shall therefore confine this discussion, on the whole, to measurements carried out at the mercury electrode. The limited data which have been published about the surface tension[47] and the differential capacity[48] of the liquid gallium electrode are entirely in keeping with what is known about the mercury electrode.

Since present-day views on the nature of the electrical double layer are so largely based on measurements of differential capacity, we discuss briefly the relevant techniques.

2. METHODS FOR MEASURING DIFFERENTIAL CAPACITY

The current literature offers a remarkable choice of methods for measuring differential capacity. These may be tentatively classified into two groups: pulse methods and a.c. methods, the latter relying on the use of sinusoidal alternating current.

The first group includes the fast surface-charging method, due to Bowden and Rideal[24], whereby the double layer capacitance is computed from charging curves recorded on an oscillograph (see also ref.21). This method has recently been improved by Brodd, Hackermann, and

McMullen[46,49], who used square-wave pulses for charging the surface. Loveland and Elving's method[50], in which a triangular waveform is applied to the (ideally polarisable) electrode and the capacitative current is displayed on an oscilloscope, also belongs to the first group. When the resistance of the electrolyte is low, the current is proportional to the capacitance of the double layer, so that the two symmetrical differential capacity curves (corresponding to the leading and the trailing edge of the triangular pulse) which appear simultaneously on the oscilloscope involve the charging and the discharging current respectively. Finally, the commutator method developed by Borisova and Proskurnin[51] should be included among the pulse techniques. This method consists in connecting the test electrode and a standard capacitor in turn to a charged condenser, and measuring the amplified potential difference with the help of a ballistic galvanometer. The throws obtained with the test electrode and the standard capacity are inversely proportional to their capacities. The main advantage of the commutator method is that measurements are taken whilst no current is flowing in the circuit. This circumvents the possible effect of ohmic impedances which, in the case of dilute solutions, can be appreciably larger than the capacitative impedance and thus impair the precision of the capacity measurements. Measurements have been successfully carried out in solutions as dilute as 10^{-5} N using the commutator method.

The principle of the a. c. method of measuring differential capacity consists in the application of a low-amplitude sinusoidal voltage to the electrode, which is independently polarised to the desired potential from a direct-current source. When the electrode is ideally polarisable the following equation gives to the value of the alternating current flowing (i):

$$i = \frac{\Delta\varphi}{\sqrt{R^2 + \frac{1}{C^2\omega^2}}}, \tag{3}$$

where $\Delta\varphi$ is the amplitude of the alternating voltage, $\omega = 2\pi\nu$ is the angular frequency, C is the double layer capacity, and R is the resistance of the solution. Eqn. (3) states that the measured current becomes proportional to the double layer capacity if the resistance of the solution is made low enough. This is the basis of Breyer and Hacobian's "tensammetric" method[52,53] of measuring differential capacity, in which the alternating current flowing through a polarographic cell containing a sufficiently concentrated solution of an inactive electrolyte is measured. If the resistive term, due to the solution, is small compared with the reactance of the electrode (*i.e.* if $R \ll 1/C\omega$), it becomes possible to evaluate the double layer capacity simply by comparing the a.c. potentials developed across the experimental cell with that across a standard capacitor, since Eqn. (3) now becomes

$$C_x \simeq C_{st}\,\frac{\Delta\varphi_{st}}{\Delta\varphi_x}, \tag{3a}$$

and the ratio $\Delta\varphi_{st}/\Delta\varphi_x$ may be measured with an oscilloscope or an a.c. valve voltmeter. This comparison method has been described in detail by Borisova, Proskurnin, and Vorsina[54,55]. It enabled Proskurnin and Frumkin to carry out the first reliable measurements of double layer capacity[27]. The comparison method, using single-phase current, has been used to measure capacity in solutions[55] as dilute as 10^{-4} N. The resonance method (Watanabe *et al.*[56]) depends on the observation of resonance in a circuit in which the double layer of an ideally polarisable electrode provides the capacitance. It can only be applied if the solutions are sufficiently concentrated, as no resonance can be observed when the ohmic resistance of the solution is too high. Lastly, the impedance bridge method must be included in the a.c. methods of measuring double layer capacity. It provides the most accurate measurements, with ideally polarised electrodes, provided that the total concentration of the electrolyte is not less than millimolar. Essentially, the method consists in keeping two of the arms of an a. c. bridge constant (non-inductive resistances, or capacitances) and matching the double layer capacity and the solution resistance with a variable capacitor and a variable resistor, connected in series. Bridge balance is observed as the disappearance of the potential difference across the bridge. The use of a bridge circuit makes it possible to match the capacitance and the resistance separately, which is particularly advantageous when the phase-lag between current and voltage is appreciably different from 90°. The application of the impedance bridge method to the measurement of differential capacity has been discussed, particularly in papers by Grahame[57-60], Melik-Gaikazyan and Dolin[61,62], Gerischer[63], and Damaskin[64].

The measured capacity of an ideally polarisable electrode will be independent of the frequency of the a.c. employed, provided that the time required for the formation of the double layer is less than one-half of the periodic time. Ferry's[65] and Grahame's[58] calculations showed that the double layer is formed in under 10^{-6} sec in 1 N solutions; the changes in double layer capacity resulting from the use of alternating current and consequent fluctuations in ionic concentration are considerably smaller than the experimental error. An unexplained frequency-dependence of capacity has nonetheless been frequently reported[4,22,23,66-68] ("capacity dispersion"). Grahame[58], Melik-Gaikazyan and Dolin[61,62], and Damaskin[64] have shown that this effect is due to the cell geometry and circuits used, and means for overcoming it have been devised. Thus, the constancy of the differential capacity of a mercury electrode has been demonstrated experimentally over the frequency range 20–500 000 c/s in 1 N KCl solution[61,62] and up to 10 000 c/s in 0.01 N KCL solution[64].

3. VIEWS ON THE STRUCTURE OF THE ELECTRICAL DOUBLE LAYER

Present-day views on the structure of the electrical double layer are based on Stern's theory[69], put forward in 1924. Whilst retaining the basic approach of the earlier theories (Helmholtz[70] and Gouy–Chapman[71,72]), Stern's theory takes into consideration the finite size, the thermal motion, and the specific adsorption of ions. Stern believes that the ionic layer consists of two parts: the fixed, or Helmholtz, part and a diffuse part. The thickness of the fixed part is of atomic dimensions, and the density of the ions which reside in it can be calculated from the Langmuir adsorption isotherm, allowing for specific adsorption forces as well as electrostatic attraction forces. The charge in the diffuse part of the double layer is calculated from Gouy and Chapman's theory. Stern's theory therefore provides the following equation for the surface charge in the case of a uni-univalent electrolyte:

$$\varepsilon = -\varepsilon_1 - \varepsilon_2 \,, \tag{4}$$

$$\varepsilon = K_{\mathrm{H}}(\varphi_a - \psi_1) = dF\left[\frac{1}{2+\frac{1}{C}\exp\left(\frac{\Phi_- - \psi_1 F}{RT}\right)} - \frac{1}{2+\frac{1}{C}\exp\left(\frac{\Phi_+ + \psi_1 F}{RT}\right)}\right] + 2\cdot\sqrt{\frac{DRT}{2\pi}}\, c\sinh\left(\frac{\psi_1 F}{2RT}\right), \tag{5}$$

where ϵ_1 is the charge in the fixed layer; ϵ_2 is the charge in the diffuse layer; K_{H} is the integral capacity of the fixed layer; φ_a is the electrode potential, measured from the point of zero charge, ψ_1 is the potential at a distance $r = d/2$ from the electrode surface (mean ionic radius); Φ_+ and Φ_- are the so-called specific adsorption potentials, assumed independent of the electrode potential; D is the dielectric constant; c is the electrolyte concentration; F is Faraday's constant.

An analysis[69,73-75] of Eqn. (5) shows that Stern's theory is in keeping with numerous experimental findings. Thus, the theory explains why the measured double layer capacity is effectively equal to the capacity of a condenser of molecular dimensions in spite of the fact that most of the charge is distributed over the diffuse layer. It can explain charge reversal of the surface, since the potential ψ_1 is not the same as the electrode potential, and can change its sign under the influence of sufficiently strong specific adsorption of ions of the appropriate sign. Since the ζ-potential in not too concentrated solutions may be equated[75] (to a first approximation) to the ψ_1 potential, Stern's theory can be used in the interpretation of electrokinetic phenomena. Besides predicting the shrinkage of the diffuse layer with increasing the electrolyte concentration, the theory gives the variation of ψ_1 potential with electrolyte concentration and with electrode potential. We can therefore assert that Stern's theory, notwithstanding later refinements, should still be regarded as providing the basic modern interpretation of the structure of the electrical double layer.

1. **The double layer in the absence of specific adsorption.** A quantitative verification of Stern's theory in the absence of specific adsorption ($\Phi_+ = \Phi_- = 0$) has been presented by Vorsina and Frumkin[76]. Assuming fairly low coverage of the surface by adsorbed ions, it can readily be shown from Eqn. (5) that

$$\varepsilon = K_{\mathrm{H}}(\varphi_a - \psi_1) = 2cdF\sinh\left(\frac{\psi_1 F}{RT}\right) + 4c\lambda F\sinh\left(\frac{\psi_1 F}{2RT}\right), \tag{6}$$

where $\lambda = \sqrt{\frac{DRT}{8\pi cF^2}}$ is the thickness of the ionic atmosphere for a uni-univalent electrolyte. The variation of φ_a, the electrode potential, with ψ_1-potential, may be derived from Eqn. (6):

$$\varphi_a = \psi_1 + \frac{2cdF}{K_{\mathrm{H}}}\sinh\left(\frac{\psi_1 F}{RT}\right) + \frac{4c\lambda F}{K_{\mathrm{H}}}\sinh\left(\frac{\psi_1 F}{2RT}\right). \tag{7}$$

However, in contrast with Stern's original assumptions, the fixed layer capacity K_{H} is not constant but varies with potential. If we assume that the fixed layer capacity depends on the sign of the adsorbed ions and varies with coverage by anions and cations as would two separate condensers connected in parallel, and if we further assume that the population of anions and cations in the fixed layer obeys Boltzmann's distribution law, we can derive the following expression for K_{H}:

$$K_{\mathrm{H}} = \frac{K_{\mathrm{H}}^{-}\exp\left(\frac{\psi_1 F}{RT}\right) + K_{\mathrm{H}}^{+}\exp\left(-\frac{\psi_1 F}{RT}\right)}{\exp\left(\frac{\psi_1 F}{RT}\right) + \exp\left(-\frac{\psi_1 F}{RT}\right)}, \tag{8}$$

where K_{H}^{+} and K_{H}^{-} are the integral capacities of the fixed layer for cations and anions respectively (assumed values $K_{\mathrm{H}}^{+} = 20\ \mu\mathrm{F\ cm^{-2}}$, $K_{\mathrm{H}}^{-} = 38\ \mu\mathrm{F\ cm^{-2}}$). From Eqns. (6), (7), and (8) we may derive the following expression for the differential capacity of the double layer

$$C = \frac{d\varepsilon}{d\varphi} = \frac{d\varepsilon}{d\psi_1}\,\frac{1}{\left(\frac{d\varphi}{d\psi_1}\right)} = \frac{K_{\mathrm{H}}A}{A + K_{\mathrm{H}} - \frac{1}{2}\left(K_{\mathrm{H}}^{-} - K_{\mathrm{H}}^{+}\right)\frac{(\varphi_a - \psi_1)F}{RT}\cosh^{-2}\left(\frac{\psi_1 F}{RT}\right)} \tag{9}$$

$$\text{where}\quad A = \frac{2cF^2}{RT}\left[d\cosh\left(\frac{\psi_1 F}{RT}\right) + \lambda\cosh\left(\frac{\psi_1 F}{2RT}\right)\right].$$

Vorsina and Frumkin[76] calculated C vs. φ curves from Eqns. (9) and (7) and compared them with differential capacity curves measured in dilute solutions of KCl or HCl. A measure of agreement was found, but the calculated curves lay appreciably below the experimental curves (see Fig. 1). It follows that the double layer in KCl or HCl solution is more densely populated than the theory predicts. Up to a point, the results may be explained by invoking the specific adsorption of chloride ions. However, certain inconsistencies arise in Stern's equation for the case of no specific adsorption ($\Phi_+ = \Phi_- = 0$). Thus, the whole of the charge of the ionic layer which is equal to the charge on the electrode, is now relegated to the diffuse layer, *i.e.* $\epsilon = -\epsilon_2$, whence, from Eqn. (4), $\epsilon_1 = 0$. The same result does not follow from Eqn. (5), and the significance of the fixed layer charge obtained for $\Phi_+ = \Phi_- = 0$ is therefore unclear. Better consistency, in the absence of specific adsorption, is found if the following equation[77] is adopted for the surface charge in a uni-univalent electrolyte:

$$\varepsilon = -\varepsilon_2 = 2\sqrt{\frac{DRT}{2\pi}}\, c\sinh\left(\frac{\psi_1 F}{2RT}\right). \tag{10}$$

This is equivalent to regarding the double layer as two capacitances connected in series: the fixed layer capacitance, C_{H}, and the diffuse layer capacitance, C_{D}:

$$\frac{1}{C} = \frac{1}{C_{\mathrm{H}}} + \frac{1}{C_{\mathrm{D}}}. \tag{11}$$

The physical significance of Eqn. (11) is easily visualised in terms of two imaginary layers of charge in the fixed layer: one equal in magnitude and opposite in sign to the charge on the electrode surface, the other equal and opposite to the charge in the diffuse layer. Since $\epsilon = -\epsilon_2$, the algebraic sum of these two hypothetical charged layers vanishes in this case, and the series combination of capacitors C_{H} and C_{D} has a common, uncharged plate.

Grahame has suggested[77] that in the absence of specific adsorption the fixed layer capacitance depends on the surface charge (ϵ) but not on the electrolyte concentration. If this is the case, a C_{H} vs. ϵ curve can be constructed by applying Eqn. (11) to differential capacity data obtained at any one concentration, and hence capacity curves for any arbitrary concentration can be derived from the observed values of C_{H} and the calculated values of C_{D}. Calculations of this type were carried out by Grahame (Fig. 2) for sodium fluoride solutions (which do not give specific adsorption) in water at different temperatures[78,79] and also in methanol[80]. The satisfactory agreement between calculated and experimental curves is convincing proof of the correctness of the assumption that the fixed layer capacity is independent of

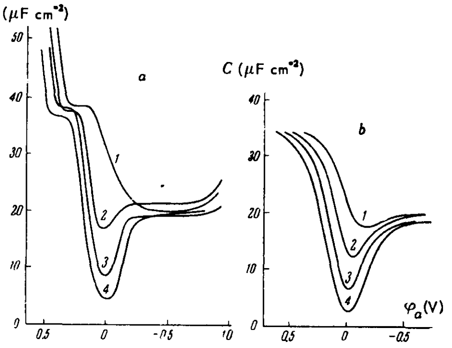

Fig. 1. Variation of differential capacity with electrode potential:

a) experimental curves, measured in the following solutions:

1) 0.1*N* KCl; 2) 0.01*N* KCl; 3) 0.001*N* KCl; 4) 0.0001*N* HCl;

b) calculated from Eqns. (9) and (7) for the same concentrations of a uni-univalent electrolyte.

the concentration of electrolyte when specific adsorption is absent. Furthermore, the classical theory of the diffuse double layer[71,72] is seen to be applicable, in practice, to a greater extent than might have been expected from the numerous simplifying assumptions made.

Actually, several improvements in the diffusion layer theory were suggested shortly after its original publication. Bikerman[81] and Freise[82] calculated the work required to convert dipolar water complexes to dipolar hydrated ion complexes, and were able to allow for the effect of ionic volume on ionic interaction (repulsion effect). Macdonald and Brachman[83] obtained an exact solution of the Debye–Hückel equation, giving the variation of local potential with distance from the polarised electrode, and Macdonald[84] applied this result to the evaluation of the static space-charge in the diffuse layer. Grahame[85] studied the effect of dielectric saturation (decrease in dielectric constant at high electric fields) on the properties of the diffuse layer, and showed that the field strength in the diffuse layer may reach the value 3×10^6 V/cm, above which a rapid drop in dielectric constant ensues. The physically observable properties of the diffuse layer (ψ_1-potential, values of the ionic components, free energy of hydration of ions) are nevertheless relatively unaffected by the onset of dielectric saturation. Sparnaay[86] further refined the theory of the diffuse layer by allowing for the ultimate ionic volume as well as for dielectric saturation. Brodowsky and Strehlow[87] also contributed to this work by showing that both effects act in the same sense and decrease the differential capacity of the diffuse layer. Finally, Kir'yanov and Levich[88], using Bogolyubov's method of correlation functions, derived a coherent statistical theory of the electrical double layer which takes account of the discrete charge distribution in the diffuse layer.

All these refinements of the theory of the diffuse layer introduce serious complications in the mathematical equations, which often cannot be solved analytically. Also, deviations from the classical diffuse layer theory are mostly confined to cases of high surface charge (as shown by Grahame[77]), where the diffusion layer capacity is large compared with that of the fixed layer. It follows, since C_H and C_D are in series connection [see Eqn. (11)], that even relatively large errors in the simple theory will usually lead to negligible errors in the description of the properties of the double layer. This conclusion was strikingly confirmed by Grahame's measurements[78-80] of double layer capacity in sodium fluoride solutions to which we have already referred. At the same time, since the classical theory[71,72] of the diffuse layer was confined to *n*-*n*-valent electrolytes[77], there was a need for extending it to include electrolytes of asymmetrical valency type. Grahame[89] solved the problem for the case of electrolytes of valency types 1 : 2 and 2 : 1.

Macdonald[90,91] attempted to formulate a mathematical theory of the fixed layer in the absence of specific adsorption. In his first paper[90] he gives a mathematical treatment of the concentration-dependence of differential capacity at the point of zero charge. The later paper[91] extends this treatment to arbitrary values of potential, taking account of dielectric saturation in the fixed layer and of the compression of the fixed layer due to strong electric fields. In this case, unlike the case of the diffuse layer, dielectric saturation has a marked effect. Using Grahame's experimental results for sodium fluoride solutions[78], Macdonald obtained a satisfactory measure of agreement between the calculated and the experimental differential capacity curves

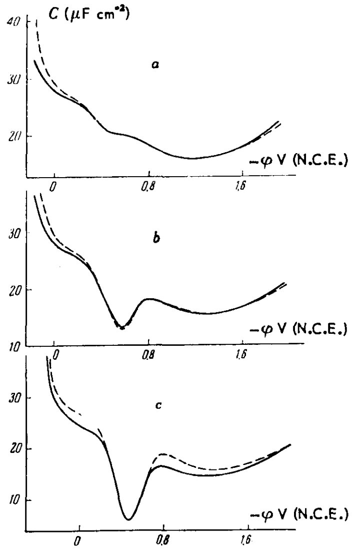

Fig. 2. Differential capacity curves in aqueous NaF solutions at 25°:

a) 0.1*N*; *b*) 0.01*N*; *c*) 0.001*N*; continuous lines: experimental; broken lines: calculated from Eqn. (11) on the basis of experimental results obtained in 0.916*N* NaF.

for a negatively charged mercury surface. As a result of this comparative work he determined a number of the parameters which characterise the properties of the fixed part of the double layer in the absence of specific adsorption. With positively charged surfaces, however, the discrepancies occurred between calculated and measured differential capacities; these were ascribed by the author to the inadequacy of the assumption of no specific adsorption of fluoride anions and that no reliance can be placed on the results.

2. The double layer in the presence of specific adsorption. The early measurements of surface tension[16,19] showed that certain anions have a striking tendency to give specific adsorption at the mercury electrode surface, an observation subsequently confirmed by differential capacity measurements[92,93]. Vorsina and Frumkin, for example, showed[92] that as the adsorbability of the anion was increased (from Cl^- to I^-) the minimum capacity, close to the point of zero charge, increased and became displaced towards more negative potentials. In the presence of I^-, a sharp minimum in the differential capacity curve is observed only if the solutions are as dilute[51] as 10^{-5} *N*, providing evidence of the strong specific adsorption of this ion. Grahame *et al.*[93] measured differential capacity curves in 12 solutions of potassium salts with different anions, and discussed their results in terms of increasing adsorbability of the anion with decreasing solubility of the corresponding mercurous salt. They concluded that the specific adsorption of anions at a mercury surface is controlled by the covalent forces arising in the crystal lattice of the resulting mercurous salt. Grahame subsequently showed[94,95] that, with the notable exception of the fluoride ion, all singly charged anions exhibit specific adsorption, to a greater or lesser extent, at the mercury electrode surface. It was as a result of this work that Grahame decided, as mentioned above, to use differential capacity curves in sodium fluoride solutions to test the theory of the double layer in the absence of specific adsorption[78-80].

Stern assumed that the specific adsorption of ions was analogous to the adsorption of gases by solid surfaces in obeying Langmuir's adsorption isotherm. The chemical potential of the adsorbed species could then be expressed as

$$\mu_i = \mu_{0i} + RT \ln \frac{\theta}{1-\theta}, \tag{12}$$

where θ is the fraction of the sites occupied by adsorbed particles. For the case of the double layer, Eqn. (12) predicts non-interaction between anion and cation adsorption, which is not acceptable in general. Esin and Markov[96] gave a more accurate expression for ϵ_1 by using a composite Langmuir isotherm for anions and cations, based on the following equations for the chemical potentials of the cations and anions which are adsorbed to different extents:

$$\left.\begin{aligned} \mu_+ &= \mu_{0+} + RT \ln \frac{\theta_+}{1-\theta_+-\theta_-} \\ \mu_- &= \mu_{0-} + RT \ln \frac{\theta_-}{1-\theta_+-\theta_-} \end{aligned}\right\} . \tag{13}$$

Kambara[97] introduced further refinements of this type into Stern's theory. In deriving the composite Langmuir isotherm Kambara made allowance for the adsorption of surface-active materials and of solvent molecules as well as for the specific adsorption of cations and anions. He obtained an expression for ϵ_1, the charge density, in terms of the ψ_1-potential, and was thus able, after making certain assumptions, to express the charge density at the electrode and the differential capacity as a function of the electrode potential. Unfortunately, all these expressions are extremely cumbersome, and Kambara's theory is therefore difficult to test. Furthermore, Parsons states[98] that the Langmuir isotherms, on which Stern's and Kambara's theories are based, is not really applicable to the specific adsorption of anions, such as I^-, Br^-, CNS^- on a mercury surface. After a detailed study of the adsorption isotherm on mercury of the surface-active iodide ion, Parsons showed[98] that the experimental results were best fitted by Temkin's equation

$$\Phi = \int_{-\infty}^{\mu} \frac{\epsilon_1}{F}\, d\mu = a\, \Gamma_-^2 , \tag{14}$$

or by any other theoretical isotherm leading to Eqn. (14) for appreciable surface coverage. In this respect Langmuir's equation is entirely unsatisfactory and fails to explain the experimental results on the adsorption of I^-, Br^-, CNS^- anions at a mercury surface. There are two reasons for this failure of Langmuir's isotherm: localised adsorption sites are hardly likely to exist at a liquid mercury surface, and furthermore the interactions between charged particles in a discrete distribution of charge, such as exists in the electrical double layer, cannot be ignored.

A further important shortcoming of Stern's, and also of Kambara's, theories is the fact that the locus of the electrical centres of specifically adsorbed ions is identified with the boundary of the diffuse layer. Stern's theory involves only a single potential (ψ_1) at the boundary of the Helmholtz layer. In his study of the experimental results on adsorption at potentials close to the electrocapillarity maximum, Grahame showed[77] that Stern's theory leads to incorrect shifts in the point of zero charge for various anions. To explain the observed shifts which are much larger than predicted by Stern's theory, we must postulate the existence of two distinct Helmholtz layers at different potentials. The locus of the electrical centres of the specifically adsorbed ions is called the inner Helmholtz plane by Grahame, who considers that only anions (with the exception of fluoride[94,95]) can be specifically adsorbed and

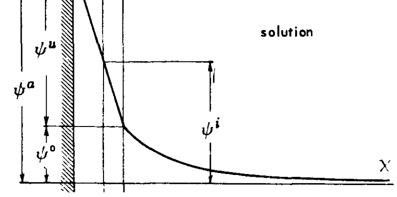

Fig. 3. Structure of the electrical double layer (after Grahame[105]):
1) inner Helmholtz plane; 2) outer Helmholtz plane.

thus give rise to an inner Helmholtz plane. Monatomic cations, which are not specifically adsorbed and are therefore excluded from the inner Helmholtz plane, cannot be part of the fixed layer, and their electrical centres may approach the surface only as far as the outer Helmholtz plane. Grahame stresses[77] that, in contrast with Stern's theory, the outer Helmholtz plane cannot be thought of as an ionic layer but merely represents the position of closest approach to the surface of ions still undergoing thermal motion. Grahame designates the potentials of the inner and the outer Helmholtz planes at ψ^i and ψ^0 respectively (see Fig. 3). Grahame's views on the electrical double layer[77,94], which deny any specific adsorption of cations, allow the charge distribution in the various parts of the double layer and the potential of the outer Helmholtz plane to be calculated, in this particular case, from differential capacity data.

Let us consider Grahame's method of calculation in some detail and confine ourselves, for simplicity, to the case of a uni-univalent electrolyte.

From the thermodynamic theory of the ideally polarisable electrode[77] [see also Eqn. (1)]:

$$F\Gamma_+ = -\int C_+ d\varphi + K_1 , \tag{15}$$

$$C_+ = \int \left(\frac{dC_+}{d\varphi}\right) d\varphi + K_2 , \tag{16}$$

$$\frac{dC_+}{d\varphi} = -F\left(\frac{\partial C}{\partial \mu}\right)_{\varphi^-} . \tag{17}$$

In these equations C_+ is the part of the differential capacity due to the presence of the cation in the double layer; K_1 and K_2 are integration constants; μ is the chemical potential in the solution; the subscript $(\ldots)_{\varphi^-}$ indicates that the derivative refers to a potential measured against that of an electrode reversible to the anion. The right-hand side of Eqn. (17) may be evaluated experimentally from the variation of differential capacity with electrolyte concentration. One can thus find $dC_+/d\varphi$ as a function of the electrode potential φ.

At sufficiently negative potentials, and in the absence of specific adsorption of cations, all the ions will be found in the diffuse layer (*i.e.* $\epsilon = -\epsilon_2$). The kinetic theory of the diffuse layer then gives the following equations:

$$F\Gamma_+ = \varepsilon_2^+ = \sqrt{\frac{DRT}{2\pi}c}\,(v + \sqrt{1+v^2} - 1) , \tag{18}$$

$$C_+ = -\frac{d\varepsilon_2^+}{d\varphi} = \frac{C}{2}\left(1 + \frac{v}{\sqrt{1+v^2}}\right) , \tag{19}$$

where ϵ_2^+ is the charge in the diffuse layer atrributable to the cation, and

$$v = \frac{\varepsilon_2}{2\sqrt{\frac{DRT}{2\pi}c}} = -\frac{\varepsilon}{2\sqrt{\frac{DRT}{2\pi}c}} .$$

From Eqns. (18) and (19) we can determine Γ_+ and C_+ uniquely, and thus derive the integration constants K_1 and K_2.* Knowing K_1 and K_2, it is a simple matter to calculate the surface density of the cation Γ_+ from Eqns. (16) and (15), and hence, using the equation

$$(\Gamma_+ - \Gamma_-)F = -\varepsilon \tag{20}$$

to find the surface density of the anion Γ_-. If no cations are specifically adsorbed at any potential:

$$F\Gamma_+ = \varepsilon_2^+ . \tag{21}$$

Thus, if we know ϵ_2^+, we can calculate the potential of the outer Helmholtz plane, ψ^0, from the kinetic theory of the diffuse layer:

$$\varepsilon_2^+ = \sqrt{\frac{DRT}{2\pi}c} \cdot \left(e^{-\frac{F\psi^0}{2RT}} - 1\right). \tag{22}$$

Finally, it is not difficult to evaluate the anion charge in the fixed layer (ϵ_1) and that in the diffuse layer (ϵ_2^-), since

$$\varepsilon_2^- = -\sqrt{\frac{DRT}{2\pi}c}\,\left(e^{\frac{F\psi^0}{2RT}} - 1\right) , \tag{23}$$

$$\varepsilon_1 = -F\Gamma_- - \varepsilon_2^- . \tag{24}$$

To calculate the potential of the inner Helmholtz plane (ψ^i) further assumptions are required. These will be discussed below.

In Stern's theory the specific adsorption is described in terms of the potentials Φ_+ and Φ_- [see Eqn. (5)], which are assumed to be independent of the electrode potential and therefore also of the surface charge. Grahame's work[77], however, showed that this assumption was contrary to the experimental data. A theory of the electrical double layer in which the influence of the electrode charge on the extent of specific adsorption is duly considered was put forward by Devanathan[99]. It assumes the presence of two Helmholtz planes: an inner plane, the site of the electrical centres of the specifically adsorbed ions which are dehydrated on the side nearest the electrode, and an outer plane (which Devanathan calls the Gouy plane) representing the locus of the electrical centres of the hydrated ions not specifically adsorbed*. Devanathan called the electrostatic capacity of the inner section of the double layer K_{H_1} and that of the section between the two Helmholtz planes K_{H_2}, and by assuming that these capacities are not a function of the electrode charge ϵ, derived the following equation for the overall differential capacity of the double layer

$$\frac{1}{C} = \frac{1}{K_{H_1}} + \left(\frac{1}{K_{H_2}} + \frac{1}{C_D}\right)\left(1 + \frac{d\varepsilon_1}{d\varepsilon}\right), \tag{25}$$

where ϵ_1 is the charge due to specifically adsorbed ions and C_D is the double layer capacity, expressed in terms of the charge in the diffuse layer ($-\epsilon - \epsilon_1$) and the electrolyte concentration. For example, in the case of a uni-univalent electrolyte at 25°,

$$C_D = 19.45\sqrt{138c + \varepsilon_2^2} , \tag{26}$$

where C_D is in μF cm^{-2}, ϵ_2 is in μC cm^{-2}, and c is in M.

Eqn (25) shows that the double layer is equivalent, according to Devanathan's theory, to three condensers connected in series, of capacities K_{H_1}, K_{H_2}, and C_D. The latter two capacities require a correction for the change in

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* K_1 and K_2 can also be derived, though less accurately, from electrocapillary curves[94].

* Devanathan identifies the concept of specifically adsorbed ions with that of ions which lose their water of hydration upon being adsorbed, and therefore dissents from the generally adopted view that specific adsorption – like other adsorptions – involves forces other than purely electrostatic ones (*e.g.*, covalent, or van der Waals forces). See also ref. 48.

specific adsorption with surface charge. The same author showed[99] that $d\epsilon_1/d\epsilon$ could be evaluated from experimental data on differential capacity by introducing certain assumptions into Eqn.(25); the charge due to specifically adsorbed ions, ϵ_1, can then be derived by numerical integration. Calculations of the surface densities of the cations and anions (Γ_+ and Γ_-) and of the shift in the point of zero charge produce results in satisfactory agreement with experiments based on this theory. Most of the parameters which appear in Eqn. (25), however, (namely K_{H_1}, K_{H_2}, and $d\epsilon_1/d\epsilon$), have to be experimentally determined. Devanathan's theory of the electrical double layer is thus seen to be essentially semi-empirical. Exception could also be taken to the assumption that the fixed layer capacities K_{H_1} and K_{H_2} are independent of the surface charge. One consequence of this assumption seems particularly difficult to accept, namely that for any electrolyte, specific adsorption can be suppressed only at the minimum of the C *vs.* ϵ curve ($\epsilon \simeq$ $\simeq -13\ \mu C\ cm^{-2}$), *i.e.* that all ions retain their hydration shell at this particular value of the surface charge. Finally, it may be noted that Devanathan's theory, like Stern's, ignores the discrete nature of the specifically adsorbed ionic charge.

Frumkin commented [73] as long ago as 1935 on the undesirability of neglecting the discrete structure of the double layer, as is done in Stern's theory. Discrepancies between this theory and experimental findings were first reported in 1939 by Esin and Markov[96], who observed an anomalously large shift in the point of zero charge as a function of potassium iodide concentration. On the basis of the equation

$$\varphi_{zc}^{(KJ)} - \varphi_{zc}^{(NaF)} = \psi_1 \simeq \text{const.} - \frac{RT}{F} \ln c_{(KI)} \qquad (27)$$

derived from Stern's theory, the zero-charge potential $\varphi_{zc}^{(KI)}$ was expected to vary linearly with $\log c_{(KI)}$, with a slope of not more than 58 mV per factor of ten change in concentration. Esin and Markov found that the relationship was indeed linear, but their experimental slope (~ 100 mV per factor of ten) exceeded the expected value by a factor of two. Esin and Shikhov explained[100] this result by postulating anion–cation dipoles on the electrode surface, situated in a hexagonal array. The difference in potential between the anion and the cation layers would then be only a fraction of the potential difference due to two separate layers of charge. No fixed anion–cation dipoles can in fact exist in the double layer, and the Esin–Shikhov model therefore leads to an even steeper variation of point of zero charge with the logarithm of KI concentration (~ 200 mV per factor of ten) than was observed in practice.

A further development of the theory of discrete ionic distribution in the double layer is due to Ershler[101]. This worker abandoned the Esin–Shikhov dipole model and put forward a different, more accurate picture of the charge distribution in the double layer for the particular case of the zero charge potential. By considering the multiple reflection of the charges of the specifically adsorbed anions between two equipotential surfaces (the outer Helmholtz plane and the metal surface) Ershler was able to prove that the potential difference between these two surfaces should be just one-half of that calculated from the Esin–Shikhov anion–cation dipole model. Ershler's theory[101] satisfactorily explained the results of experiments on the dependence of the shift in zero-charge potential upon the concentration of specifically adsorbed anions[96,102]. Gurenkov subsequently showed[103] that Ershler's theory was equally satisfactory when applied to experiments on the concentration-dependence of adsorption potential at the solution/air interface, although it had originally been developed for the metal/solution interface. It should be noted that the principles underlying the calculation of adsorption potentials in concentrated solutions[102,103] were put forward by Frumkin[104].

More recently, Grahame[105,106] has developed Ershler's views and applied them to the case of charged surfaces, and has studied the potential drop in the diffuse layer. According to Grahame[105],

$$\varphi_a = \psi^u + \psi^0 = \psi^V + \psi^{02} + \psi^0, \qquad (28)$$

where φ_a is the electrode potential relative to the point of zero charge in a non-adsorbed electrolyte (*e.g.* NaF); ψ^u is the potential drop in the fixed layer, made up of ψ^V (potential difference due to specifically adsorbed ions) and ψ^{02} (potential difference arising from the electronic charge of the surface, see Fig. 3). Furthermore,

$$\psi^{02} = \int_0^\varepsilon \frac{1}{C^{02}} d\varepsilon, \qquad (29)$$

where C^{02} is the differential capacity of the fixed layer at constant specific adsorption of anions, introduced by Grahame:

$$C^{02} = \left(\frac{\partial \varepsilon}{\partial \psi^u}\right)_{\varepsilon_1}. \qquad (30)$$

Knowing φ^0, the potential of the outer Helmholtz plane [see Eqn. (22)], the potential drop across the fixed layer, ψ^u, may be found from Eqn. (28), and C^{02} may then be evaluated for any arbitrary surface charge using Eqn. (30). Grahame's calculations[106] showed that C^{02} is practically independent of ϵ_1, and should therefore be the same for all anions, since at $\epsilon_1 = 0$ the value of C^{02} is not affected by the nature of the anion. This result greatly simplifies the subsequent calculations. In practice, once ψ^{02} has been found by numerical integration of Eqn. (29), it is not a difficult matter to derive ψ^V from Eqn. (28), *i.e.* to evaluate the potential drop in the fixed layer arising from the presence of specifically adsorbed anions. According to the Ershler–Grahame theory[101,105], which postulates a hexagonal array of specifically adsorbed ions on the surface and multiple reflections of their charges between the equipotential surfaces of the metal and of the outer Helmholtz plane,

$$\frac{d\psi^V}{d \ln a_\pm} = \frac{1}{\dfrac{RT}{F\psi^V} - \dfrac{d\psi^i}{d\psi^V}} \frac{RT}{F} \qquad (31)$$
$$[\varepsilon = \text{const}],$$

where $a_\pm$ is the mean activity of the electrolyte. Eqn. (31) yields a value of $d\psi^i/d\psi^V$ and thus finally leads to a calculated value for ψ^i, the potential of the inner Helmholtz plane. It should be noted that an entirely self-consistent mathematical theory, able to take account of the discrete nature of the charges in the fixed layer, has very recently been developed by Kir'yanov and Levich. Their analysis has confirmed the correctness of Eqn. (31), which lacked a really firm basis in Ershler's[101] and in Grahame's[105] earlier derivations.

In the whole of Grahame's work the assumption is made that cations are not specifically adsorbed at a mercury electrode surface over the entire accessible potential range [see Eqn. (21)]. The assumption is not strictly correct, however, since a few inorganic cations can undergo excess adsorption to a moderate extent.

Vorsina and Frumkin[107] were the first to conclude, from differential capacity data, that the La^{3+} and Th^{4+} cations are specifically adsorbed to some extent at a mercury surface.

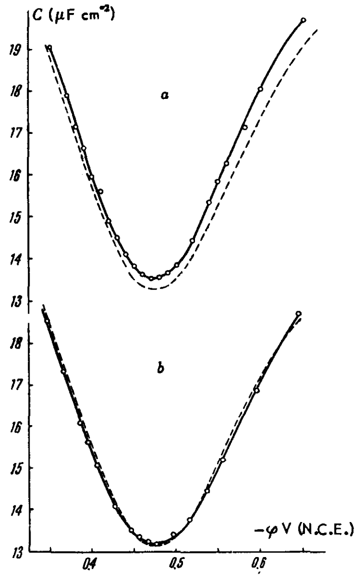

Fig. 4. Portions of differential capacity curves in the neighbourhood of the point of zero charge in 0.01*N* solutions of (*a*) CsF and (*b*) NaF, at 25°. Points and full curves : experimental; dotted curves : calculated from Eqn.(11) on the basis of experimental results obtained in 0.9*N* solutions.

Grahame himself showed[108] that when the mercury surface is negatively charged the double layer capacitance in 0.1 *N* aqueous chloride solutions increases in the sequence $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, but he attributes this effect to changes in the capacity of the fixed layer, arising from the different cation radii and the different dielectric saturation in the fixed layer. The difference in capacity for the cations Li^+, Na^+, and K^+ is even more striking in methanol solutions[109]. The work of Frumkin, Damaskin, and Nikolaeva-Fedorovich[110,111] suggests a ready explanation for the increase in capacity in the series Li^+ to Cs^+ in terms of a relatively small amount of specific adsorption of cations, increasing with ionic radius.

It can be shown, on the other hand, that the difference in differential capacity between solutions of, say, NaF and CsF is not entirely explicable on the grounds of changes in the capacity of the fixed layer. Indeed, it has already been stressed that, in the absence of specific adsorption, the electrical double layer is equivalent to two condensers of capacities C_D and C_H connected in series [see Eqn. (11)], such that the fixed layer capacity *C*, whilst being a function of the charge on the electrode, is at the same time independent of the electrolyte concentration. Fig. 4 shows portions of differential capacity curves in the neighbourhood of the point of zero charge for 0.01 *N* sodium fluoride and caesium fluoride solutions, as measured by the present author, together with *C vs.* φ curves calculated for the same solutions by substituting data obtained in 0.9 *N* NaF and CsF solutions into Eqn. (11). Clearly, the calculated and the experimental capacity curve coincide only for the sodium fluoride solution, and therefore the assumed absence of specific adsorption of Na^+ and F^- ions is confirmed in this case. With caesium fluoride, on the other hand, the experimental *C vs.* φ curve lies above the calculated curve, and this shows directly that the Cs^+ cation must undergo slight specific adsorption. The presence of some specific adsorption in the case of some inorganic cations is further confirmed by electrocapillarity and zero charge potential measurements[111], and receives indirect support from our extensive knowledge of the kinetics of the electrolytic reduction of numerous ions at the mercury electrode[112].

The effects resulting from the specific adsorption of Cs^+ and La^{3+} are relatively small in comparison with those which accompany the adsorption of anions. There are some inorganic cations, however, such as Tl^+, whose specific adsorbability is entirely comparable with that of the anions Cl^- and Br^-. The adsorption of Tl^+ on mercury causes a sharp drop in the electrocapillary maximum, which is shifted towards more positive potentials[113]. Thallium cations are also strongly adsorbed on a platinum surface[114]. Grahame's theory of the double layer, which postulates that cations are not specifically adsorbed, must therefore be regarded as somewhat approximate.

We should also note that the theory developed by Grahame is not applicable to concentrated electrolytes, when the negative adsorption of ions begins to swamp the electrostatic interaction of these ions with the charged surface. Frumkin and Iofa[115] showed how ion adsorption in concentrated solutions could be evaluated from electrocapillary curves, and Iofa, Ustinskii, and Eiman[116] followed up this suggestion in the case of hydrochloric, hydrobromic, and sulphuric acids. As expected, they found that on the cathodic branch, and for relatively low HCl concentrations, Γ_+ is positive and $(-\Gamma_-)$ is negative. As the acid concentration is increased, in addition to the electrostatic adsorption, general negative ion adsorption begins to be noticeable, and Γ_+ decreases. In really concentrated HCl solutions (> 10 *N*) the adsorption of hydroxonium cations on the negatively charged mercury surface can no longer be calculated from Eqn. (21), basic to Grahame's theory; furthermore, it is actually a negative quantity, since under these conditions the negative adsorption of H_3O^+ ions outweighs their electrostatic attraction. In concentrated sulphuric acid solutions (10.0 – 12.3 *N*) this effect is even more apparent[116].

These specific cation adsorption effects, and the negative adsorption of ions in concentrated solutions, are a searching test for the applicability of Grahame's theory of the electrical double layer. Nevertheless, calculations based on his theory can in many cases lead to important parameters, characteristic of the double layer, which can be used in explaining the kinetics of electrochemical reactions[117].

3. Double layer in the presence of organic surface-active materials. Many organic compounds are adsorbed at the mercury electrode surface. Gouy showed[17,18], as long ago as 1906, that adsorbed organic material can lower the interfacial tension of mercury significantly. His experiments indicated a decrease in the adsorption of neutral organic molecules as the potential drop at the electrode/electrolyte interface was increased, and complete desorption at high enough surface charges. Electrocapillary curves measured in the presence of organic impurities showed breaks of varying degrees of sharpness. The desorption of organic substances at high surface charges arises from the increase in the energy

stored in the double layer capacity when the layer of organic molecules, of low dielectric constant, is replaced by a layer of water molecules whose dielectric constant is significantly higher even allowing for saturation effects[91].

Frumkin developed a quantitative theory[118] of the influence of an electric field on the adsorption of neutral molecules in which the equation of state of the adsorbed layer is considered. Evaluating the attractive forces between adsorbed molecules, he finds the following relationships between the depression of interfacial tension ($\Delta\sigma$), the surface coverage ($\theta = \Gamma/\Gamma_m$), and the concentration of surface-active material (c):

$$\frac{\Delta\sigma}{A} = -\ln(1-\theta) - a\theta^2, \tag{32}$$

$$Bc = \frac{\theta}{1-\theta}e^{-2a\theta}, \tag{33}$$

where A, B, and a are constants such that $A = RT\Gamma_m$, a is a measure of the mutual attraction between adsorbed molecules, and B gives the effect of electrode potential upon the adsorption:

$$B = B_0 \exp\left[-\frac{\frac{1}{2}C_0\varphi_a^2 - \frac{1}{2}C'\varphi_a(\varphi_a - 2\varphi_N)}{RT\Gamma_m}\right], \tag{34}$$

where C_0 and C' denote the capacity of the double layer at $\theta = 0$ and $\theta = 1$ respectively, and φ_N is the shift in point of zero charge when the surface is covered by the adsorbate.

Frumkin's theory[118] satisfactorily explains the measured effects of dissolved surface-active organic substances on the interfacial tension of mercury.

In Butler's theory[119] an attempt is made to explain the observed electrocapillary curves in terms of the molecular properties of the adsorbate (the polarisability of the organic molecules is particularly stressed). However, Butler's theory relies on experimental measurements of interfacial tension to give the dipole moments of the adsorbed molecules. Furthermore, by assuming that Henry's law is applicable, the theory leads to an incorrect relationship between the adsorption of an organic substance and its concentration in solution.

Lippmann's Eqn. (2), applied to electrocapillarity data, predicts for differential capacity curves in the presence of organic additives a region of low capacity (~4–5 $\mu F\ cm^{-2}$) bounded on both sides by desorption peaks. According to Frumkin[118], the extent of adsorption in fact varies linearly with surface charge. It is, therefore, an easy matter to derive the following equation for the differential capacity:

$$C = C_0(1-\theta) + C'\theta + (\varepsilon' - \varepsilon_0)\frac{d\theta}{d\varphi}, \tag{35}$$

where ϵ_0 and ϵ' denote the surface charge at $\theta = 0$ and $\theta = 1$ respectively. The last term in Eqn. (35) is a pseudo-capacity connected with the adsorption–desorption process; this parameter gives rise to peaks in the differential capacity curves. For sufficiently large surface charges, whether positive or negative, $\theta \to 0$, so that one expects from Eqn. (35) that capacity curves measured with and without organic impurities should coalesce in these regions. That such is indeed the case was first demonstrated by Proskurnin and Frumkin[27], who found that differential capacity curves in the presence of n-octyl alcohol were of the expected form. Capacity curves of a similar form were reported by Ksenofontov, Proskurnin, and Gorodetskaya[120] in solutions of ethanol, n-butanol, and phenol. The double layer differential capacity method has since become widely used for studying the adsorption of organic substances at electrode surfaces. For example, it was applied in an investigation[121] of the structure of the thin films formed at the mercury/solution interface by palmitic, oleic, and myristic acids, and by cetyl alcohol. Other recorded uses of the method include studies of the adsorption of valeric acid and other functional derivatives containing five carbon atoms[122] and of the adsorption of various polyelectrolytes, both dissociated and undissociated[123]. Differential capacity measurements enabled Melik-Gaikazyan[124] to demonstrate the formation of multimolecular layers on the surface of a mercury electrode exposed to solutions of n-octanol and n-hexanol. Multimolecular layer formation is accompanied by an even more striking drop in capacity (to as little as 0.9 $\mu F\ cm^{-2}$). Using differential capacity data, Laitinen and Moiser[125] calculated adsorption isotherms on mercury for thirty different organic compounds, and found that the adsorption could be described sufficiently accurately by a Langmuir equation. The adsorption on mercury of the surface-active tetra-alkylammonium cation was studied[126] by the differential capacity method. It was shown that bulky organic cations, such as $[(C_4H_9)_4N]^+$, behave like neutral surface-active molecules on the mercury surface. Thus, in spite of the electrostatic attractive forces, the tetrabutylammonium cation is desorbed from the mercury surface at sufficiently negative potentials, giving a characteristic peak on the differential capacity curve.

More recently, Breiter and Delahay[127] have compared data on the adsorption of n-amyl alcohol on mercury, calculated thermodynamically from electrocapillary curves, with others derived from measurements of double layer differential capacity using Eqn. (35). The good agreement of the two sets of results confirmed the essential correctness of Eqn. (35), which is now commonly used in studies of the adsorption of organic compounds by the differential capacity method.

In a number of cases the differential capacity curve takes an even more complicated form in the presence of organic surface-active molecules and ions. Thus, Loveland and Elving[128] observed four instead of two capacity peaks, due to desorption, in oscillographically displayed differential capacity curves measured in saturated n-heptyl and n-octyl alcohols. They ascribed the two outer peaks to complete desorption of alcohol molecules, and the two inner peaks to the formation (or disappearance) of a second layer of adsorbed molecules which constitutes a micellar film at low electrode charges. Even brief bubbling of an inert gas through the solution is sufficient to decrease the concentration of alcohol in the solution to the point where the differential capacity curve assumes the normal shape with two desorption peaks. Gupta also concluded[129] that condensed, micellar films can be formed, as a result of his "tensammetric" study of the adsorption of methyl orange on mercury. He found entirely similar capacity peaks, due to the formation and the disappearance of micellar films; he also found peaks of this type in the adsorption on mercury of long-chain alkyl sulphonate anions (12 or more carbon atoms)[130,131], and of sodium laurate and caprylate[132].

In the absence of complicating multilayers and micellar films of surface-active organic molecules or ions, differential capacity curves are satisfactorily accounted for by Frumkin's theory[118], at least where the adsorption of saturated aliphatic compounds is concerned. This theory has been extended by American workers[122] and used to establish the variation of differential capacity with polarisation and adsorption. Frumkin's theory[118] can also explain the S-shaped adsorption isotherms observed with strongly interacting surface-active molecules[133,134], and with large organic cations[135].

As shown by Gerovich *et al.*[136-138] and also by Blomgren and Bockris[139], the π-electrons present in aromatic and in certain cyclic and aliphatic unsaturated compounds causes these substances to be adsorbed on a positively charged mercury electrode surface. An increase in the positive charge of the surface does not induce desorption: the adsorption of organic molecules containing π-electrons cannot therefore be described as a function of the electrode potential by Frumkin's theory[118]. An attempt was recently made by Parsons[140] to develop a general thermodynamic theory of the structure of the electrical double layer in the presence of adsorbed organic molecules and ions, but no quantitative test could be made as the existing experimental data were inadequate.

Whilst inorganic ions are adsorbed on a mercury surface so rapidly that the time required to form the electrical double layer cannot be measured, even by the most recent methods[61,62], the situation is quite different in the presence of large organic molecules or ions. The kinetics of the adsorption of an organic substance on the mercury electrode surface may be followed by an a.c. method (Frumkin and Melik-Gaikazyan[141,142]). By studying the frequency-dependence of the differential capacity in the neighbourhood of the desorption peaks in solutions containing normal saturated alcohols, Melik-Gaikazyan was able to show, on the basis of Frumkin's theory, that the diffusion of alcohol molecules towards the mercury surface was the slow stage in the adsorption of these alcohols. Frumkin's theory[141] considers only two limiting cases: the rate of the process is determined either by the diffusion of the organic molecule towards the electrode surface or by the adsorption itself. Berzins and Delahay[143], at the cost of introducing some complication into the theory, produced a general solution of the problem, dealing with both the diffusion and the adsorption process at the same time. Their method enables rates of adsorption exchange of up to $\sim 10^{-5}$ mole cm^{-2} sec^{-1} to be measured, corresponding to a time of adsorption (or desorption) of 10^{-4} sec, depending on the high-frequency sensitivity of the impedance bridge used. Lorenz *et al.*[144,145] also contributed to this aspect of the problem. They studied the kinetics of adsorption of a number of organic compounds at the mercury electrode by high-frequency (25–100 kc/sec) differential capacity measurements, and showed that the adsorption time, though measurable, was small. Thus, a rate of adsorption exchange of the order of 10^{-4} mole cm^{-2} sec^{-1} was observed with n-butyl, iso-amyl, and benzyl alcohols, with phenol, methyl ethyl ketone, n-oleic acid, chloroform, and with a number of other organic compounds. Since the maximum extent of adsorption for these substances is (according to Lorenz) about 10^{-9} mole cm^{-2}, the time-constant is in every case $\leq 10^{-5}$ sec. On the other hand, the rate of double condensation which, according to Lorenz[133,134], takes place with organic molecules having sufficiently long carbon chains, is much less than the rate of adsorption. Thus, in the case of the higher fatty acids (C_6, C_8, and C_9) the time-constant for double condensation lies between 10^{-1} and 10^{-3} sec. However, if no double condensation is involved in the overall adsorption process, which includes the diffusion of organic molecules to the electrode surface, the diffusion stage becomes the slowest and determines the rate of the whole process. This is in accordance with Frumkin and Melik-Gaikazyan's conclusions[141,142]. In this connection, Delahay *et al.*[146-146] have made a detailed study of diffusion kinetics in specific systems which is applicable to the transfer of surface-active organic molecules from the bulk of the solution to the electrode surface during the establishment of adsorption equilibrium. Working on the linear portion of the Langmuir adsorption isotherm, *i.e.* near the origin, these authors concluded[146,147] that when the adsorbate is present at low concentrations a considerable time, of the order of minutes, elapses before adsorption equilibrium is established. One must therefore use a stationary rather than a dropping mercury electrode when studying the adsorption of organic substances. If the complete adsorption isotherm of Langmuir is considered (and this can only be done numerically, using a calculator) the time required for the attainment of adsorption equilibrium is found to be somewhat shorter[148], but nevertheless longer than the drop period of the conventional polarographs (3–5 sec). Frumkin and Damaskin's investigation[135] of the effect of the concentration of the $[(C_4H_9)_4N]^+$ cation on surface coverage, using the dropping mercury electrode, demonstrated that in the maximum adsorption region the number of adsorbed ions is determined almost exclusively by ionic diffusion to the mercury surface. This is in agreement with the conclusions of Delahay *et al.*[146-148].

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THE DISSOLUTION OF METALS IN FUSED HALIDES

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CONTENTS

I. INTRODUCTION

The dissolution of metals in fused salts is of exceptional importance for many electrometallurgical and thermal processes, such as the production of titanium, magnesium, aluminium, sodium, etc. The ability of metals to dissolve in a fused electrolyte is the most important cause of decrease in current efficiency and deterioration of performance in electrolysis. Moreover, the kinetics of metal thermite processes, such as the magnesium thermite preparation of titanium, also appear to be related to interaction of the metals in the salt phase. Finally, in recent years a successful start has been made in the application of a method of refining metals, based on the reaction of the latter with a fused salt. There are reports of the use of this method for the purification of nickel, and a similar method for refining aluminium has already found general acceptance. All this indicates the considerable practical importance of the question of metal dissolution.

The theoretical side of the question is of no less importance, however. The study of solutions of metals in fused salts yields important information on the nature of reaction in ionic media and on characteristic features of the liquid state. Solutions of metals provide a clear illustration of Mendeleev's well-known hypothesis regarding the chemical nature of solutions.

The dissolution of metals in fused salts was discovered in 1807 by Davy[1,2], who established that during the electrolysis of fused KOH, or when metallic potassium is fused with potassium hydroxide, the melt becomes coloured. Later an analogous phenomenon was observed when a number of other metals were fused with their salts, particularly in the Na + NaCl, K + KCl,[3-6] Rb + RbCl, Cs + CsCl,[7,8] Pb + $PbCl_2$,[9] and other systems[10,11]. It was established that lithium colours its salts black, lead brown, potassium violet, etc., and that all these colour changes are associated with dissolution of the metal in the fused salts. It was also shown that the solubility of metals in fused salts depends on the nature of the metal and salt, the composition of the metallic and salt phases, and the temperature[10]. When a melt containing dissolved metal is frozen, the metal is usually found as metallic particles of colloidal dimensions, and on this basis Lorenz[9] put forward the hypothesis that solutions of metals in fused salts are colloidal in character.

For a long time Lorenz's hypothesis had many supporters, so that in industry the terms "pyrosol" and "metal fog" are still used to describe solutions of metals. Later studies[10] showed, however, that solutions of metals in fused salts exhibit all the properties of true solutions and are moreover optically homogeneous[12-14], so that Lorenz's hypothesis should now be rejected. The appearance of colloidal metal particles when a melt freezes is probably due to displacement of the chemical equilibrium between metal and fused salt with decrease in temperature.

The established fact that true solutions are formed by metals in fused salts does not settle the question of the nature of these solutions. Three viewpoints exist.

1) It may be assumed that the metal dissolves in the salt in the form of atoms, which retain their individuality and are evenly distributed throughout the whole volume of the solution, for example, by introduction into vacancies in the quasi-crystalline structure of the liquid salt. The possibility of atomic dissolution of metals was first discussed by Hettich[15], and recently this hypothesis has been intensively developed by Cubicciotti and coworkers[16,17].

2) It may be assumed that the dissolution of metals in fused salts is due to chemical reaction between the electrolyte and the metal with the formation of ions of lower valency (sub-ions)[10,11,18]. In other words the dissolution of metals is assumed to involve equilibria of the type

$$Pb + Pb^{2+} \rightleftharpoons 2Pb^{+},$$
$$Hg + Hg^{2+} \rightleftharpoons Hg_2^{2+}\quad, \text{ etc.}$$

Although in some cases (Hg, Tl, Al) sub-ions are undoubtedly formed, in others, particularly that of the alkali metals, the possibility that ions of lower valency exist is not so obvious, and it is necessary to assume[15] that "atom-ion" complexes are formed, for example

$$Na + Na^{+} \rightleftharpoons (Na{-}Na^{+}).$$

The majority of sub-compounds, if they do exist in fused salts, cannot be isolated in the pure state at room temperature.

3) Finally, we may start from the similarity in many properties of fused salts and ionic crystals and consider solutions of metals in fused salts as structural units similar to colour centres (*F*-centres). In this case it would be correct to describe solutions of metals as ion-electronic liquids, whose possible formation was first pointed out by Ol'shanskii[19,20]. This viewpoint has not yet been developed as fully as it should.

II. SUB-COMPOUNDS

Since most workers at present tend to attribute the dissolution of metals in fused salts to the formation of sub-ions, we shall in this section examine data on the formation of ions and compounds of lower valency.

The valency shown by elements in their compounds is determined by their electronic structures; for example, for Na $1s^2 2s^2 2p^6 3s^1$, for Mg $1s^2 2s^2 2p^6 3s^2$, and for Al $1s^2 2s^2 2p^6 3s^2 3p^1$. In ionic compounds these elements normally lose electrons from the outer *M* level and acquire the neon structure $1s^2 2s^2 2p^6$, showing valencies of 1, 2, and 3 respectively. The situation is more complex for metals of the sub-groups, such as Hg ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2$), Tl ($\ldots 6s^2 6p^1$), Pb ($\ldots 6s^2 6p^2$), and Bi ($\ldots 6s^2 6p^3$). The maximum valency of these elements corresponds to the loss of electrons from the outer *s* and *p* levels, so that ions with an outer shell of 18 electrons are formed. These metals can, however, form ions of lower valency in addition to the compounds with the highest degree of oxidation. Thus mercury with the Hg^{2+} ion in aqueous solutions forms a singly-charged ion with one 6*s* electron in the outer shell. The equilibrium constants for the reaction $Hg^{2+} + Hg \rightleftharpoons Hg_2^{2+}$, together with X-ray diffraction data for compounds of monovalent mercury[21], show that in this case there is formed a dimer Hg_2^{2+}, in which the bond between the two mercury atoms is formed by a pair of *s* electrons. Thallium forms compounds in which it shows valencies of either +3 or +1*. In the latter case the thallium atom loses the 6*p* electron and retains the two 6*s* electrons in its outer shell. Lead and bismuth, in addition to Pb^{4+} and Bi^{5+} ions, form Pb^{2+} and Bi^{3+} ions, which are much more stable in aqueous solution and which also have two 6*s* electrons in the outer shell.

If the term "sub-compounds" is used to describe compounds of lower valencies of metals, the Hg_2^{2+}, Tl^{+}, Pb^{2+}, and Bi^{3+} ions are sub-ions of the corresponding elements. The fact that the electronic structure of these ions are identical and that intermediate oxidation states (Tl^{2+}, Pb^{3+}, etc.) do not exist, indicates that stable ions of lower valency exist as a result of coupling of two 6*s* electrons. This is shown particularly clearly in the case of mercury, where a pair of 6*s* electrons is coupled by dimerisation.

From this viewpoint the existence of Al^{+}, Cd_2^{2+}, Ca_2^{2+} ions, etc., is quite probable, and spectroscopic studies show that monovalent halides of aluminium, the alkaline-earth metals, zinc, cadmium, etc., exist in the vapour state at high temperatures[22]. The most stable of these compounds appear to be the aluminium sub halides[23,24]. Russell *et al.*[25,26] studied the equilibrium between $AlCl_3$ vapour and liquid aluminium,

$$AlCl_3 + 2Al \rightleftharpoons 3AlCl, \tag{a}$$

by a flow method involving the passage of a gaseous mixture of $AlCl_3$ and argon through molten aluminium with subsequent analysis of the gas composition. Analogous measurements were also made by Semenkovich[27,28], who determined the free energy of formation of aluminium sub-

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* The existence of divalent thallium and its analogues (Ga and In) has been reported. As will be shown later, this is unlikely, since such compounds are probably complexes containing Tl^{+} and Tl^{3+}.

chloride according to reaction (a):

$$\Delta G = 76780 - 52.75\,T \text{ kcal mole}^{-1}. \qquad (1)$$

Thus at ~1200° the subchloride predominates in the gas phase over aluminium ($\Delta G < 0$).

Gross *et al.*[29] showed that aluminium subchloride is formed when aluminium is heated in fused NaCl to 750°–1000°:

$$\mathrm{NaCl + Al \rightleftharpoons AlCl + Na}. \qquad \text{(b)}$$

The enthalpy of formation of AlCl at 298°K, calculated from experimental data, was given as 16.0 kcal mole^{-1} by Semenkovich[28] and as 17.0 kcal mole^{-1} by Weiss[30]. The entropy of formation of AlCl is +54.1 cal mole^{-1} deg^{-1}.

A phenomenon which has for long been known in electrochemistry is the negative difference-effect[31], that is, the liberation of hydrogen at the anode during the anodic dissolution of a number of metals in aqueous solutions. This phenomenon was first discovered by Beetz[32] for magnesium anodes and by Wohler and Buff for aluminium anodes[33]. Beetz established that the magnesium anode becomes covered by a black film which is decomposed by water with the evolution of hydrogen, and he suggested that the film contains magnesium suboxide Mg_2O. Later, Baborovsky[34] confirmed the evolution of hydrogen from a magnesium anode and established that the anodic current efficiency of the magnesium amounts to ~150% and depends only to a slight extent on the composition and concentration of the solution, the current density, or the temperature.

By studying the anodic current efficiency during the dissolution of metals in aqueous solutions, it is possible to determine the apparent valency $\tilde{n}$ of the metal dissolving. Recent studies[35-39] have shown that for many metals the values are unusually low and may even be non integral (Table 1), indicating that the difference-effect is not such a rare phenomenon.

The mechanism of the negative difference-effect has not yet been finally established, and different workers give different explanations. This phenomenon has perhaps been best studied for the case of magnesium, so that we shall examine the data for this metal in more detail*.

Bodfross[40,41] established that the potential of a magnesium electrode is independent of the Mg^{2+} ion concentration in the solution but changes considerably with change in the acidity of the solution. With mechanical displacement of the electrode its potential is shifted to more negative values. Bodfross related these properties of the magnesium electrode to the potential-determining reactions

$$\mathrm{Mg \rightleftharpoons Mg^{+} + \varepsilon},$$
$$\mathrm{Mg^{+} + H^{+} \longrightarrow Mg^{2+} + {}^{1}/_{2}H_2}.$$

TABLE 1. Apparent valency during the anodic dissolution of metals in aqueous solutions[38].

M	Be	Al	Mg	Zn	Ti	Ga	U	In	Mn	Hg
Normal valency	2	3	2	2	3	3	4	3	3	2
$\tilde{n}$	1	1.3	1.2	1.4	1.5	1	1.4	1	1.7	1

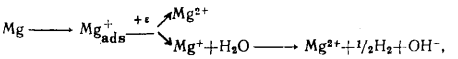
Faivre and Michel[42] and Brouchere[43] showed by X-ray structure analysis that the dark-grey film formed on a magnesium anode during dissolution is magnesium oxide containing excess Mg atoms in the lattice.

Petti *et al.*[37] and Kokoulina and Kabanov[44,45] studied the apparent valency of magnesium during its anodic dissolution and established that the values of $\tilde{n}$ are independent of the current density and concentration of the solution, but are determined by the potential of the anode (Table 2).

TABLE 2. Dependence of $\tilde{n}$ on the nature of the solution and on the anode potential[44,45].

Solution	Concentration, N	i_a, mA cm^{-2}	φ, V	$\tilde{n}$
$MgCl_2$	0.1—4.0	150	—1.7	1.26
$MgBr_2$	0.1—1.0	100	—1.62	1.30
$MgSO_4$	0.01—1.0	100	—1.55	1.35
$MgSO_4$+ +K_2CrO_4	1.0 0.05	100	—1.5	1.30
$KClO_3$	1.5	6.4	—1.3	1.64

Kokoulina and Kabanov explained the dependence of the apparent valency of the dissolving magnesium on the potential by assuming that the anodic process takes place according to the scheme



$$\mathrm{Mg \longrightarrow Mg^{+}_{ads} \xrightarrow{+\varepsilon} Mg^{2+}}$$
$$\mathrm{Mg^{+}_{ads} \longrightarrow Mg^{+} + H_2O \longrightarrow Mg^{2+} + {}^{1}/_{2}H_2 + OH^{-}},$$

in which the slowest stage is the oxidation of Mg to Mg^{+}. They showed that in this case the apparent valency is given by the equation

$$\tilde{n} = \frac{1 + 2k\,(\exp \beta\varphi F/RT)}{1 + k\,(\exp \beta\varphi F/RT)}, \qquad (2)$$

which shows qualitative agreement with experiment.

Other authors[46-48] reached an analogous conclusion, and it has been suggested that monovalent magnesium is formed as Mg_2^{2+}, although no experimental data in support of this were given.

Other data indicate the possible formation of extremely unstable compounds of monovalent magnesium. Thus McEwen *et al.*[49] showed that during the electrolysis of solutions containing various organic compounds with magnesium electrodes, reduction processes take place in the anolyte. For example, dimethylbenzophenone and azoxybenzene are reduced to tetra-*p*-tolylethylene and azobenzene respectively. This phenomenon is also attributed to the formation of Mg^{+} ions with strong reducing properties. Runge[50] pointed out that the formation of subhalides explains the reduction of many organic compounds by a mixture of Mg + MgI_2 (2MgI) and organomagnesium compounds RMgX, which apparently dissociate according to the scheme

$$\mathrm{RMgX \rightleftharpoons R + MgX},$$

where X is a halogen atom and R an organic radical.

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* Work on aluminium has been reviewed by Belyaev and Firsanova[24].

Some idea of the stability of the subhalides of different metals can be obtained by calculating their heats of formation from the elements, and this has been done by Grimm and Herzfeld[51], Belozerskii[10], and Irmann[52]. Thus the formation of aluminium monochloride

$$\mathrm{Al(solid)} + \tfrac{1}{2}\mathrm{Cl_2(gas)} = \mathrm{AlCl(solid)}$$

can be broken down into the following stages: (1) dissociation of the gaseous chlorine molecules to atoms (heat of dissolution $\frac{1}{2}D$); (2) sublimation of solid aluminium (heat of sublimation σ); (3) ionisation of aluminium atoms (ionisation potential I); (4) attachment of electrons to gaseous chlorine atoms (electron affinity E); and (5) formation of the AlCl crystal lattice from the ions (lattice energy of the subchloride U); the heat of formation of the subchloride is then

$$W = U + E - I - {}^1/_2D - \sigma. \tag{3}$$

Values of the heats of stages 1–4 are known. The greatest difficulty is encountered in the determination of the lattice energy of the subchloride. Earlier, this involved not only the use of extremely approximate relationships but also the tacit assumption that laws derived for purely ionic lattices were applicable to sub-compounds. It is, however, possible to determine the lattice energy of a subhalide with sufficient accuracy using the equation put forward by Yatsimirskii[53] for the energy of a lattice in which the bonds have a high degree of covalent character:

$$U - U_0 + 250\,\{0.5 + 2\cdot 10^3(I - E - U_0)\}, \tag{4}$$

where U_0 is the lattice energy of the corresponding compound, calculated from Kapustinskii's equation

$$U_0 = \frac{574.4}{r_C + r_A}\left(1 - \frac{0.345}{r_C + r_A}\right), \tag{5}$$

where r_C and r_A are radii of cation and anion.

In calculations with formula (4) it is necessary to know the radii of the sub-ions. These may be found on the assumption that the radius of a sub-ion is equal to the radius of the atom with the same electronic structure. This is confirmed for the case of the Tl^+ ion (1.49 Å), whose radius is equal to that of the isoelectronic mercury atom Hg (1.50 Å).

The data for calculating the heats of formation of subhalides are given in Table 3. The values of I and σ are taken from Mishchenko and Ravdel'[54] and of E and D from Latimer[55]. The values obtained for the lattice energies and heats of formation of the subhalides are given in Table 4, which also gives for comparison the heats of formation of the normal halides of the corresponding metals (W^*). The reliability of these results is confirmed by comparison of the calculated data in Tables 4 with the experimental values of the heats of formation[28,29,55]:

	TlCl	TlBr	TlI	InCl	AlCl
W_{exp}, kcal mole^{-1}	48.99	41.2	29.7	44.5	16.0–17.0

in which the discrepancy does not exceed 10%.

Comparison of the values of W and W^* in Table 4 shows that in most cases the subhalides cannot be stable at room temperature and should decompose into the corresponding metal and normal salt, the only exceptions being the subhalides of Tl, In, and Ga. With increase in temperature, however, the stability of the subhalides can apparently increase, as in the case of aluminium subchloride[28].

TABLE 3. Thermochemical characteristics of ions, kcal mole^{-1}.

Ion	I	σ	r, Å	Ion	I	σ	r, Å	Ion	E	$^1/_2D$	r, Å
Mg^+	177.7	35.9	1.91	Zn^+	216.0	31.0	1.27	F^-	93.5	32.2	1.33
Ca^+	142.2	46.0	2.36	Cd^+	206.0	27.0	1.44	Cl^-	88.2	28.9	1.81
Sr^+	132.8	39.2	2.53	In^+	134.8	58.2	1.49	Br^-	81.6	26.9	1.96
Ba^+	121.6	42.0	2.74	Ga^+	139.8	66.0	1.33	I^-	74.6	25.4	2.20
Tl^+	142.3	44.5	1.49	Sn^+	140.6	72.0	1.62				
Al^+	139.5	75.0	1.60	Pb^+	172.5	46.3	1.70				
Hg^+	242.6	14.5	1.44	Sb^+	200.7	60.8	1.40				
Bi^+	169.4	49.7	1.75								

TABLE 4. Lattice energies and heats of formation of subhalides and normal salts (198° K).

Subhalide	U, kcal mole^{-1}	W, kcal mole^{-1}	Halide	W^*, kcal mole^{-1}	Subhalide	U, kcal mole^{-1}	W, kcal mole^{-1}	Halide	W^*, kcal mole^{-1}
MgF	189.4	37.1	MgF_2	263.5	AlF	187.7	34.5	AlF_3	311.0
MgCl	179.3	25.0	$MgCl_2$	153.4	AlCl	173.8	18.6	$AlCl_3$	166.2
MgBr	179.8	21.6	$MgBr_2$	123.7	AlBr	170.2	10.4	$AlBr_3$	125.8
MgI	178.6	14.2	MgI_2	86.0	AlI	168.8	3.0	AlI_3	75.2
CaF	168.2	41.0	CaF_2	290.3	TlF	193.3	67.8	TlF_3	—
CaCl	157.9	29.0	$CaCl_2$	190.0	TlCl	177.5	50.0	$TlCl_3$	—
CaBr	157.9	24.4	$CaBr_2$	161.3	TlBr	175.5	43.4	$TlBr_3$	—
CaI	156.7	17.7	CaI_2	127.8	TlI	171.5	33.9	TlI_3	—
SrF	159.1	48.4	SrF_2	290.3	ZnCl	210.7	23.0	$ZnCl_2$	99.4
SrCl	151.8	39.1	$SrCl_2$	198.0	CdCl	202.1	28.4	$CdCl_2$	93.0
SrBr	151.7	34,4	$SrBr_2$	171.1	InCl	175.5	41.8	$InCl_3$	128.4
SrI	153.7	30.9	SrI_2	135.5	GaCl	181.9	35.4	$GaCl_3$	125.4
BaF	151.4	49,1	BaF_2	286.9	SnCl	173.8	20.5	$SnCl_2$	83.6
BaCl	144.5	40.2	$BaCl_2$	205.6	PbCl	182.4	22.9	$PbCl_2$	85.8
BaBr	144.6	35.7	$BaBr_2$	180.4	SbCl	200.9	–1.3	$SbCl_3$	91.6
BaI	144.0	29.6	BaI_2	144.0	BiCl	180.1	20.3	$BiCl_3$	90.8

The experimental detection of subhalides has also been reported. Thus Borchers[56] reports the formation of the salts CaCl, SrCl, and BaCl; and Frary and Berman[57] and Ravier[58], in a study of the composition of the violet cathodic deposit formed during the electrolysis of fused magnesium chloride, concluded that it consisted of Mg_2O and MgCl. Guntz and Benoit[18] reported the preparation of strontium, barium, and calcium subhalides and gave the following data for the heats of reaction at room temperature:

$$\mathrm{Ca + CaCl_2 \longrightarrow 2CaCl} \qquad Q = 2.7\ \mathrm{kcal},$$
$$\mathrm{Sr + SrCl_2 \longrightarrow 2SrCl} \qquad Q = 14.6\ \mathrm{kcal},$$
$$\mathrm{Ba + BaCl_2 \longrightarrow 2BaCl} \qquad Q = 16.5\ \mathrm{kcal},$$

but these results differ considerably from those obtained by the above calculations.

There are also reports[59] of the isolation of almost pure bismuth subchloride, which can be kept *in vacuo* at 180° for a prolonged period but which decomposes rapidly in air or on cooling.

Many authors have noted the marked influence of temperature on the stability of subhalides. Thus Guntz[60] states that lithium subchloride is stable in the narrow temperature range 500°–700°. According to Wöhler and Rodewald[61], calcium subchloride is stable above 800°, while silver subfluoride Ag_2F decomposes above 90°.

Analysis of the available experimental material on the existence of sub-compounds shows that much of it is unreliable. The calculated values of the heats of formation, however, cannot form the basis for a complete rejection of the possible formation of sub-compounds. In the case of mercury, for example, calculation of the heats of formation of the subhalides gives the values

$$\begin{array}{lccc} & \mathrm{HgCl} & \mathrm{HgBr} & \mathrm{HgI} \\ W = & 30 & 25 & 15\ \mathrm{kcal\,mole^{-1}}, \end{array}$$

whereas the actual values of the heats of formation of Hg_2Cl_2, Hg_2Br_2, and Hg_2I_2 are double these (kcal mole^{-1}): 63.3, 49.4, and 28.9, due to dimerisation of the monovalent ions. This dimerisation is not exceptional. As is shown below, analogous dimers appear to be formed by bismuth (Bi_2^{2+}), cadmium (Cd_2^{2+}), and possibly the alkaline-earth metals (Ca_2^{2+}. etc.).

III. COLOUR CENTRES IN IONIC CRYSTALS

Most solid salts, and in particular almost all halides, exhibit a slight ionic conductivity due to the presence of lattice defects. As early as 1903, however, Ioffe[62] discovered that, when irradiated with X-rays, crystals of sodium chloride become coloured and acquire the property of photoconductivity. This phenomenon was later studied in detail by Roentgen and Ioffe[63], Tartakovskii[64], and others[65,66]. It was established that the production of colour under the influence of X-rays is shown not only by crystals of all alkali-metal halides[67], but also by the halides of the alkaline-earth metals (CaF_2,[68,69] SrF_2, $SrCl_2$, and BaF_2 [70,71]) and transition metals (CdF_2 [72]).

This phenomenon has now been studied in considerable detail and a large quantity of experimental data and theoretical work on the nature of colour production in crystals has been reviewed in detail by Seitz[73,74], Pohl[75], and Saint-James[76]. Since this work has been published chiefly in specialised physical literature, we shall give the chief results below.

The cause of the production of colour in crystals is the appearance of electrons in the conduction band, as a result of which a new light-absorption band is produced and the crystal acquires colour. Under certain conditions this colour may be retained for several years.

Experiment shows that colour can be produced in crystals by various methods, which can be conveniently divided into two groups[66]: (A) irradiation of the crystal with X-rays or with beams of electrons or neutrons; this is accompanied by excitation of electrons and their transfer to the conduction band; (B) introduction into the crystal of excess metal atoms, by heating the salt in metal vapour or by passing direct current through the crystal. In the former case the metal atoms absorbed by the crystal are ionised and the electrons enter the conduction band. In the latter case the electrons enter the crystal from the metal cathode, which is usually sharply pointed.

The production of colour in crystals takes place fairly rapidly at elevated temperatures. The rate of production of colour and its intensity increase exponentially with temperature [proportional to $\exp(-\frac{\mathrm{const.}}{T})$]. At low temperatures the coloured crystals are dielectrics, but on heating or illumination they acquire considerable electronic conductivity. The electrical conductivity of coloured crystals also increases exponentially with temperature. If a direct current is passed through a heated coloured crystal, the colour front moves to the anode and disappears there, and both the conductivity of the crystal and the current at constant voltage decrease.

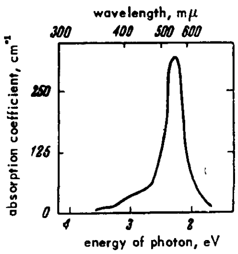

Fig. 1. *F*-absorption band for a KCl crystal; concentration of colour centres 1.15×10^{18} cm^{-3}; $K_{\max}$ = = 310 cm^{-1}.

TABLE 5. Position of absorption band maxima for alkali-metal halide crystals.

Crystal	Maximum of *F*-band	Crystal	Maximum of *F*-band	Crystal	Maximum of *F*-band
LiF	257	NaF	340	KF	455
LiCl	395	NaCl	470	KCl	556
LiBr	452	NaBr	500	KBr	630
LiI	531	NaI	609	KI	720

The colour of the crystal and the appearance of the new absorption band, and also the electronic conductivity, which increases with increase in temperature, result from the localisation, in energy levels lying below the conduction band, of the electrons introduced into the crystal by one of the above methods. These local electronic states are usually called *F*-centres or colour centres. Their properties are independent of the means by which the crystals are coloured. An absorption band for a coloured KCl crystal is shown in Fig. 1. The maximum at 556 mμ corresponds to the absorption by the *F*-centres. The position of the maximum depends on the nature of the salt. Table 5 gives the positions of the *F*-absorption band maxima for alkali-metal halide crystals[76]. The position of the maximum of the *F*-absorption band is independent of the nature of the alkali metal in whose vapour the crystal is heated.

If the crystal is coloured by irradiation, holes, that is, vacant levels from which electrons have moved, are produced, and electrons are promoted to the conduction band. With the passage of time, the excited electrons recombine with the holes, that is, they return to the ground state and the crystal loses its colour. The decolorisation of the crystal is accelerated considerably when the crystal is heated or illuminated. If the crystal is coloured by the introduction of electrons from outside (by heating in metal vapour or by electrolysis), the colour is extremely stable, since recombination in this case is impossible. These crystals can be decolorised either by heating in vacuum, causing the alkali metal to volatilise from the crystal, or by heating followed by slow cooling, which leads to coagulation of the alkali metal. In the latter case the F-absorption band disappears and the colour of the crystal changes to that due to the colloidal metal.

The concentration of colour centres varies with the method by which the colour is produced. Under certain conditions it may reach 10^{19}–10^{20} centres/cm^3, which corresponds to an excess metal atom concentration of 0.1–1.0 at.%. Particularly high concentrations of F-centres are attained by introducing electrons from outside. Buckel and Hirsch[77] raised the concentration of alkali metal in the crystal (KCl, NaCl, KBr) to 10 at.%. The concentration of F-centres, however, was not more than 1.1%, the rest of the metal being present in the colloidal state.

The properties of F-centres are readily explained[65,66] if it is assumed that they are electrons which have replaced halide ions at the crystal lattice sites. This localisation of current carriers takes place not only in purely ionic crystals, but also in typical semiconductors. There is no essential difference between an NaCl crystal heated in sodium vapour and containing excess Na^+ ions and F-centres, and a crystal of cuprous oxide heated in oxygen and containing excess O^{2-} ions and conductivity holes. The only difference is that the absorption band for the cuprous oxide lies in the infra-red and not in the visible region of the spectrum, and its formation does not change the colour of the crystal.

The conditions for equilibrium between a crystal and metal vapour were examined by Mott and Gurney [65]. By calculating the free energy change for the removal of one metal atom from the vapour (ΔF_v) and for the introduction of one atom of metal into the crystal (ΔF_c) and equating the two, they obtained an approximate equation for calculating the equilibrium concentration of F-centres in unit volume (n_F):

$$n_F = n_M \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{-W_F/kT}, \tag{6}$$

where n_M is the concentration of metal atoms in the vapour, m the mass of a metal atom, h and k are Planck's and Boltzmann's constants, and W_F is the work done in introducing one metal atom into the crystal, that is the work of formation of an F-centre.

This relationship has been confirmed experimentally. From experimental data, Pohl[67] calculated W_F for different crystals and obtained the values -0.10 eV (-2.3 kcal) for KCl and -0.25 eV (-5.4 kcal) for KBr. Thus the dissolution of a metal atom in a halide crystal is accompanied by a gain of energy.

The mechanism of formation of F-centres when crystals are heated in the vapour of the corresponding metals was explained by Mott and Gurney as follows. One of the metal atoms is adsorbed on the surface of the crystal, and after a time interval this atom loses its electron, which enters the conduction band and begins to drift into the interior of the crystal. At the same time one of the negative ions is successively displaced from the internal layers of the crystal to the surface and occupies a position next to the positive ion. The anionic vacancy thus produced captures the electron and forms an F-centre. The localised electron can be regarded as being shared by six positive ions (in the NaCl lattice). On heating, the localised electrons are lifted from their positions (dissociation of the F-centres) and give the crystal electronic conductivity.

An important property of F-centres is that if an alkali metal is dissolved in any fused alkali-metal halide and the melt is cooled, typical F-absorption bands, characteristic of the given salt, are formed on freezing. This means that the F-centres can exist only in the presence of standard lattice defects, which do not occur in the liquid salt.

It is also apparent, however, that there is a direct link between the F-centres and the metal dissolved in the salt. We shall examine this question in more detail below, in discussing the absorption spectra of solutions of metals in fused salts.

IV. SOLUBILITY OF METALS IN PURE SALTS

It is convenient to examine the solubility of metals in fused salts with reference to their position in the Periodic Table.

(a) The solubility of alkali metals. The dissolution of alkali metals in fused halides has been studied by a number of workers. Lorenz and Winzer[78] found that the solubility of sodium in fused NaCl increases from 10 mole % to 15 mole % when the temperature increases from 810° to 850°. Similar results were obtained by Belozerskii[10,11], who found that the solubility of potassium in potassium chloride is ~8 mole % at 800°.

The most complete study of the solubility of alkali metals in fused halides was made by Bredig *et al.*[79–82], who recorded the fusion diagrams for the Na–NaX, K–KX, and Cs–CsX systems (where X = F, Cl, Br, or I). Some of these are given in Fig. 2, which shows horizontal lines corresponding to monotectic reactions and indicates complete miscibility of metal and salt above certain limiting temperatures, given in Table 6, which also gives the temperatures of the monotectic reactions. In general the limiting temperature decreases for a given metal in the halide series

$$MF > MCl > MBr > MI.$$

The monotectic temperature changes in the same direction. The solubility increases on going from sodium to caesium, and caesium is completely miscible with liquid sodium fluoride in all proportions.

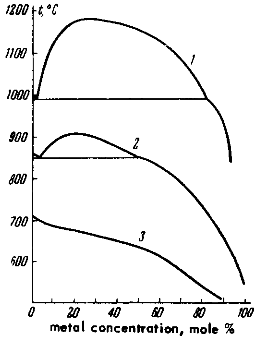

Fig. 2. Fusion diagrams for the systems: 1) Na–NaF; 2) K–KF; 3) Cs–CsF.

TABLE 6. Limiting temperatures ($t_{\lim}$) for the existence of two liquid phases and monotectic temperatures for the K–KX and Na–NaX systems[69, 70].

System	$t_{\lim}$, °C	Monotectic temp., °C
Na — NaF	1180	990
Na — NaCl	1080	795
Na — NaBr	1026	740
Na — NaI	1033	657
K — KF	904	849
K — KCl	790	752
K — KBr	728	708
K — KI	717	658

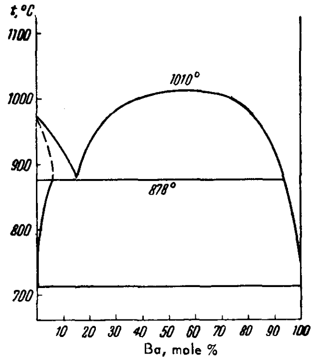

Fig. 3. Fusion diagram for the Ba–BaCl$_2$ system.

TABLE 7. Solubility of the alkaline-earth metals in fused halides.

Metal	Salt	t, °C	Solubility, at.%	
			Cubicciotti's data	Guntz and Benoit's data
Mg	MgCl$_2$	720	—	0.55**
		800	0.92*	0.82**
		900	1.20*	1.28**
	MgI$_2$	900	1.25*	
		1000	1.31*	
Ca	CaCl$_2$	900	16	—
		1000	13	5.7
	CaI$_2$	1000	—	9.6
Sr	SrF$_2$	1000	—	20.0
	SrCl$_2$	1000	—	24.6
	SrBr$_2$	900	21	—
		1000	22	35
	SrI$_2$	900	27	—
		1000	35	40
Ba	BaF$_2$	1050	—	22
	BaCl$_2$	900	30	—
		1000	28	—
		1050	—	28
	BaBr$_2$	900	18	—
		1000	22	—
		1050	—	37
	BaI$_2$	1050	—	39

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* Zhurin's data[83, 84].

** Bukun and Ukshe's data[85].

(b) **The solubility of the alkaline-earth metals.** The dissolution of the alkaline-earth metals in fused halides has been studied by Wöhler and Rodewald[61], Guntz and Benoit[18], Zhurin[83,84], and others[85]. Recently, Cubicciotti *et al.*[16,86,87] studied the fusion diagrams for the alkaline-earth metal–halide systems Ba–BaCl$_2$, Ba–BaBr$_2$, Sr–SrCl$_2$, Sr–SrI$_2$, and Ca–CaCl$_2$. In this work it was noted that at certain concentrations, solutions of salt in metal and of metal in salt form two immiscible layers. The solid formed when the salt-rich phase freezes, reacts violently with water evolving hydrogen. Complete mutual solubility of the metal and salt was not observed even at high temperatures (1100°), in contrast to the case of the alkali metals. Later, however, Schäfer and Niklas[88] showed that Cubicciotti's studies were inexact, and that in the Ba–BaCl$_2$ system, for example, complete mutual solubility can be attained at 1010°. The corresponding fusion diagram (Fig. 3) is very similar to those of the alkali metal–halide systems.

Table 7, which is compiled from various sources, gives values for the solubility of the alkaline-earth metals in the fused halides, and shows that these solubilities can be measured only approximately. Some conclusions can, however, be reached. Thus it is undoubtedly true that the solubility of the alkaline-earth metals increases in the series

$$\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$$

and decreases in the series

$$\text{iodide} > \text{bromide} > \text{chloride} > \text{fluoride},$$

in agreement with the corresponding data for the alkali metals.

(c) **The solubility of heavy metals.** Data on the solubility of metals in fused halides have been published. The solubilities of lead[89-91], cadmium[90,92-96], bismuth[88,97-100], cerium[101-103], and others have been studied in detail, and for many of these the fusion diagrams of the metal–salt systems have been obtained (Figs. 4 and 5). Collected solubility data are given in Table 8.

In most cases, increase in temperature is accompanied by an increase in the solubility of the metal in the fused salt. Corbett, von Winbush, and Albers[96] showed that for systems with a solubility < 2%, the logarithm of the solubility is a linear function of $1/T$.[83,84]

The Bi–BiCl$_3$ system is a special case, since Bi and BiCl$_3$ show complete mutual solubility above 780°.[104] The solubility of Bi in BiCl$_3$ increases with increase in temperature from 200° to 320°, then decreases with further

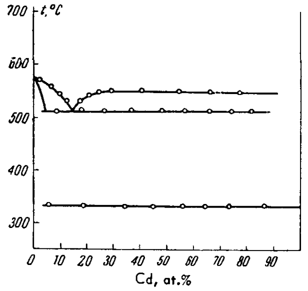

Fig. 4. Fusion diagram for the Cd–CdCl$_2$ system.

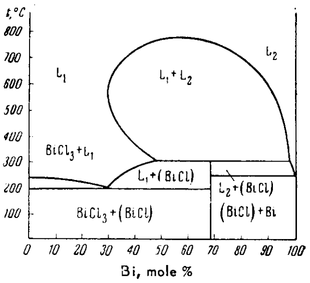

Fig. 5. Fusion diagram for the Bi–BiCl$_3$ system.

TABLE 8. Solubility of heavy metals in fused halides.

Metal	Salt	t, °C	Solubility, at.%	References
Zn	$ZnCl_2$	500 600 700	0.182 0.61 1.64	95
	ZnI_2	500 600 670	0.28 0.87 1.65	95
Cd	$CdCl_2$	530 600 690	12.5 16.0 15.6	92, 93, 105
	$CdBr_2$	600	14.0	92
	CdI_2	410 610	0.63 1.5 5.7	95 92
Hg	$HgCl_2$ HgI_2	500 500	50 25	92 92
Ga	$GaCl_3$ $GaBr_3$ GaI_3	230	2 9 40	95
In	InX_3	230	50	95
Tl	TlX_3	230	50	95
Sn	$SnCl_2$ $SnBr_2$	500 500	0.003 0.009	95 95
Pb	$PbCl_2$	500 700	0.060 0.056	95 106
	PbI_2	500 600 700	0.05 0.15 0.41	92 95 94
Sb	$SbCl_3$ SbI_3	273 300 400	0.018 3.5 5.8	95
Ce	$CeCl_3$	800	9.5	103
Bi	$BiCl_3$ $BiBr_3$	270 270	33 40	104 95

increase in temperature to 550°, and increases again above 550°.

For a series of metals in the same Group of the Periodic System at constant temperature, the solubility (Table 8) increases with increase in the atomic weight of the metal, that is for a given halide the solubility increases in the series

$$\text{Zn} < \text{Cd} < \text{Hg}$$
$$\text{Ga} < \text{In, Tl}$$
$$\text{Sn} < \text{Pb}$$
$$\text{Sb} < \text{Bi},$$

in agreement with the analogous relationships for the alkali and alkaline-earth metals.

For metals of the Third, Fourth, and Fifth Groups, changing the anion increases the solubility in the series

chloride < bromide < iodide,

in agreement with the corresponding change for the alkali and alkaline-earth metals. The same order is observed for zinc solutions, but in the case of cadmium the reverse order is shown and the solubility increases from the iodide to the chloride.

Corbett, von Winbush, and Albers[95] noted that the standard free energy changes for the disproportionation of solid mercurous halides are 8.0 kcal mole^{-1}, 6.6 kcal mole^{-1}, and 2.5 kcal mole^{-1} for the chloride, bromide, and iodide respectively, indicating that the order of stability of the mercury sub-compounds is similar to the order of solubilities for cadmium. A characteristic feature is that although the stability of the halide complexes of most metals in aqueous solution decreases from the fluoride to the iodide, the reverse order is shown by complexes of cadmium and mercury[107]. This is attributed to the tendency of mercury and cadmium to form covalent donor π-bonds whose strength increases in the series chloride < bromide < iodide. In this case we can assume that both the solubility and the stability of the sub-compounds should decrease with increase in the stability of the bond between the "normal" cation and the anion.

Data on the dissolution of a number of other heavy metals have recently been published. Cubicciotti and Johnson[108,109] reported the high solubility (up to 7.5 at.%) of nickel in nickel chloride. Corbett *et al.*[94,110-113] studied the fusion diagrams of gallium halides and established the existence of the compounds GaX, GaX_2, and GaX_3. A mixture of gallium iodides was formed when gallium was heated with elementary iodine to 350°–500°. On fusion the gallium di-iodide (m.p. 211°), disproportionated to GaI and GaI_3.

Clark, Griswold, and Kleinberg[114] obtained the InCl–$InCl_3$ phase diagram and noted the formation of a congruently melting compound, In_2Cl_3, which they assumed to be the complex salt $In_3^{(I)}[In^{(III)}Cl_6]$.

Corbett[113,115] also studied the Pr–$PrCl_3$, Nd–$NdCl_3$, and Nd–NdI_3 equilibria. The fusion diagrams indicate that the compounds $PrCl_{2.34}$ (978°), $NdCl_2$ (950°), NdI_2 (970°) and the compound $NdCl_{2.3}$, melting incongruently at 700°, are formed in these systems. Their structures are not yet clear.

V. INFLUENCE OF FOREIGN CATIONS ON THE SOLUBILITY OF METALS

In this section we shall examine the influence of foreign cations of less noble metals on the solubility. Only a few data are available.

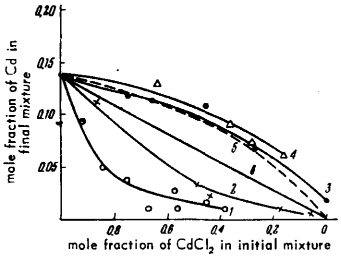

Fig. 6. Solubility of cadmium in binary salt systems: 1) $CdCl_2$–KCl; 2) $CdCl_2$–$CaCl_2$; 3) $CdCl_2$–$MgCl_2$; 4) $CdCl_2$–$CeCl_3$; 5) calculated curve for a regular solution; 6) calculated curve for an ideal solution.

TABLE 9. Polarising power of cations (P)*

M^{n+}	R, Å	$P=\frac{z}{R^2}$
Cd^{2+}	1.03	(1.90)
K^+	1.33	0.56
Ca^{2+}	1.06	1.76
Mg^{2+}	0.78	3.28
Ce^{3+}	1.01	(2.94)

Cubicciotti[17] studied the dissolution of cadmium in binary salt melts containing KCl, $CaCl_2$, $MgCl_2$, and $CeCl_3$, all of which decrease the solubility of cadmium, the efficiency of the additives decreasing in the series (Fig. 6)

$$KCl > CaCl_2 > MgCl_2,\ CeCl_3.$$

The influence of a foreign cation on the solubility of cadmium in cadmium chloride depends on its polarising power (Table 9). The K^+ and Ca^{2+} ions, whose polarising powers are much less than that of Cd^{2+}, decrease the solubility to a much greater extent than might be expected if the effect of the foreign salt were merely simple dilution of the salt phase in accordance with the law of mass action (curve *6* in Fig. 6). The reverse is true of Mg^{2+} and Ce^{3+}, which have a greater polarising power than Cd^{2+}.

Since the polarising power characterises quantitatively the interaction between the cations and anions in the salt, the observed relationship indicates a direct link between this interaction and the solubility. The "stronger" Mg^{2+} and Ce^{3+} cations decrease the energy of the Cd^{2+}–Cl^- bond and thus increase the solubility of cadmium compared with that in an ideal ionic solution, whereas the "weaker" cations, by increasing the energy of the Cd^{2+}–Cl^- bond, decrease the solubility.

These ideas lead to the suggestion that the solubility of cadmium should be proportional to the activity of $CdCl_2$ in the salt phase. This can be verified if the $CdCl_2$ solutions are regular. Denoting the solubility of cadmium by s and the cadmium chloride concentration by x_1, we obtain by the law of mass action

$$K=\frac{s\gamma_s}{x_1\gamma_1},\tag{7}$$

where γ_s and γ_1 are the corresponding activity coefficients. Assuming γ_s = const. and, in accordance with the theory of regular ionic solutions[116],

$$\log\gamma_1=A(1-x_1)^2,\tag{8}$$

we find

$$\log\frac{s}{x_1}=\log\frac{k}{\gamma_s}+A(1-x_1)^2,\tag{9}$$

where A is a constant. The broken line in Fig. 6 gives the solubility curve for Cd in $CdCl_2$–$MgCl_2$ with appropriate choice of the constants k/γ_s and A, and shows that satisfactory agreement with experiment can be obtained. Analogous results can also be obtained for the $CdCl_2$–$CeCl_3$ system, but for $CdCl_2$–KCl and $CdCl_2$–$CaCl_2$ mixtures this relationship is not confirmed, probably because these solutions are not regular. The results obtained by Cubicciotti[17] were explained in terms of his own theory, which does not, however, agree with a number of facts, particularly the difference in the influence of $CaCl_2$ and $MgCl_2$ on the solubility of cadmium.

Analogous results were obtained[86] in a study of the solubility of Bi in $BiCl_3$–NaCl and $BiCl_3$–$CaCl_2$ mixtures. The Na^+ cation, which has a lower polarising power, decreased the solubility of bismuth to a greater extent than the Ca^{2+} cation.

The influence of foreign cations on the solubility of magnesium in a chloride melt was studied by Zhurin[83,84] and in more detail by Bukun and Ukshe[85], who showed that at a given magnesium chloride concentration the solubility decreases with decrease in the polarising power of the foreign cation (Table 10).

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* The polarising power of Cd^{2+} and Ce^{3+}, generally speaking, is greater than z/R^2, since these ions do not have the electronic structure of an inert gas.

The influence of cations of metals more noble than the metal dissolving is complicated by equilibria of the type $Mg + PbCl_2 \rightleftharpoons MgCl_2 + Pb$, which are outside the scope of the present article. It is nevertheless of interest to examine how the solubility is affected by dilution of the metallic phase by a more noble metal. Heymann *et al.*[116-119] showed that for the Cd–Bi–$CdCl_2$ system the solubility is proportional to the concentration of dissolving metal in the alloy:

$$s = k_0 x_M \tag{10}$$

Similar results were obtained by Zhurin[84] for the Mg–Al–$MgCl_2$ system (Table 11). A deviation from Eqn. (10) was observed[105] for Na–Pb(Cd) alloys, and the authors attributed this to the non-ideal nature of the metal solutions.

VI. CRYOSCOPIC STUDIES OF SOLUTIONS OF METALS IN FUSED SALTS

Since solutions of metals are true solutions, the application of the Raoult–Van't Hoff law for the dependence of the freezing point depression on the concentration of solute should give information on the structure of the dissolved species. Since

$$\Delta T_f = \nu K_f m, \tag{11}$$

where T_f is the m.p. of the pure solvent, m the molal solute concentration, $K_f = \frac{RT_f^2 M_0}{1000\, L_f}$ the cryoscopic constant; L_f is the heat of fusion of the pure solvent, and M_0 its molecular weight, we can, by comparing the experimental value of the cryoscopic constant K_f with the calculated value, find the number of particles of new species formed when one atom of metal dissolves (ν).

TABLE 10. Solubility of magnesium at 800° in a melt of 50 mole % $MgCl_2$ + 50 mole % MCl_n[85].

MCl_n	KCl	NaCl	$BaCl_2$	$SrCl_2$	$CaCl_2$	LiCl
z_M/R_M^2	0.56	1.04	0.98	1.34	1.76	1.64
$s \times 10^2$, at.%	15.2	17.4	34.2	37.2	42.0	40.4

TABLE 11. Solubility at 800° of magnesium diluted with aluminium[84].

Metal phase compn., %		s, at.% × 10	$k_0 \times 10^4$
Mg	Al		
100	0	94	47
79	21	82	51
67	33	56	42
49	51	45	46
		average	46.5

This calculation can be carried out, for example, for solutions of potassium and sodium in their halides (Table 12). The data of Bredig and coworkers were used for the heats of fusion, melting points[120], solution concentrations x (mole fractions), and ΔT_f.[79,80,82] In all cases ν = 0.5–0.7, indicating that one species is formed in solution for every two atoms of dissolved metal. In other words, the dissolution of sodium and potassium is accompanied by the formation of Na_2 and K_2 molecules. It should be emphasised that these are molecules and not double ions, since reaction of the type

$$Na^+ + Na \longrightarrow Na_2^+,$$

corresponds to the formation of one dissolved species for every metal atom. The fact that the value of ν, particularly for sodium, is greater than 0.5 was attributed by Bredig and Bronstein[82] to partial dissociation of the molecule

$$Na_2 \rightleftarrows 2Na.$$

Dissociation according to the scheme

$$Na_2 + 2Na^+ \rightleftarrows 2Na_2^+.$$

is also possible.

Similar calculations by Cubicciotti and coworkers[108] showed that when nickel dissolves in $NiCl_2$, up to Ni concentrations of 7.4 at.%, the freezing point depression corresponds to the formation in solution of two new species for every dissolved nickel atom, indicating that the dissolution of nickel involves the reaction

$$Ni + Ni^{2+} \rightarrow 2Ni^{+}.$$

Another method of interpreting the results of cryoscopic measurements involves the use of the approximate Schröder equation for the liquidus line

$$\ln x = -\frac{L_f \Delta T_f}{RT_f(T_f + \Delta T_f)}, \tag{12}$$

where x is the mole fraction of the solvent.

Grjotheim, Gronvold, and Krogh-Moe[121] investigated freezing point depressions for the dissolution of cadmium in cadmium chloride. The value of x depends on the structural model of the solution. By assuming different structural models, it is possible to calculate the heat of fusion L_f and compare it with experimental data. Thus for Cd–$CdCl_2$ we have:

1. For the reaction $Cd + Cd^{2+} = Cd_2^{2+}$

$$x_{Cd^{2+}} = (n_{CdCl_2} - n_{Cd})/n_{CdCl_2}, \quad L_f = 5.4 \text{ kcal mole}^{-1},$$

where n_i is the number of moles of the i-th component.

TABLE 12. Structure of sodium and potassium dissolved in halides.

Salt	T_f, °K	L_f, kcal × mole^{-1}	ΔT_f, °K	$x \cdot 10^2$	K_f	ν	Salt	T_f, °K	L_f, kcal × mole^{-1}	ΔT_f, °K	$x \cdot 10^2$	K_f	ν
NaF	1268	7.8	5	2.5	13.7	0.60	KF	1131	6.75	9	45	18.8	0.60
NaCl	1073	6.7	5	2.1	18.5	0.73	KCl	1043	6.34	18	10	26.6	0.54
NaBr	1020	6.24	7	2.9	33.2	0.72	KBr	1007	6.10	26	17	32.4	0.46
NaI	933	5.64	3	1.6	49.0	0.55	KI	954	5.74	23	12	48.5	0.57

2. For the reaction $Cd + Cd^{2+} = 2Cd^{+}$

$$x_{Cd_2^{2+}} = (n_{CdCl_2} - n_{Cd})/(n_{CdCl_2} + n_{Cd}), \quad L_f = 10.4 \text{ kcal mole}^{-1}.$$

3. For the atomic dissolution of cadmium

$$x_{Cd^{2+}} = n_{CdCl_2}/(n_{CdCl_2} + n_{Cd}), \quad L_f = 4.3 \text{ kcal mole}^{-1}.$$

The experimental value is L_f = 5.3 kcal mole^{-1}, indicating that Cd_2^{2+} ions are formed in solution.

Analogous calculation from published data[108] for Ni in $NiCl_2$ gives a value ~10 kcal mole^{-1} for L_f assuming that Ni_2^{2+} is formed and ~20 kcal mole^{-1} assuming that Ni^{+} is formed. This confirms that the Ni dissolves as singly-charged Ni^{+} ions, since the experimental heat of fusion of nickel chloride is 18.5 kcal mole^{-1}.

Mellors and Senderoff[103] carried out an analogous analysis of the dissolution of Ce in $CeCl_3$. The calculated values of the heat of fusion of $CeCl_3$, assuming the formation of an atomic solution, Ce^{+} ions, and Ce^{2+} ions, are 6.0 kcal mole^{-1}, 9.0 kcal mole^{-1}, and 18.0 kcal mole^{-1} respectively. Comparison with the actual heat of fusion $L_f \simeq 8$ kcal mole^{-1}, shows that Ce^{+} ions are formed.

Bredig[122] and Mayer *et al.*[123] examined the structure of solutions of Bi in $BiCl_3$ on the basis of cryoscopic data. The following dissolution reactions were assumed:

$$\begin{array}{ll} Bi \rightarrow \text{atomic Bi} & 2Bi + BiCl_3 \rightarrow Bi_3Cl_3, \\ 2Bi \rightarrow Bi_2, & 8Bi + 4BiCl_3 \rightarrow 3Bi_4Cl_4, \\ 2Bi + BiCl_3 \rightarrow 3BiCl, & Bi + 2BiCl_3 \rightarrow 3BiCl_2, \\ 4Bi + 2BiCl_3 \rightarrow 3Bi_2Cl_2, & Bi + BiCl_3 \rightarrow Bi_2Cl_3 . \end{array}$$

The heat of fusion of $BiCl_3$, was found to be 5.5 kcal mole^{-1} by Bredig[122], and 5.7 kcal mole^{-1} by Mayer *et al.*[123], and best agreement with experimental data is obtained assuming the formation of Bi_2Cl_2 (Fig. 7) or the dimeric ion $(:Bi::Bi:)^{2+}$, by analogy with the $(Hg:Hg)^{2+}$ ion. Dissociation of the dimer above 400° is possible.

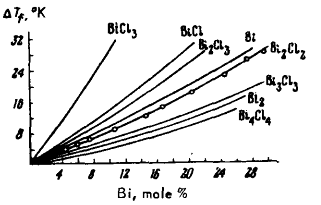

Fig. 7. Comparison of experimental data for the depression of the freezing point of $BiCl_3$ by Bi with the calculated values obtained for different structural schemes for the solutions.

VII. INFLUENCE OF THE DISSOLUTION OF METALS ON THE VAPOUR PRESSURE OF FUSED SALTS

Cubicciotti *et al.*[124] studied the vapour pressure of $BiCl_3$ in equilibrium with Bi in the range 210°–410° and showed that the vapour consisted of monomeric $BiCl_3$ and that the vapour pressure is related to the temperature by the expression

$$\log p = p_0 + \frac{b}{T} . \tag{13}$$

The dependence of the vapour pressure on concentration shows positive deviations from Raoult's law, indicating that the bismuth dissolves as neutral aggregates of the type Bi_n or as polymeric ions, for example

$$2Bi + Bi^{3+} \rightleftarrows 3Bi^{+},$$
$$3n\,Bi^{+} \rightleftarrows 3Bi_n^{n+}.$$

The nature and structure of the dissolved bismuth were discussed by Corbett[59,125] and Bredig[122]. Corbett concluded that the deviations from ideal behaviour can be attributed to the formation of the polymer Bi_4Cl_4 at temperatures up to 360° and of more complex polymers at higher temperatures. According to Bredig[122], the data can be explained equally readily by assuming the formation of the dimer Bi_2Cl_2, which is converted to Bi_2 at higher temperatures. Analogous results have been obtained for Bi–$BiBr_3$.[126] The equilibrium

$$3Bi_2X_2 \rightleftarrows 2Bi_2 + 2BiX_3,$$

according to Bredig, exists at all temperatures but is displaced to the right with increase in temperature. The equilibrium constant of this reaction for Bi–$BiBr_3$, for example,

$$K = \frac{[Bi_2X_2]^3}{[BiX_3]\,[Bi_2]^2} \tag{14}$$

decreases from 0.05 at 300° to 10^{-4} at 400°.

This explanation does not contradict cryoscopic data and also explains the complete miscibility of Bi and $BiCl_3$ at high temperatures[104], for if the dissolution of the bismuth involved merely the formation of singly-charged ions, the solubility could not exceed 33 at.%, whereas Bredig's hypothesis postulates that the complete miscibility is due to mixing of the Bi_2 dimers with the subhalide Bi_2X_2, no Bi^{3+} ions apparently remaining.

Cubicciotti and Keneshea[127] also studied the vapour pressure BiI_3 over Bi–BiI_3 solutions. Unlike the chloride and bromide systems, this system shows ideal behaviour up to Bi concentrations of 30–35 at.%. The equilibrium

$$BiI_3 \rightleftharpoons \tfrac{3}{2}I_2(\text{gas}) + Bi(\text{soln.})$$

is established. No explanation for the unique behaviour of this system has been given.

VIII. VOLUME EFFECTS ACCOMPANYING THE DISSOLUTION OF METALS IN FUSED SALTS

The influence of the dissolution of metals on molar volume was also studied by Cubicciotti and Keneshea[126–130] in the case of bismuth solutions. They established that in all cases the density of the solutions decreases linearly with temperature

$$\rho = \alpha - \beta t.$$

The quantity α increases and the temperature coefficient β decreases slightly with increasing concentration of bismuth (Table 13).

TABLE 13. Change in density of $Bi-BiX_3$ solutions with change in concentration (by interpolation from Cubicciotti's data).

x_{Bi}, at.%	$BiCl_3$		$BiBr_3$		BiI_3	
	α	$\beta \times 10^3$	α	$\beta \times 10^3$	α	$\beta \times 10^3$
0	4.42	2.20	5.25	2.40	5.56	2.22
10	4.58	2.06	5.39	2.20	5.67	2.10
20	4.85	2.08	5.54	2.00	5.79	1.95
30	5.19	2.15	5.71	1,85	5,94	1.75

If we assume that the subchloride Bi_2Cl_2 is formed in solution of the molar volume of the solution can be calculated from the formula

$$\tilde{V} = \frac{x_{Bi_2Cl_2} M_{Bi_2Cl_2} + (1 - x_{Bi_2Cl_2}) M_{BiCl_3}}{\rho} = \frac{489 x_{Bi_2Cl_2} + 315.4\,(1 - x_{Bi_2Cl_2})}{\rho}, \quad (15)$$

where x is the mole fraction and M the molecular weight. Here

$$x_{Bi_2Cl_2} = \frac{3x_{Bi}}{4 - 3x_{Bi}}, \quad (16)$$

where x_{Bi} is the mole fraction of dissolved metal and the molar volume of the Bi_2Cl_2 dimer in the solution is defined as

$$\varnothing_{Bi_2Cl_2} = \frac{\tilde{V} - (1 - x_{Bi_2Cl_2})\,\tilde{V}_{BiCl_3}}{x_{Bi_2Cl_2}}, \quad (17)$$

where $\tilde{V}_{BiCl_3}$ is the molar volume of pure bismuth chloride. Analogous equations can be written for the other halides. Calculation shows that in the concentration range $x_{Bi} = 0.05-0.20$ ($x_{Bi_2X_2} = 0.04-0.18$) the partial molar volume of the dimer is almost independent of the concentration of the solution and is close to $\tilde{V}_{BiX_3}$. The fact that the partial molar volume of Bi_2X_2 is constant indicates that solutions of Bi in BiX_3 approximate to ideal behaviour if they are regarded as $Bi_2X_2-BiX_3$ mixtures.

Thus measurements of the density of $Bi-BiX_3$ solutions agree with the assumption that Bi_2X_2 is formed. Analogous calculations can also be made, however, assuming that bismuth dissolves as atoms. There are no grounds for rejecting the latter hypothesis.

IX. POTENTIOMETRIC STUDIES OF SOLUTIONS OF METALS

Karpachev and Stromberg[106,131] were the first to make a potentiometric study of solutions of metals in fused salts. The procedure involves the determination of the dependence of the potential of an inert carbon electrode on the concentration of dissolved metal. The electrode potential, like an ordinary redox potential, is determined by the ratio of the concentrations of dissolved metal to that of normal chloride and if the latter remains constant, the potential obeys the Nernst equation

$$\varphi = \varphi_0 - b \log x.$$

The value of the prelogarithmic coefficient b is determined by the mechanism of the dissolution. If this involves the formation of M^+ ions, $b = 2.3\,RT/F$, if M_2^{2+} ions or M atoms are formed, $b = 2.3\,RT/2F$, etc. For solutions of cadmium in $CdCl_2 + KCl-NaCl$ (1 : 1) at 700° the experimental value of $b = 0.092$, indicating that dissolution of cadmium takes place according to the reaction

$$Cd + Cd^{2+} \longrightarrow Cd_2^{2+}$$

or

$$Cd_M \longrightarrow Cd_{diss}$$

For solutions of lead in $PbCl_2$ at 700°, $b = 0.185$, *i.e.*

$$Pb + Pb^{2+} \longrightarrow 2Pb^+,$$

which agrees with the results of cryoscopic measurements.

Using potentiometric measurements, Karpachev and Stromberg determined the composition of a saturated solution from the point at which the potential of the carbon electrode ceased to change when the metal was introduced into the cell by cathodic deposition. The quantity of metal liberated was calculated from the quantity of electricity passed. The results of the solubility measurements made in this way are given in Table 14. The solubility of lead in $PbCl_2$ at 700° is 0.056 mole%, which agrees well with other data.

Although the solubility of Cd in a KCl–NaCl (1 : 1) melt is very small, it is nevertheless significant and when recalculated in volume units amounts to ~0.0059 M. The Cd concentration in the vapour above the metal at 1 atm and 700° also amounts to ~0.006 M, so that it is natural to assume that part of the cadmium "volatilises" into the melt in atomic form.

Senderoff and Mellors[132] made a potentiometric study of solutions of cerium in cerium chloride and found that the e.m.f. of the cell

$$Ce \mid CeCl_3, \text{ sat. with } Ce \parallel CeCl_3 \mid Ce$$

in the temperature range 820°–920° exceeds the calculated value by 0.7 V. Since in the authors' opinion the junction potential in the cell cannot exceed 60 mV, this difference can only be ascribed to an equilibrium of the type

$$4CeCl_3 + 2Ce \rightleftarrows 3Ce^+ + 3CeCl_4^-.$$

Analogous e.m.f. values were obtained with inert Mo electrodes. The e.m.f., for Ce concentrations in the melt between 8.7 mole % and zero, was related to x_{Ce} by the equation

$$\varphi = \varphi_0 + b \log \frac{[Ce^{3+}]}{[Ce^+]}, \quad (18)$$

with a prelogarithmic factor equal to 0.115 V, indicating that Ce^+ ions are formed. In Senderof and Mellors'

TABLE 14. Solubility of cadmium in $CdCl_2-KCl-NaCl$ at 700°.

Concn. of $CdCl_2$ in NaCl–KCl, mole %	0	1.0	2.0	3.0	5.0	6.5	10.0	25.0	50.0
Solubility of Cd, at.%	0.025	0.034	0.042	0.053	0.071	0.081	0.110	0.465	2.34

opinion, the dissolution of cerium should lead to formation of the complex

$$Ce^{(I)}[Ce^{(III)}Cl_4].$$

Finally, Smirnov and Chukreev[133,134] made a potentiometric study of the dissolution of beryllium in $BeCl_2$ + + KCl–LiCl at 400°–900°. Assuming that Be on dissolution forms singly-charged Be^+ ions, they measured the potential of an inert molybdenum electrode in the melt and found the equilibrium constant of the reaction

$$Be(solid) + Be^{2+} \rightleftharpoons 2Be^+$$

to be given by

$$k = \exp\left(2.36 - \frac{4904}{T}\right). \tag{19}$$

X. ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF METALS IN FUSED SALTS

The electrical conductivity of solutions of metals in fused salts was studied by Aten[93,135,136] and Bredig and Bronstein[137]. The latter made a systematic study of the electrical conductivity of solutions of sodium and potassium in their fused chlorides and bromides (Figs. 8 and 9).

The dissolution of the alkali metals in all cases leads to an increase in the conductivity. Bredig and Bronstein calculated the equivalent conductance of the dissolved metal, assuming additivity of the molar volumes, from the equation

$$\lambda_M = \frac{\kappa_{soln}\tilde{V} - x_1\lambda_{salt}}{x_2}, \tag{20}$$

where x_1 and x_2 are the mole fractions of the metal and salt, λ_{salt} is the molar conductance of the pure salt, κ_{soln} the specific conductivity of the solution, and $\tilde{V}$ the molar volume of the solution. With increase in the concentration of dissolved metal, λ_{Na} decreases whereas λ_K increases (Fig. 9).

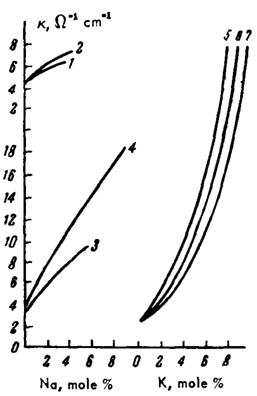

Fig. 8. Specific conductance of solutions of metals in fused salts:
1) Na–NaCl, 845°; 2) Na–NaCl, 890°;
3) Na–NaBr, 805°; 4) Na–NaBr, 895°;
5) K–KBr, 870°; 6) K–KBr, 760°;
7) K–KCl, 820°.

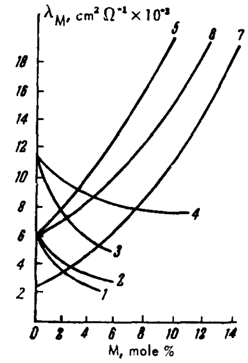

Fig. 9. Equivalent conductance of metal dissolved in a fused salt. Numbering same as in Fig. 8.

These facts require special explanation. In Bronstein and Bredig's opinion, the electrons should be relatively weakly bound to the dissolved metal atoms, so that the conductivity of the solution becomes partly electronic in character, and increases with increase in concentration. In addition, however, association of dissolved particles (Na_2) is possible, and this apparently leads to a decrease in λ_{Na} with increase in the Na concentration in the solution. The decrease in the equivalent conductance of the solution due to association can hardly be more than 1–2 $cm^2\Omega^{-1}$ per mole % of dissolved metal, whereas the increase in the equivalent conductance due to the electronic contribution reaches 100 $cm^2\Omega^{-1}$ per mole % of metal. It is assumed that almost no association of potassium takes place in solution, although this does not agree with cryoscopic data. Bronstein and Bredig assumed that the electronic conductance in the melt involved the transfer of electrons between ions of different states of oxidation. This mechanism is similar to proton transfer in aqueous solution.

Aten studied the electrical conductivity of solutions of Bi in $BiCl_3$ and of Cd in $CdCl_2$ (Table 15). The decrease in the conductivity produced by the dissolution of cadmium increases with increase in the metal concentration. On dissolution of bismuth, the conductivity of the solution at first increases, but starts to decrease when the concentration is increased above 15 at.%.

Aten calculated the molar conductance (λ_{Cd}) of dissolved cadmium and found the value 8 $\Omega\,cm^{-2}$ at 600°, whereas the molar conductance of pure $CdCl_2$ is higher by one order of magnitude (110 $\Omega\,cm^{-2}$). According to Bronstein and Bredig, this is due to formation of the dimer Cd_2^{2+}; there

TABLE 15. Electrical conductivity of solutions of Bi in $BiCl_3$ and of Cd in $CdCl_2$.

Bi, at.%	κ, Ω^{-1} cm^{-1}		Cd, at.%	κ, Ω^{-1} cm^{-1}	
	300°	350°		580°	600°
0	0.498	0,554	0	1,907	1,968
5.2	0.506	0,585	2.5	1.898	1.959
10.1	0.507	0.605	5.0	1,884	1.945
20,5	0.481	0,607	7,5	1,867	1.928
31,1	0.405	0,549	10,0	1.845	1.906

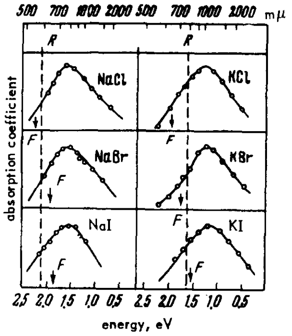

Fig. 10. Absorption bands of Na and K dissolved in their fused halides. *R* gives the position of the absorption lines of gaseous Na and K atoms.

is apparently no electronic contribution to the conductivity in this case. The mechanism of conduction in bismuth solutions is more complicated. It may be assumed that at low concentrations of dissolved metal, there is a slight electronic conductivity, which disappears at high concentrations due to association or to the change

$$2Bi_2^{2+} \longrightarrow Bi^{2+} + Bi_2.$$

Senderof and Mellors[132] measured the electrical conductivity of solutions of Ce in $CeCl_3$ and found that at 840° the conductivity of the melt increases from 0.92 $\Omega^{-1}\,cm^{-1}$ for pure $CeCl_3$ to 3.76 $\Omega^{-1}\,cm^{-1}$ for a saturated solution of Ce in $CeCl_3$. This fourfold increase in the conductivity for a Ce content of $\sim 9\%$ can hardly be due to the higher mobility of the Ce^+ ions and in this case it is most probable that the increase in conductivity is due to electron transfer.

Since Aten, on the basis of measurements of the electrical conductivity of $Cd-CdCl_2$, concluded that cadmium dissolves as uncharged species, it is of interest to describe the experiments of Grjotheim[121], who showed that the dissolved metal takes part in the transfer of current. Electrolysis was carried out in a quartz U-tube, fitted with a porous alundum partition impregnated with pure $CdCl_2$. Both sections of the vessel were filled with $Cd-CdCl_2$ solution and on application of a direct current the colour front entered the partition and moved rapidly towards the cathode, indicating that the colour of the cadmium solutions is due to positively charged species.

XI. MAGNETIC AND SPECTROSCOPIC STUDIES OF SOLUTIONS OF METALS IN FUSED SALTS

The effect of a magnetic field on a body is determined by the electronic structures of the atoms or ions[138]. When the magnetic field influences only the movement of the electrons in the atoms and ions, the substance is diamagnetic, that is, it is repelled by the magnetic field. When the atoms or ions have a permanent magnetic moment, the substance is attracted towards the magnetic field, that is, it exhibits paramagnetic properties.

Paramagnetism is caused by the presence of unpaired electrons, so that the presence of ions such as Cd^+, Bi^+, and Ga^{2+} should be detectable by the appearance of paramagnetic properties when metals dissolve in fused salts. Unfortunately, there are few data on the magnetic properties of such systems.

Erlich and Gentsch[139,140] isolated calcium subchloride as pale-yellow crystals with density 2.45. The product, however, did not show paramagnetic properties, indicating the formation of Ca_2^{2+} ions. The magnetic susceptibility of solutions of Cd in $CdCl_2$ has been studied[121,141]. Since the cadmium solutions were found to be diamagnetic, the measurements confirmed that Cd_2^{2+} ions are formed. McMullan and Corbett[111] showed that gallium dichloride, $GaCl_2$, is diamagnetic, indicating that the Ga_2^{4+} ion or the complex $Ga^{(I)}[Ga^{(III)}Cl_4]$ is formed. Corbett[59] also noted the diamagnetism of bismuth monochloride, which agrees with the hypothesis that Bi_2^{2+} dimers are formed. Thus in all these cases the sub-ions are diamagnetic, confirming the tendency towards the formation of stable ions with filled *s*-orbitals.

The most important data on the nature of solutions in fused salts are probably obtainable from spectroscopic studies. The absorption spectra of alkali metals dissolved in fused halides have been studied[67,71,142]. Broad absorption bands (Fig. 10) were obtained with maxima at $\lambda = 790$ mμ for Na and 980 mμ for K. It may be assumed that these bands are produced from the first absorption lines of the atoms, with wavelengths 590 mμ for Na and 770 mμ for K. The displacement of the centre of the absorption band is ~ 200 mμ and the broadening of the bands is ~ 700 mμ (1 eV). The fact that there is no splitting of the energy levels of the alkali-metal atoms indicates that the perturbing field (due to the salt ions) is spherically symmetrical. In other words, the nature of the absorption spectra in these cases indicates that the solutions contain no stable compounds of dissolved atoms and normal ions (Na_2^+, K_2^+). The displacement of the maximum and the broadening of the absorption band indicate a marked expansion of the outer electronic orbital, that is a weakening of the bond between the electron and the metal atom. As already mentioned, *F*-centres are formed in the melt on freezing. If this is related to the appearance of lattice defects in the solid crystal, we would also expect that the electrons may be fairly readily displaced from ion to ion in the liquid salt, since the potential well for an electron is shallow in both solid and liquid salt.

Woodward *et al.*[143] recorded the Raman spectrum for molten gallium dichloride at 190° and showed that it has the structure $Ga^+[GaCl_4^-]$, and not $Cl_2Ga-GaCl_2$ as previously suggested[144]. An analogous conclusion was reached by Garton and Powell[145] on the basis of an X-ray diffraction study of $GaCl_2$ crystals. The study of the Raman spectra confirmed the existence of Hg_2^{2+} ions, containing a metal-to-metal bond, in mercurous chloride[146]. A similar structure for the calcium sub-ion was suggested by Erlich and Gentsch[140] on the basis of an X-ray analysis of CaCl.

XII. DISSOLUTION OF METALS IN ELECTROCHEMICAL PROCESSES

The dissolution of metals in fused salts has a significant effect on the current efficiency during electrolysis. Lorenz[9,147] suggested that the main reason for the deviation from Faraday's law during the electrolysis of fused salts is the dissolution of the metal being deposited at the cathode and its subsequent oxidation at the anode. For example, during the electrolysis of lead chloride the overall cathodic processes are

$$Pb^{2+} + 2\varepsilon \longrightarrow Pb$$
$$Pb + Pb^{2+} \longrightarrow 2Pb^+,$$

and the anodic process involves the reaction

$$Pb^+ - \varepsilon \longrightarrow Pb^{2+}.$$

The decrease in the cathodic current efficiency is determined by the conditions for the transport of dissolved metal from the cathode to the anode and therefore depends to a considerable extent on the geometry of the electrolytic cell, the shape and size of the electrodes, the distance between them, and other factors determining the hydrodynamics of the electrolyte[148-154]. The most complete analysis of the influence of electrolysis conditions on the current efficiency in fused electrolytes was made by Bukhbinder[155].

Aten[136] suggested that the mechanism of metal loss can be related to electron transfer in solutions of metals in fused salts. Yanagase and Derge[156] studied the electrolysis of antimony sulphide Sb_2S_3 at 635°–690° and $i = 0.25$–1.5 A cm^{-2} with a carbon cathode and a liquid metal anode, and attributed the low current efficiency to partial electronic conductivity. No one has confirmed this experimentally for fused chlorides.

Spooner[157] noted the depolarising action of the process

$$Pb + PbS \longrightarrow Pb_2S$$

during the electrolysis of PbS in a chloride melt.

Antipin[158-160] analysed the shape of the cathodic polarisation curves for the electrodeposition of aluminium from cryolite–alumina melts and concluded that instead of the proposed reduction reaction

$$Al^{3+} + 3\varepsilon \rightarrow Al,$$

the reduction processes at the cathode involved the formation of sub-ions:

$$2Na^+ + \varepsilon \rightarrow Na_2^+,$$
$$Al^{3+} + 2\varepsilon \rightarrow Al^+,$$
$$Al^+ + \varepsilon \rightarrow Al,$$
$$Na_2^+ + \varepsilon \rightarrow 2Na.$$

Each of these reactions corresponds to a definite branch on the polarisation curve. Antipin also detected two branches on the polarisation curves for the electrolysis of $PbCl_2$, AgCl, and other fused chlorides, and explained these on the assumption that the primary processes involve the formation of sub-ions (Ag_2^+, Pb^+).

Sucki[162-164] studied the electrolysis of fused calcium chlorides and showed that until the electrolyte is saturated with metal, the cathodic process is

$$Ca^{2+} + 2\varepsilon \rightarrow Ca,$$

but that after saturation and at low current densities, the primary process is accompanied by the reduction

$$Ca_2^{2+} + 2\varepsilon \rightarrow 2Ca.$$

Under these conditions the reaction $2Ca^{2+} \rightarrow Ca_2^{2+}$ apparently does not occur.

According to Sucki, the following processes are possible in the electrolysis of fused KCl and NaCl

$$K^+ (Na^+) + x\varepsilon \rightarrow K (Na) \text{ (dissolved)},$$
$$K (Na) \text{ (dissolved)} + y\varepsilon \rightarrow K (Na) \quad (\text{where } x + y = 1),$$

and

$$K^+ (Na^+) + \varepsilon \rightarrow K (Na).$$

Smirnov and Chukreev[165] established that during the anodic dissolution of beryllium in a KCl–LiCl melt, Be^+ ions are formed in addition to Be^{2+} ions, and the ratio Be^+/Be^{2+} increases with decrease in current density (Table 16), accompanied by a shift of the anode potential towards more negative values. Since the dissolution of beryllium takes place without polarisation, the potential shift can be due only to a change in the $[Be^{2+}]/[Be^+]$ ratio in the melt, in accordance with the Nernst equation

$$\varphi = \varphi_0 + \frac{RT}{F} \ln \frac{[Be^{2+}]}{[Be^+]}$$

Calculation confirms this assumption.

It has been established[24,166,167] that Al^+ ions are formed during the dissolution of aluminium in fused salts. Belyaev[167] also noted the formation of Sn^+ during the dissolution of tin in a chloride melt. The anodic current efficiency was 120% for aluminium and 200% for tin, but decreased rapidly with increase in the anodic current density.

TABLE 16. Influence of current density on the current efficiency for the dissolution of beryllium.

i, A cm^{-2}	Current efficiency, %	Fraction	
		Be^+	Be^{2+}
0.004	135.5	0.357	0.643
0.005	124.0	0.242	0.758
0.05	113.5	0.137	0.863
0.4	109.5	0.095	0.905
0.5	106.5	0.065	0.935

XIII. CONCLUSION

In concluding this examination of the dissolution of metals in fused salts we must point out that despite the recent intensified interest in this question, no final solution has yet been reached. Although in many cases the phenomenon can be related to the formation of sub-compounds, under certain conditions the formation of atomic solutions is undoubtedly possible, particularly in the case of the alkali metals. Certain data obtained from the study of solutions of bismuth and alkali metals show the existence of the equilibrium

sub-ion ⇌ dissolved atom,

in addition to the equilibrium

normal ion ⇌ sub-ion.

The dissolved atoms and ions also undoubtedly tend to polymerise.

Comparison of the properties of solutions of metals in fused salts and in solid crystals (F-centres) suggests their close similarity. In systems containing normal metal ions and sub-ions, the excess electrons are evidently not localised on definite atoms but move freely from one to another. Dimerisation of the sub-ions hinders this process by deepening the potential box for the electron. Nevertheless, it may be assumed that electronic conductivity is shown by solutions of metals, although the conductivity should be not metallic but semiconducting in character. Thus a given solution at relatively low temperatures close to the melting point of the salt can be regarded as a system containing chiefly normal ions and sub-ions, while the same solution at high temperatures can be regarded as a solution of excess electrons; more or less prolonged localisation of the electrons on individual metal ions is possible only on dimerisation. This viewpoint explains the behaviour of a number of systems, including Bi–$BiCl_3$, Ca–$CaCl_2$, etc., which show complete miscibility at high temperatures.

A solution to the problem of the nature of fused salts is evidently to be found by treating these as special semiconducting systems, which according to Ol'shanskii, can be classified as ionic–electronic liquids.

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TECHNETIUM — ELEMENT 43

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CONTENTS

HISTORY OF DISCOVERY

In 1871 Mendeleev predicted the existence of the element with atomic number 43, which he called "ekamanganese", and determined its position in the Periodic System[1]. However, the element remained unknown for a long time. Numerous attempts to find it in nature, based on its presumed analogy to manganese and certain platinum metals, were unsuccessful[2-13]. A typical example is the work of Ogawa[8] who claimed to have isolated a new element from molybdenite, thorianite, and certain other minerals. This "new element" had many of the properties predicted for element 43. Ogawa called it "nipponium" and described the properties of several of its compounds.

In 1925 Noddack and Tacke[12] announced the discovery, from X-ray spectroscopic data, of element 43 for which they proposed the name "masurium". The data given below show that the X-ray lines which they ascribed to element 43 approximately correspond to calculations from Moseley's relation with allowance for the screening constant.

	$K_{\alpha 1}$	$K_{\alpha 2}$	$K_{\beta 1}$
Observed wavelength, Å	0.672	0.675	0.601
Calculated wavelength, Å	0.6734	0.6779	0.6000

The relative intensity of the masurium and rhenium lines suggested identical content of both elements in the specimens studied*. From its position in the Periodic System, Noddack described some of the physical and chemical properties of masurium. He suggested that it should have an atomic weight between 98 and 99, density of 11.5, and melting point of 2300°. Its lower oxides (MaO, Ma_2O_3, MaO_2) should be yellow in colour and probably insoluble in acids. The higher oxides (MaO_3 and Ma_2O_7) should be lightly coloured and on reaction with water should yield acids analogous to manganic and permanganic.

About a year later Prandtl[13] proved Noddack's results to have been erroneous. Thus for a long time there has been no reliable experimental proof of the existence of stable isotopes of element 43, although evidence from nuclear physics suggests that such stable isotopes should exist[14].

Various nuclear reactions appear to be the only source of technetium. The element was first prepared in 1937 by Segrè and Perrier[15] by the bombardment of molybdenum nuclei with deuterons. Since this was the first preparation of an artificial element, Segrè and Perrier called it "technetium"**. Later many other nuclear reactions leading to the formation of various isotopes of this element studied.

At present nuclear fission of uranium is the principal source of technetium in relatively large quantities[17]. One of the most long-lived isotopes of technetium, ^{99}Tc, is formed in the nuclear reactor, among other products. The

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* Later Noddack showed that the lines of masurium are much weaker than those of rhenium.

** From τεχνητός "artificial" (Ed. of Translation).

TABLE 1. Technetium isotopes 1161.

Mass number	Type of decay*	Half-life	Energy of radiation, MeV		Mode of formation
			β	γ	
92	EC, β^+	4.5 min	4.1	1.3	${}^{92}\text{Mo}(d,\ 2n){}^{92}\text{Tc}$
93*m*	EC, IT	45 min		0.39	${}^{92}\text{Mo}(d,\ n){}^{93m}\text{Tc}$
93	EC, β^+	2.7 h	0.8	1.3	${}^{92}\text{Mo}(d,\ n){}^{93}\text{Tc}$
94	β^+ (75%) EC (25%)	53 min	2.4	0.87 (98%), 3.27 (2%)	${}^{94}\text{Mo}(p,\ n){}^{94}\text{Tc}$; ${}^{94}\text{Mo}(d,\ 2n){}^{94}\text{Tc}$ ${}^{94}\text{Ru}\xrightarrow{\beta^+}{}^{94}\text{Tc}$
95*m*	EC(96%) β^-(0.2–0.6%) IT(3%)	60 days	0.4	0.039	${}^{92}\text{Mo}(a,\ p){}^{95m}\text{Tc}$; ${}^{95}\text{Mo}(p,\ n){}^{95m}\text{Tc}$; ${}^{95}\text{Mo}(d,\ 2n){}^{95m}\text{Tc}$; ${}^{95}\text{Ru}(n,\ p){}^{95m}\text{Tc}$
95	EC	20 h		0.93 (5%), 1.07 (5%), 0.76 (90%)	${}^{95}\text{Mo}(p,\ n){}^{95}\text{Tc}$; ${}^{95}\text{Mo}(d,\ 2n){}^{95}\text{Tc}$; ${}^{92}\text{Mo}(a,\ p){}^{95}\text{Tc}$; ${}^{94}\text{Mo}(d,\ n){}^{95}\text{Tc}$; ${}^{95}\text{Ru}\xrightarrow{\beta^+}{}^{95}\text{Tc}$
96*m*	IT	52 min		0.034	${}^{96}\text{Mo}(p,\ n){}^{96m}\text{Tc}$
96	EC	4.2 days		0.238, 0.312, 0.415 0.560, 0.771, 0.806 0.842, 1.078, 1.119 1.187	${}^{93}\text{Nb}(a,\ n){}^{96}\text{Tc}$; ${}^{95}\text{Mo}(d,\ n){}^{96}\text{Tc}$; ${}^{96}\text{Mo}(d,\ 2n){}^{96}\text{Tc}$
97*m*	IT	90 days		0.096	${}^{97}\text{Mo}(d,\ 2n){}^{9\,m1}\text{Tc}$; ${}^{97}\text{Mo}(p,\ n){}^{97m}\text{Tc}$; ${}^{97}\text{Ru}\xrightarrow{EC}{}^{97m}\text{Tc}$; ${}^{96}\text{Mo}(d,\ n){}^{97m}\text{Tc}$
97	EC	> 10^4 years			${}^{97}\text{Mo}(d,\ 2n){}^{97}\text{Tc}$; ${}^{97m}\text{Tc}\xrightarrow{IT}{}^{97}\text{Tc}$
98	β^-, EC	> 10^5 years	2.1	0.2, 0.86	${}^{98}\text{Mo}(p,\ n){}^{98}\text{Tc}$
99*m*	IT	6 h		0.0020 ± 0.0001 0.1403 ± 0.0005 0.1423 ± 0.0005	${}^{99}\text{Mo}\xrightarrow[67\ \text{min}]{\beta^-}$ $\xrightarrow{87\%}{}^{99m}\text{Tc}\ \downarrow\text{IT}$ $\xrightarrow{13\%}{}^{99}\text{Tc}\xrightarrow{\beta^-}{}^{99}\text{Ru}$; ${}^{99}\text{Ru}\ (n,\ p){}^{99m}\text{Tc}$
99	β^-	2.12×10^5 years	0.293	No γ	${}^{99m}\text{Tc}\xrightarrow{IT}{}^{99}\text{Tc}$; U(fission)${}^{99}\text{Tc}$
100	β^-	15.8 – 17.5 sec	2.4	0.6	${}^{100}\text{Mo}(p,\ n){}^{100}\text{Tc}$
101	β^-	14.3 – 16.5 min	1.2	0.3	${}^{100}\text{Mo}(d,\ n){}^{101}\text{Tc}$; ${}^{102}\text{Ru}(\gamma,\ p){}^{101}\text{Tc}$; ${}^{103}\text{Rh}(\gamma,\ 2p){}^{101}\text{Tc}$
102	β^-	25 sec			U(fission) ...
104	β^-	3.8 ± 0.2 sec			
105	β^-	short			
107	β^-	1.5 sec			

* EC—orbital electron capture; IT—isomeric transition; β^+—positron emission; β^+—negatron (negative β^- particle) emission.

yield of the isotope in the fission of uranium-235 induced by thermal neutrons is approximately 6.2%. Hahn's rough calculations show that the production of 10^4 g of plutonium in a uranium reactor is accompanied by the accumulation of approximately 150 g of ^{99}Tc together with other fission products[18]. According to other data a 10^5 kW reactor produces approximately 2.5 g of technetium in 24 h†. The power of this reactor corresponds to a production of approximately 100 g of plutonium in 24 h. Hence the preparation of 10 kg of plutonium leads to the formation of approximately 250 g of technetium. The total quantity of technetium obtained in various plutonium-producing plants apparently amounts to tens or even hundreds of kilograms: the chemistry of technetium can therefore be investigated as thoroughly as that of many other elements.

Up to the present 19 isotopes and nuclear isomers of technetium have been synthesised. The methods used and some of the characteristics of the nuclei are given in Table 1.

Interesting work has been done on the effect of electron density[19-21], pressure[22], and temperature[23], on the fission constant (λ) of ^{99}Tc.

IDENTIFICATION OF THE ISOTOPES OF ELEMENT 43

The activity arising on irradiation of molybdenum with deuterons and neutrons has been assigned to element 43 by means of chemical[24-28] and other methods[29]. Chemical identification consists in observing the behaviour of radioactive isotopes during the separation of carrier elements introduced into the irradiated solution. If the activity follows a particular carrier element, it must be associated with a radioactive isotope of this element or its close analogue.

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† The quantity of technetium obtainable by irradiating Mo with deuterons is approximately 10^{-10}g.

The following method has been used for the chemical identification of element 43 prepared by the Mo (*d*, *n*) Tc reaction. The surface of the irradiated molybdenum target was dissolved in a mixture of nitric and hydrochloric acids, and the solution was evaporated to dryness. The residue was dissolved in water containing a few drops of concentrated ammonia and the resulting solution was divided into several portions. The (*d*, *n*) reaction might have formed radioactive isotopes of zirconium, niobium, tantalum, and ruthenium either in the main reaction with the target element or in side reactions with the target element and impurities. Hence the number of carriers required was limited to those elements and rhenium, which was used as the closest analogue of element 43 available.

Zirconium sulphate was added to the first part of the solution and the zirconium was precipitated as ZrO_2 with ammonia. The precipitate was found to be completely inactive. The second part of the solution was treated with an alkaline solution of tantalate and Ta_2O_5 was precipitated with dilute sulphuric acid. Again the precipitate proved inactive. Potassium perrhenate was added to the third part of the solution and the molybdenum present was precipitated as the 8-hydroxyquinoline complex. The precipitate contained only a small part of the activity which was completely lost on reprecipitation. Hence, appreciable quantities of radioactive molybdenum isotopes were also absent from the irradiated target. These results suggest that the activity in the target might have been due either to technetium or ruthenium isotopes. To distinguish between those two possibilities, rhenium sulphide was precipitated from the filtrate remaining after the removal of the molybdenum. The precipitate was dissolved in 5% sodium hydroxide and the hot solution was treated with an excess of hydrogen peroxide. A ruthenium salt was then added, the solution was acidified with dilute sulphuric acid, and the perrhenate was precipitated with nitron. The activity passed quantitatively into the precipitate. This constitutes a proof that irradiation of molybdenum does, in fact, lead to the formation of isotopes of element 43.

Later some technetium isotopes were identified by means of specific filters, the method being based on characteristic X-ray absorptions observed during isomeric transitions in specially selected substances[29].

Recently Spitsyn and Kuzina[30] isolated technetium from molybdenum trioxide irradiated with thermal neutrons in a nuclear reactor and identified ^{99}Tc by chemical, radiometric, and spectroscopic methods. The spectroscopic determination was made in a glass three-prism spectrograph in a camera (f = 1300 cm) with automatic collimation. The spectrum obtained on combustion of the specimen contained characteristic technetium lines.

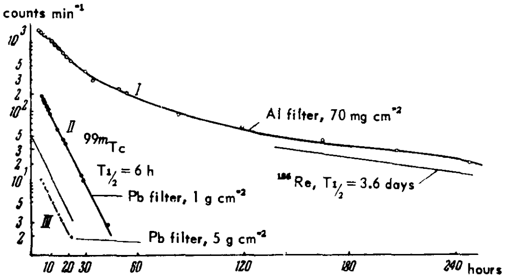
POSSIBLE NATURAL OCCURRENCE OF RADIOACTIVE TECHNETIUM ISOTOPES

Detailed investigation of the properties of the artificially produced technetium, and in particular the thorough study of its emission spectrum carried out in 1950 by Meggers and Scribner[31], allowed a further search for this element in nature to be undertaken. In 1951 Moore suggested that certain weak lines in the solar spectrum might be due to ionised technetium[32]. A year later Merrill[33], using the 100 inch telescope, obtained spectra of young stars containing technetium lines. These results suggest that technetium is synthesised in S-type stars.

From a thorough investigation of the solar spectrum (lines at 3195–3125 Å and 3298–3286 Å) Hibenet *et al.*[34] found that the technetium content in the sun amounts to $2.1 \times 10^{-11} - 2.6 \times 10^{-11}$ [the units are not given in the Russian text (Ed. of Translation)]. Herr[35] described an attempt to find naturally occurring long-lived technetium isotopes. Rhenium-containing molybdenum minerals were processed to yield approximately 370 g of molybdenite with 0.3% of rhenium. A technetium-containing rhenium fraction was obtained by distilling the material with $HClO_4$. To avoid losses of technetium, all operations were carried out in the presence of a short-lived radioactive technetium isotope as a tracer: $As(C_6H_5)_4ReO_4.As(C_6H_5)_4TcO_4$ was precipitated from the rhenium fraction. As much rhenium as possible was then removed by repeated distillation from $HClO_4$ and precipitation from 9 *N* hydrochloric acid with hydrogen sulphide. From the solution, which was markedly enriched with technetium (the technetium was still present, however, in virtually tracer quantity), approximately 1.5 mg of copper sulphide was precipitated. The sulphide with the coprecipitated technetium was subjected to neutron irradiation in a reactor (neutron flux 1.2×10^{12} neutron cm^{-2} sec^{-1}). Particular interest attaches in this connection to the ^{99m}Tc nuclear isomer of technetium (half-life 6.6 h). Observation in the irradiated solution of an activity corresponding to this half-life would constitute evidence that ^{99m}Tc was present and was formed as a result of neutron capture by the nucleus of ^{98}Tc. However, it was necessary to bear in mind that ^{99m}Tc might have arisen also through neutron capture by ^{98}Mo and subsequent fission of ^{99}Mo:

$$^{98}\mathrm{Mo}(n, \gamma)^{99}\mathrm{Mo} \xrightarrow{\beta^-} {}^{99m}\mathrm{Tc}.$$

Control experiments with much greater amounts of molybdenum showed that, in analogous conditions, the (*n*, *γ*) reaction can lead only to a very small ^{99m}Tc activity.



Although thorough chemical purification of the irradiated specimen excluded the possibility of the presence of molybdenum, the activity corresponding to ^{99m}Tc was nevertheless found. Curve *I* in the Figure shows the change with time of the activity obtained after 9 h irradiation in a reactor and measured using a 70 mg cm^{-2} aluminium filter. The curve is non-linear throughout its length and reveals the presence of a long-lived component with half-life corresponding to ^{186}Re. The purification used had not therefore completely removed all the rhenium. Curves *II* and *III* show the change in the activity measured with lead filters, and the observed half-life is very close to that of ^{99m}Tc. This activity may be ascribed to tracer quantities of ^{99m}Tc formed as a result of neutron capture by ^{98}Tc present in very small quantities in the irradiated specimen.

In 1956 Boyd and coworkers[36] carried out a search for technetium in various minerals using spectrochemical, radioactivation, and mass-spectrometric methods. The results (Table 2) show that technetium is present in some minerals in vanishingly small quantities. The authors suggest the technetium is formed in the earth's crust, on the one hand, by the radioactivation of molybdenum, niobium, and ruthenium with hard cosmic rays, and on the other, by spontaneous uranium fission.

TABLE 2. Technetium content in some materials.

Specimen	Method of determination	Technetium content, g kg^{-1}
MoS_2 (Climax, Colorado)	spectroscopic	$< 4 \times 10^{-10}$
Pure $KReO_4$	"	$< 8 \times 10^{-*}$
Pure $KReO_4$	"	$< 8 \times 10^{-9}$
MoS_2 (Nevada)	"	$< 1.5 \times 10^{-8}$
MoS_2 (Miami, Arizona)	spectrophotometric	$< 1.8 \times 10^{-7}$
MoS_2 (Miami, Arizona)	activation	$< 10^{-9}$
MoS_2 (Miami, Arizona)	spectroscopic	$< 1.7 \times 10^{-9}$
MoS_2 (Miami, Arizona)	activation	$\sim 8.3 \times 10^{-11}$
MoS_2 (Nevada)	"	1.3×10^{-10}
Osmium-iridium concentrate	spectroscopic	$< 1.6 \times 10^{-8}$
Volatile Mo combustion products	"	$< 1.3 \times 10^{-8}$
Yttrotantalite (West Africa)	mass-spectrometric	$< 6 \times 10^{-11}$
Iron-nickel meteorite	spectroscopic	$< 4.5 \times 10^{-10}$

* [Value not given in Russian text. (Ed. of Translation)].

ELECTRONIC CONFIGURATION AND VALENCE STATES OF TECHNETIUM

The spectrum of the neutral technetium atom has not so far been interpreted. It is probable that the electronic configuration of technetium atoms in the ground state is $4s^24p^64d^65s(^6D_{9/2})$ or $4s^24p^64d^55s^2(^6S_{5/2})$.[37]

Since the properties of technetium are similar to those of rhenium, the chemistry of which is known in some detail, technetium may be expected to exhibit valence states +7, +6, +5, +4, +2, and -1. At the present time the oxidation states established experimentally are -1 (doubtful), 0, +2, +4, +5, +6, and +7.[37] The most characteristic and stable valence state is +7.

ELEMENTAL TECHNETIUM

Flagg and Bleidner[38] appear to have been the first to prepare invisible films of metallic technetium. A molybdenum plate was irradiated with deuterons, dissolved in aqua regia, and the solution was evaporated to dryness with an excess of ammonia. The evaporation with ammonia was repeated until the MoO_3 precipitate became perfectly white. It was dissolved in 15 *N* ammonia solution, which was then acidified with hydrochloric acid and treated with ammonium acetate. The solution was heated to boiling and molybdenum was precipitated with a tenfold excess of 1 *N* silver nitrate. The precipitate of Ag_2MoO_4 was filtered off and washed with 0.5% silver nitrate. The excess of silver nitrate was then removed from the filtrate by precipitation with NH_4I, aqua regia was added to the filtrate, and the mixture heated with simultaneous addition of nitric acid. Finally, concentrated sulphuric acid was added, the solution was heated until the appearance of heavy fumes, diluted with distilled water, and electrolysed. An invisible radioactive film was obtained on the electrode surface.

The first "visible" specimens of technetium compounds were obtained by Parker and coworkers[39], who isolated it in milligram quantities from uranium fission products by means of remote-manipulation methods. A rod of irradiated uranium was dissolved in 30% hydrochloric acid. The UCl_4 formed was oxidised with 30% hydrogen peroxide to UO_2Cl_2, the excess of H_2O_2 being removed by treatment with liquid bromine. The uranyl chloride solution was treated with $PtCl_2$ and technetium sulphide was coprecipitated with PtS by hydrogen sulphide. The sulphide precipitate was dissolved in a mixture of 30% hydrogen peroxide and 19% ammonia, and then evaporated to dryness. The pink precipitate obtained contained ammonium pertechnate. Further separation was effected by distilling Tc_2O_7 from 18 *N* sulphuric acid. Later studies on the preparation of macroquantities of technetium itself and its compounds are based on this work.

Metallic technetium, approximately 100 μg, was obtained in 1948 by Fried[40], and then in fractions of a gram by many other investigators[41-43]. Fried used very pure ammonium pertechnate, NH_4TcO_4, as the starting material. A hot solution of ammonium pertechnate in 4 *N* hydrochloric acid (technetium concentration 1 mg ml^{-1}) was placed in a conical micro(test-tube) and hydrogen sulphide was passed in. The slowly formed dark-brown precipitate of technetium sulphide (Tc_2S_7) was separated by centrifugation, thoroughly washed, and dried in a vacuum at room temperature. The sulphide was then placed in a quartz capillary; this was joined to an apparatus which provided an atmosphere of hydrogen over the heated specimen and also permitted the removal of volatile and gaseous reduction products. Successive treatment of Tc_2S_7 with hydrogen at 1100° followed by the removal of the volatile products gave the first macrospecimen of metallic technetium. Mooney confirmed, from X-ray diffraction data, that the product was in fact the element[44]. When large quantities of technetium from fission products became available, another group of investigators[45] obtained 0.6 g specimens of spectroscopically pure technetium. The starting material was an isomorphous mixture $As(C_6H_5)_4ClO_4.As(C_6H_5)_4TcO_4$. The precipitate, which is extremely stable to the action of the usual reagents, was decomposed with a mixture of concentrated sulphuric and perchloric acid. About 0.2 g of technetium [initially present in 3–4 g of $As(C_6H_5)_4ClO_4$], dissolved in 1000 ml of concentrated sulphuric acid, was electrolysed for 24 h in a cell with a large platinum cathode (current density 10 mA cm^{-2} at 2–3 V). The black precipitate formed as a result of electrolysis was transferred to a glass distillation apparatus and dissolved in a mixture of 5 ml each of concentrated nitric, perchloric, and sulphuric acids. After the initially very rapid dissolution ceased, the technetium was distilled from perchloric acid as Tc_2O_7 into dilute ammonia solution. The distillate was acidified with hydrochloric acid, treated with bromine water, and then technetium sulphide was precipitated; its coagulation was accelerated by heating on a water-bath. The freshly precipitated technetium sulphide readily dissolved in a mixture of NH_4OH and H_2O_2. The mixture of $(NH_4)_2SO_4$ + NH_4TcO_4 formed on evaporation of the solution was reduced with hydrogen in a platinum boat. The first stage was carried out at low temperature to avoid loss of technetium through sublimation of the lower oxides. In the final stage at 500°–600°, $(NH_4)_2SO_4$ sublimed off and very pure specimens of metallic technetium were obtained.

PROPERTIES OF METALLIC TECHNETIUM

Metallic technetium is a silver-brown* mass, tarnishing in moist air. X-Ray diffraction studies[46-48] have established that metallic technetium has a hexagonal close-packed structure, fully analogous to the neighbouring elements — rhenium, ruthenium, and osmium. The unit cell contains two atoms and has the following parameters: $a = 2.735 \pm 0.001$ Å; $c = 4.391 \pm 0.0001$ Å. The density calculated from X-ray diffraction data (on the assumption that the atomic weight is 99) is 11.487 g cm^{-3}. The atomic weight determined from chemical analysis of milligram quantities of Tc_2O_7 was found to be 98.8 ± 0.1,[45] in fair agreement with the mass-spectrographic determination (98.813). The melting point of technetium should be about 2300°. Among other physical properties the comparatively recently established superconductivity of technetium is noteworthy[49]. The critical temperature (the temperature at which superconductivity becomes apparent) for elemental technetium is highest among those known for elements (T_{cr} = 11.2°K). The superconductivity was studied with ^{99}Tc specimens of high purity (99.9%). The paramagnetic susceptibility is 2.5×10^{-6} g^{-1} at 102°K, 2.7×10^{-6} g^{-1} at 298°K, and 2.9×10^{-6} g^{-1} at 780°K, *i.e.* it is much greater than for rhenium[50]. One of the most interesting nuclear properties of ^{99}Tc is its very low capture cross-section for thermal neutrons.

According to Fried's data[40], subsequently confirmed by Cobble *et al.*[45], metallic technetium does not dissolve in cold or hot concentrated or dilute hydrochloric acid. Unlike metallic rhenium it does not appreciably dissolve in a mixture of hydrogen peroxide and aqueous ammonia. The metal readily dissolves in aqua regia and in nitric acid. On combustion in oxygen, technetium yields a pink oxide, Tc_2O_7, which is volatile at 300°. Elemental technetium reacts with much greater difficulty with chlorine than does rhenium.

Although the specific activity of pure technetium is small (17 mc mg^{-1}), it can on occasion present a serious radiation hazard. Its dry preparations give a radiation dose at the surface of 10 r h^{-1} per 100 mg. Fortunately the radiation from technetium (β-particles with maximum energy of 300 keV) is almost completely absorbed by the walls of the usual chemical ware. Data on the specific radiological toxicity of technetium are not at present available.

COMPOUNDS OF TECHNETIUM(VII)

The +7 oxidation state is the most stable and characteristic one of technetium. This state arises as a result of direct high-temperature oxidation of technetium with oxygen and also when its solutions are treated with reagents such as nitric acid, aqua regia, etc.[51] The existence of the heptavalent state, and in particular of the pertechnate ion, was established in the early stages of the study of the chemistry of technetium from purely radiochemical investigations. The presence of heptavalent technetium in solutions is also indicated by its coprecipitation with perrhenates and perchlorates. Segrè *et al.*[27], studying the possibility of the separation of technetium from its closest analogue, rhenium, determined the crystallisation coefficient* for the $KReO_4-KTcO_4-H_2O$ system. The experiments were carried out as follows. To a solution of $KReO_4$ a definite quantity of a technetium solution was added. The mixture was partly evaporated at a constant temperature, until crystals appeared, and then the activity of the crystals and the mother liquor was determined. The mean value of the crystallisation coefficient was found to be 2.6; however, the values obtained from separate experiments varied between 2.2 and 3.7. The considerable scatter was apparently due to insufficiently defined experimental conditions and to the imperfect technique of the measurements. Similar experiments made with caesium perrhenate as the macrocomponent yielded a crystallisation coefficient of 0.75. Other possible carriers for heptavalent technetium (the pertechnate ion) are thallium, nitron, and tetraphenylarsonium perrhenate[45].

It is probable that, like rhenium, technetium distils as Tc_2O_7, formed by dehydration of $HTcO_4$. The high volatility of technetium(VII) has been observed in various experiments: (a) after deuteron bombardment of a target made from compressed molybdenum trioxide with added rhenium, technetium sublimes together with Re_2O_7 when the mixture is heated to 550° in a stream of oxygen, the MoO_3 remaining in the target[15]; (b) when a mixture of technetium and rhenium is distilled from concentrated perchloric acid, technetium appears in the first fraction, whereas rhenium distils only in the last fractions; (c) in the distillation from hot concentrated sulphuric acid solutions technetium volatilises showly, whereas rhenium distils over quickly and quantitatively. When such solutions are treated with a strong oxidising agent (for example potassium dichromate), technetium volatilises more rapidly and more fully than rhenium[52,53].

Chromatography of very dilute solutions of technetium[38] has shown that it is present in anionic form in $H_2SO_4 + HNO_3$ solutions. When such solutions are passed through a column of "acid" alumina (known to absorb anions) technetium is fully absorbed; but it is not absorbed on "basic" alumina which is known to absorb cations. When solutions of technetium are treated with certain reducing agents (HCl, $SnCl_2$, etc.), definite changes in its chromatographic behaviour take place. These changes (decrease in the absorption on "acid" alumina and increase in the absorption on the "basic" form) may be related to the reducing action of these reagents, *i.e.* to a transition from the anionic to cationic form of technetium.

Hall and Johns[54] studied the ion exchange of technetium(VII) in very dilute solutions on IRA-400 anion-exchange resin. In alkaline solution, technetium, like molybdenum, is retained on the resin; when molybdenum is eluted with 10% sodium carbonate or 1 *N* $K_2C_2O_4$, technetium remains on the resin, but can be subsequently eluted with 0.5 M solution of sodium thiocyanate. These data show that in

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* Boyd [J. Chem. Educ., 36, 3 (1959)] states that technetium is a silver-*grey* mass (Ed. of Translation).

* This was termed the 'partition coefficient between solution and solid salt' by the original authors (Ed. of Translation).

very dilute acid solutions technetium is present as the anion TcO_4^-.

The redox potential for the process $Tc \rightarrow TcO_4^-$ has been calculated from the results of experiments on cathodic reduction in very dilute oxidised solutions of technetium and from a comparison with the standard redox potentials for the processes $Mn \rightarrow MnO_4^-$ and $Re \rightarrow ReO_4^-$. The resulting potential, -0.41 V, lies between -0.78 (standard redox potential for the reaction $Mn + 4H_2O = MnO_4^- + 8H^+ + 7e$) and -0.15 (standard redox potential for the reaction $Re + 4H_2O = ReO_4^- + 8H^+ + 7e$). [38,55].

The studies of Boyd and coworkers[41] on macroquantities of technetium have produced quite convincing evidence of the existence of the higher oxide Tc_2O_7 and the corresponding acid, $HTcO_4$. Fried[40], who first studied the combustion of metallic technetium, suggested that the oxide formed has the formula TcO_3. However, later studies showed that the formula is Tc_2O_7. In these experiments, Boyd[41] burnt a quantity of metallic technetium in dry oxygen at 400°–600°. The light, yellow hygroscopic oxide formed (m.p. 113° ± ± 0.1°) was purified by sublimation in a quartz tube. A definite quantity was dissolved in water and titrated potentiometrically with 0.05 M ammonia solution. The curves obtained were characteristic of strong monobasic acids. The neutralised solution was evaporated to dryness in a platinum dish at 95° and the residue weighed. Results of two such experiments are summarised in Table 3. It is interesting that, as shown by X-ray diffraction studies, the oxide is not isomorphous with the analogous rhenium compound.

In further experiments Boyd and coworkers[41] isolated a hydrate of Tc_2O_7 and established its composition. A 1 M aqueous solution of Tc_2O_7 was slowly evaporated at room temperature over concentrated sulphuric acid. The solution became first yellow, then dark yellow, dark red, and finally dark-red hygroscopic crystals separated. These, on being left in air, avidly absorbed water. It was suggested that the crystals were of the hydrate $Tc_2O_7.H_2O$. A solution containing an exact quantity of the hydrate was neutralised with ammonia, evaporated, dried, and the weight of the residue (NH_4TcO_4) determined. The results of the analysis of the yellow-red substance obtained on evaporation of an aqueous solution of Tc_2O_7 at constant temperature are given in Table 4, which shows that the composition of the dark-red crystals corresponds to the formula $Tc_2O_7.H_2O$ or, in other words, to "anhydrous $HTcO_4$". Thus, unlike the colourless perrhenic acid, the corresponding acid of technetium is intensely coloured. The form of the potentiometric titration curves shows that pertechnic acid is a fairly strong monobasic acid..

TABLE 3.

Wt. of ppt., mg	No. of milliequiv. expected for Tc_2O_7	No. of milliequiv. expected for TcO_3	Milliequiv. of OH^- required for neutralisation
157.7 70.11	1.017 0.4524	2.146 0.9538	1.019 0.4561
milliequiv. of NH_4TcO_4 obtained			1.020 0.4564

TABLE 4.

Wt. of Tc_2O_7 hydrate, mg	Wt. of NH_4TcO_4 formed, mg	Mol. wt. of hydrate	Tc_2O_7 : : H_2O
98.1	108.5	327.4	0.97
98.5	108.5	328.6	1.02

Some salts of pertechnic acid have been obtained in weighable quantities. For example, ammonium pertechnate (NH_4TcO_4) may be obtained by direct neutralisation with ammonia and evaporation of an aqueous solution of Tc_2O_7, or by evaporation of a solution obtained by dissolving Tc_2S_7 in a mixture of NH_4OH and H_2O_2. Pure NH_4TcO_4 is a crystalline non-hygroscopic pink substance which shows no signs of decomposition on heating at 100° for several hours. The salts NH_4TcO_4, $KTcO_4$, and $AgTcO_4$ have the structure of the $CaWO_4$ type[47]. Aqueous solutions of pertechnate absorb intensely in the ultra-violet, which fact may be used for the quantitative determination of technetium. At wavelengths of 2470 Å and 2890 Å, Beer's law holds up to 10^{-3} M concentrations of pertechnate ions. It is possible to determine in this way as little as 10^{-8} g of technetium[41].

The reduction of pertechnate ions in very dilute solutions with various reagents has been studied[27]. Zinc, tin, nickel, lead, mercury, and copper in sulphuric acid solutions, and a 1 : 1 mixture of concentrated hydrochloric acid and 20% stannous chloride solution lead to quantitative precipitation of technetium. This shows that the TcO_4^- ion is reduced either to free technetium or to an insoluble oxide.

The preparation of weighable quantities of pure Tc_2O_7 and $HTcO_4$ allowed their thermodynamic properties to be investigated; they are of considerable interest for the more profound understanding of the chemistry of the elements in the second subgroup of Group VII in the Periodic System. The vapour pressures of $HTcO_4$ and its solutions have been determined. The vapour pressures over solid and liquid Tc_2O_7 at 20° are 0.65 and 1.0 mm Hg respectively. The variation of the vapour pressure of the solid and liquid technetium oxide can be expressed by the following equations:

$$\log P \text{ (mm)} = -\frac{7.969}{T} - 8.97 \log T + 41.11,$$

$$\log P \text{ (mm)} = -\frac{6264}{T} - 12.59 \log T + 48.36.$$

When hydrogen sulphide is passed through acid solutions of pertechnates, technetium(VII) sulphide is formed. Parker and coworkers[39] found that technetium sulphide may be coprecipitated with carriers (rhenium and copper) from 100 ml of solution acidified with aqueous hydrochloric acid (0.4–5 *N* HCl). This was studied in detail in an examination of the dependence of the precipitation of microquantities of technetium on time and on the concentration of hydrochloric acid[24]. There are also indications that technetium sulphide may be precipitated from ammonia solutions. Technetium sulphide is often the end-product in general schemes for the purification and concentration of the element.

The sulphide readily dissolves in a cold mixture of ammonia and hydrogen peroxide, yielding a light-green solution. It is also soluble in cold ammonia itself, like Re_2S_7. Somewhat unexpectedly, Tc_2S_7 is insoluble in ammonium polysulphide solution despite the fact that the latter contains an excess of NH_4OH. Further studies with weighable quantities of the material should explain these results.

When a solution of $KTcO_4$ in 18 M H_2SO_4 is treated with 12 M HCl, TcO_3Cl is formed; this can be extracted with carbon tetrachloride, chloroform, or hexane[56]. Another oxyhalide of technetium, TcO_3F, is formed when $HTcO_4$ or Tc_2O_7 reacts with UF_4.[57] Technetium(VII) can be readily reduced to lower oxidation states with hydrochloric acid, thiocyanate[58], and anion-exchange resins[59].

COMPOUNDS OF TECHNETIUM(VI)

The existence of technetium(VI) has been revealed by polarographic studies[60]. Polarography of alkaline (2 *N* NaOH) solutions of heptavalent technetium has revealed waves corresponding to the reduction of technetium(VII) to technetium(VI) and of technetium(VI) to technetium(II). Furthermore, the hexavalent state arises in the reduction of heptavalent technetium with "mild" reducing agents (for example hydrazine hydrate) in alkali in the cold, and in the irradiation of molybdenum blue with neutrons. Technetium(VI) is not extracted with ketones and pyridine and is not appreciably coprecipitated with ferric hydroxide. However, it is quantitatively coprecipitated with the 8-hydroxyquinoline complex of molybdenum and with silver and lead molybdates.

Comparison of the standard redox potentials of the MnO_4^{2-}/MnO_4^- and ReO_4^{2-}/ReO_4^- systems in alkali solutions, -0.567 and 0.7 V, suggests that under analogous conditions the potential of the TcO_4^{2-}/TcO_4^- system should be about 0.2 V. This indicates that in alkaline solutions technetium(VI) should be relatively stable. However, according to Boyd[67], technetium(VI) in aqueous solutions should disproportionate to the (IV) and (VII) states. These processes should be faster, the lower the alkalinity of the solution, and in fact, when an alkaline solution of technetium(VI) is diluted so that the alkali concentration falls to 0.02 – 0.05 *N*, disproportionation does take place. At equilibrium, the ratio of the +7 and +4 forms is 2 : 1, whereas the +6 form has almost completely disappeared. The disproportionation apparently takes place similarly to that of manganese and rhenium:

$$3TcO_4^{2-} + 2H_2O \rightleftharpoons 2TcO_4^- + TcO_2 + 4OH^-.$$

COMPOUNDS OF TECHNETIUM(V)

The existence of technetium in the +5 state of oxidation can only be inferred from polarographic studies of technetium(VII) solutions. Polarographic reduction of technetium(VII) in 1 M solution of hydrochloric acid yielded two waves, one of which was due to the reduction of technetium(VII) to technetium(V).[33] When TcO_4^- is reduced in 6 – 8 M HCl at 100°, technetium in the +5 state is formed during the first 2 h, and can be extracted with xylene (partition coefficient > 30)[62].

COMPOUNDS OF TECHNETIUM(IV)

The existence of technetium compounds in the +4 state of oxidation has been established with certainty. The first evidence of this was obtained in experiments with sub-microquantities of technetium, which showed that the element is quantitatively precipitated with platinum(IV) sulphide from acid solutions (0.25 – 11 M H_2SO_4). The behaviour of very small quantities of technetium in acid solutions is very reminiscent of the behaviour of manganese dioxide. Like rhenium[63], technetium(IV), in the presence of the thiocyanate ion, is extracted with ethyl ether from 3 *N* hydrochloric acid; the species extracted appears to be the complex ion $Tc(SCN)_6^{2-}$.

In 1953 Cobble and coworkers[64], using microquantities of technetium, developed a number of methods for the preparation of the dioxide. TcO_2 is obtained when aqueous solutions of NH_4TcO_4 are reduced with zinc and hydrochloric acid or by pyrolysis of NH_4TcO_4. According to Nelson and coworkers[50], the product obtained by the reduction of ammonium pertechnate with zinc and hydrochloric acid has the composition $TcO_2 . 1.6H_2O$. The composition and structure of the oxide obtained by pyrolysis were established by chemical and X-ray analyses. Technetium dioxide can also be obtained by the electrolytic reduction of technetium(VII) at a platinum electrode[60] in alkaline solution.

Compared with the analogous oxides of manganese and rhenium, technetium dioxide is more stable to heat. Whereas MnO_2 loses oxygen at high temperatures to form MnO, and ReO_2 disproportionates to Re and Re_2O_7, TcO_2 volatilises without decomposition. On heating to 300°, $TcO_2 . 1.6H_2O$ is completely dehydrated, and at 900° – 1100° the anhydrous TcO_2 distils. X-Ray analysis of the distillate has shown it to be identical with the TcO_2 obtained by pyrolysis of $HTcO_4$.

Technetium dioxide reacts with chlorine on heating to 300°, yielding readily hydrolysable products which can be separated by distillation. In oxygen or in air the dioxide is oxidised to Tc_2O_7.

Using macroquantities of technetium, Nelson[50] obtained another compound of technetium(IV), K_2TcCl_6, by reducing ammonium pertechnate with potassium iodide in hydrochloric acid solution. X-Ray analysis has shown that the compound has a cubic lattice and is isomorphous with the analogous rhenium compound. It hydrolyses in more acid solutions than the rhenium analogue, yielding hydrated technetium dioxide, $TcO_2.2H_2O$.

Technetium(IV) chloride was obtained by allowing carbon tetrachloride to react with Tc_2O_7 at 400°, the yield being 79%. $TcCl_4$ consists of fine, blood-red, easily hydrolysable crystals[65]. It is interesting that under these conditions rhenium yields $ReCl_3$ and $ReCl_5$. Thus in this respect technetium resembles more closely manganese than rhenium. Furthermore, $TcCl_4$ can be readily obtained in the pure state, showing it to be more stable than $MnCl_4$.

COMPOUNDS OF TECHNETIUM IN +3, +2, +1, and -1 OXIDATION STATES

Compounds of technetium(III), predicted by Noddack[12], are completely unknown although rhenium(III) compounds have been studied in some detail.

The evidence for the existence of technetium(II) is unreliable. Indications of its existence come from polarographic studies and from studies on the coprecipitation of technetium with divalent-metal sulphides (copper and cadmium)[66].

There appear to be no data at present on the existence of technetium(I). The corresponding rhenium compounds are obtained by reducing a dilute solution of perrhenic acid with zinc and hydrochloric acid. The black precipitate formed is soluble in nitric acid and bromine water, its composition corresponding to $Re_2O.H_2O$.

The evidence for the existence of technetium in the -1 state of oxidation comes so far only from polarographic studies[67]. However, the corresponding rhenium compounds have been studied and isolated in a fairly pure state.

METHODS FOR THE ISOLATION OF RADIOACTIVE TECHNETIUM ISOTOPES

The methods at present available for the isolation of technetium isotopes from fission products or from cyclotron targets can be divided into the following principal classes.

1. Extraction[35,39,68–73].
2. Chromatographic[54,74–80].
3. Distillation[15,52,53,81].
4. Electrochemical[82].

The method described by Tribalat[68] for the separation of technetium from uranium-fission products is an example of the extraction methods. Irradiated uranium oxide is dissolved in dilute H_2SO_4, the solution is treated with ammonium persulphate, and the elemental iodine formed is extracted with toluene. The aqueous solution is boiled, neutralised with $(NH_4)_2CO_3$, and again treated with ammonium persulphate. Technetium(VII) is then extracted with a chloroform solution of tetraphenylarsonium chloride. Radiochemically-pure technetium preparations are obtained in this way.

Chromatographic methods for the isolation of technetium have found wide application recently. A method using anion-exchange resins, IRA-400 and others has been described[54]. Neutron-irradiated metallic molybdenum is dissolved in 10% NaOH in the presence of 30% H_2O_2. Under these conditions technetium is present as sodium pertechnate. The excess of H_2O_2 is removed by boiling, and the solution is passed through a chromatographic column filled with Amberlite IRA-400 resin in perchlorate form. Molybdenum can be eluted from the column with 10% NaOH, technetium being firmly held by the resin under these conditions. It can be subsequently eluted with ammonium thiocyanate solution. Kuzina and Spitsyn[83] have described a chromatographic purification of technetium concentrates isolated from neutron-irradiated MoO_3. Technetium is purified by passing the concentrate in nitric acid solution (pH 2) through KU-2 cation exchanger.

Methods based on the distillation of technetium oxide at 550°, or of technetium(VII) from H_2SO_4 in a weak current of air, are very convenient in a number of cases. Lincober and coworkers[52] and Glendenin[53] isolated technetium by distillation from perchlorate solution. To remove traces of molybdenum, the distillation was repeated several times. However, ruthenium, as RuO_4, also distils from perchlorate solution, but can be separated from the distillate by reduction with alcohol which precipitates a mixture of ruthenium(III) and ruthenium(IV) oxides which are sparingly soluble and do not entrain technetium(VII).

An electrochemical method for the isolation of technetium has been described by Barrett[82].

Methods for the separation of technetium from its closest analogue, rhenium, have considerable importance since the latter is often used as a carrier for technetium. The following methods are at present available.

1. A mixture of Tc and Re metals or sulphides is distilled in a stream of chlorine as the chlorides. Rhenium is distilled from the product at 300° in a vacuum, and technetium chloride decomposes, the metal remaining in the residue[84].
2. Technetium and rhenium can be separated by virtue of the fact that technetium sulphide is soluble in 9 *N* HCl, whereas rhenium sulphide is not. Repeated precipitation of Re_2S_7 with hydrogen sulphide from 9 *N* HCl leads to complete separation.
3. In a convenient chromatographic method[74], the sulphides of rhenium and technetium are dissolved in ammonia and the solution is passed through a Dowex-2 (sulphate form) column. Both elements are retained on the resin, but technetium can be eluted with 0.1 M ammonium thiocyanate solution at pH 8.3 – 8.5.
4. Technetium can be separated from rhenium, as TcO_2, by electrochemical reduction at a platinum cathode at 1.1 V. The concentration of technetium should not exceed 10^{-4} M and must be lower than that of rhenium[60].
5. For the separation of small quantities of radioactive technetium and rhenium isotopes, a method based on the different stabilities of the phthalocyanine complexes of the two metals is used.

APPLICATIONS OF TECHNETIUM

As already mentioned, the most long-lived technetium isotope (^{99}Tc) has an extremely low neutron-capture cross-section. This, together with its exceptional stability to corrosion, makes metallic technetium suitable for use in the construction of reactors[85] (at present this is being done). In view of its corrosion inhibiting properties [for iron and steel (Ed. of Translation)], it may find application in the manufacture of precision instruments[61]. It is also very probable that technetium may be employed as a semiconductor.

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THE EVOLUTION OF BIOCATALYSTS

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CONTENTS

I. INTRODUCTION

There are a number of different aspects to the evolution of biological catalysts which are of interest to a wide circle of chemists. The first appears from a comparison of the effects achieved by our ordinary catalysts with the virtually unlimited possibilities of the highly organised enzymic systems of the living cell.

Anyone familiar with the difficulties involved in the selection of a suitable catalyst and accustomed to using catalysts at high pressures and temperatures is bound to be impressed by the performance of the biological catalysts, which can oxidise sulphur directly to sulphuric acid at low temperatures, fix nitrogen at atmospheric pressure, synthesise methane, oxidise naphthalene, induce the reaction of hydrogen with oxygen, and form penicillin, polypeptides and proteins. What is more, these catalysts both originate and sustain the processes which we understand by the term "life".

However, our knowledge of enzymes falls far short of that of catalysis, especially so far as the general theoretical principles are concerned. For this reason the theoretical study of the action of biocatalysts deserves close attention.

The organic catalysts and the "models" of enzymes are obviously less difficult objects of study, and the advances achieved with a series of models provide the foundation for a development of theoretical concepts. Such concepts will be different from those inferred from a study of non-enzymic catalysis; and, in particular, it should be kept in mind that the theoretical analysis of the action of catalytic systems, characteristic of the living cell, is still in the embryonic stage.

Another aspect is their immediate relation to biochemical evolution. These catalysts, functioning so effectively in nature, are the result of a specific "selection", of whose mechanism we have very little knowledge. For this reason a comparison between enzymes and those compounds whose properties are similar to those of the biological catalysts merits especial attention. Such a comparison shows at once that although there is a very large number of "similar" substances, the types of structures inherent in enzymes are considerably fewer.

The purpose of the present review is not so much to describe different pathways of varying plausibility for the chemical evolution of biocatalysts, but rather to analyse the physicochemical properties of the relatively small number of the biocatalysts "selected" to be a basis for the catalytic mechanisms of life.

We shall attempt to characterise the possible catalytic reactions of the non-biogenic stage — processes which prepared organic compounds for a higher form of organisation and which represent a transition towards the biological evolution proper. We shall then consider the properties of the catalytic processes in biological specimens as we find them today. After briefly describing the most important aspects of protein biocatalysts, we shall deal with those innumerable compounds which can model the functions of proteins and enzymes, in particular the metal complexes.

A comparison of the properties of the two types of compounds can bring out certain important features concerning the selection factors.

We shall conclude by analysing the general tendencies in the development of catalytic systems united by different kinds of bonds, and their thermodynamic aspect.

Information about the actual pathways of the synthesis of biocatalysts is very sketchy, but even more so is our knowledge of their changes in the course of time.

Since life began to develop some 10^9 years ago[1], the structures that the biocatalysts acquired in the course of evolution can be taken to reflect the general principles governing the totality of processes in an open system — a system involving a "flux" of energy throughout the long period of its existence. Thermodynamics gives no general answer to the question as to how a system which is continuously subjected to the different energy influences of the outside world and which changes its mass would evolve. Biological specimens provide experimental material (obtained without the participitation of the experimenter) from which we can judge what exactly is happening in such a system. At this point the question may be asked: why are we so concerned only with enzymes? The answer is that all the processes which the cell uses to sustain its existence, or, from the chemist's viewpoint, to provide the required level of stability, are catalytic; in the words of I.P.Pavlov, the enzymes are the very "originators of life". The development of catalytic and autocatalytic functions is one of the most characteristic signs of biochemical evolution. If the equilibrium in isolated thermodynamic systems is described by extremal values of the characteristic functions, then its analogue for the constantly developing systems is the establishment of stable and reproducible structures with low entropy, which are capable of producing entropy by means of catalytic mechanisms. Thus, the quasi-equilibrium in an open system is characterised by the reproduction and development of a structure which is protected from chaotic decomposition by systems of co-ordinately functioning catalysts.

In his report at the symposium on the origin of life Calvin[1] pointed out that autocatalysis was one of the selection factors operating throughout the period of chemical evolution. As an example he cited the system consisting of bivalent copper ions and molecular hydrogen; this system is stable as long as it does not contain an ion of monovalent copper; if by any chance this ion appears, it catalyses the reduction of bivalent copper by hydrogen with practically complete conversion. This is undoubtedly autocatalysis — one of the most manifest agents of selection.

Nevertheless, autocatalytic processes are incomparably less frequent than catalytic ones, and primary process may be postulated to account for the preservation of certain types of molecules. Out of a multitude of reactions which take place in a mixture of compounds, a particular compound A is not affected or changed by precisely that process which it catalyses. This is true even if A catalyses several reactions. Hence, the molecules which are least changed in a complex of reactions are those catalysing the largest number of processes; they "outlive" the others, and ultimately form a catalytic system capable of warding off practically all the chemical attacks inherent in a given medium, *i.e.* a system compatible with the maximum number of reactions. This is exemplified by the development of the enzymes of the oxidase type, which are stable to the action of oxygen, and yet catalyse its use in the synthesis of the compounds which are necessary for the reproduction of the whole system.

These organisms are well adapted precisely to those media in which autocatalysis and "compatibility" initiated their development. Put in completely hostile media, they perish as a result of non-catalytic processes. Organisms can survive if they are capable of building new types of catalysts which can eliminate the destructive influences. Thus, most insects die under the effect of certain chlorine derivatives, *e.g.* DDT, but some resistant species are capable of producing an enzyme which destroys DDT by splitting off hydrogen chloride; in other words they owe their survival to a catalytic mechanism. This is the general principle of all protective processes which organisms use for keeping their structure unchanged, and for counteracting all noxious substances.

At the outset of chemical evolution, catalysis played only a subsidiary role. The main factors were radiation and electrical discharges, and the reactions probably propagated by means of radical diffusion. Calvin estimates that chemical evolution began about 2.5×10^9 years ago[1].

According to Rubey, the earth's first atmosphere consisted of carbon dioxide, nitrogen, carbon monoxide, and water vapour; Oparin thinks that in the early stages of development the earth had a reducing atmosphere, containing methane, ammonia, water, hydrogen sulphide, and hydrogen[2,3].

It is extremely difficult to assess what sort of reactions were possible in the earth's atmosphere and on its surface in the pre-biological period. Our only criterion is the thermodynamic possibility of a particular process; but even there we are very often limited by our ignorance of the temperatures and pressures which existed at the time. It is even more difficult to compare the number of the most probable non-catalytic reactions with the processes which probably took place in the presence of catalysts.

The non-catalytic processes which undoubtedly played an important role in the pre-biological period were the following: (1) the photochemical decomposition of water followed by the oxidation of ammonia to nitrogen, and of hydrocarbons to alcohols, aldehydes, and acids; (2) the photochemical decomposition of ammonia resulting in the formation of free radicals and hydrazine, and probably of a whole series of nitrogen-containing organic compounds; (3) the photochemical decomposition of methane and its conversion to other hydrocarbons, notably olefines; (4) the photochemical formation of formaldehyde from carbon dioxide and water; (5) the formation of methylamine from methane and ammonia (at 500°); (6) the condensation of acetylene with formaldehyde, and with other organic compounds, such as alcohols, esters, etc.; (7) the reaction of methane or ethylene with carbon monoxide in the presence of an electric discharge, forming aldehydes; (8) the reaction of nitrogen with acetylene in the presence of an electric discharge, to give hydrogen cyanide; (9) the reaction of hydrogen cyanide with acetylene, yielding pyridine; (10) the reaction of carbon monoxide with ammonia in the presence of an electric discharge, forming urea; (11) the formation of mercaptans from olefines and hydrogen sulphide; (12) the formation of phosphoric acids as a result of the chain oxidation of phosphine; (13) the formation of cyanamide; (14) the formation of phosphoguanidine from cyanamide and ammonium phosphite[3].

Miller carried out a series of experiments which attracted considerable interest. He subjected a mixture of hydrogen, methane, ammonia, and water vapour to the action of an electric discharge generated by a high-frequency Tesla apparatus. In some experiments he also used a silent discharge. The analysis of the products obtained gave considerable quantities of glycine, alanine, sarcosine, aspartic, glutamic, and formic acids, together with a series of other organic compounds. The addition of iron ammonium alum to the system caused no essential change in the qualitative or quantitative composition of the reaction products[4].

In an attempt to verify Oparin's view that ultra-violet radiation from the sun was one of the fundamental sources of energy in the pre-biological period, Pavlovskaya and Pasynskii irradiated a mixed solution of formaldehyde, nitrates, and ammonium chloride for 20 h with the light of a PRK-2 lamp, and obtained a series of amino-acids[5].

In Urey's opinion, organic compounds were formed in the atmosphere as a result of the action of ultra-violet radiation and electric discharges[6]. Miller thinks that hydrogen atoms, formed by the photolysis of methane, ammonia, or water, reacted with carbon monoxide yielding formaldehyde or glyoxal; active nitrogen was able to react with methane and other hydrocarbons, yielding hydrocyanic acid. It seems that this process involved the participation of H atoms and NH_2 radicals. High-energy radiation probably played a subsidiary role. In 1951–1952 some organic compounds were synthesised from carbon dioxide and water by the action of fast α-particles from a 40 MeV cyclotron. Formic acid was produced in small amounts; formaldehyde was formed only in the presence of iron ions, which, in Miller's view, served as reducing agents; oxidative conditions, apparently, are not favourable for the synthesis of organic compounds[7].

We shall not consider the other more complicated processes whose non-catalytic character is doubtful. Instead, we shall deal with a number of reactions which proceed in the presence of catalysts. The hydration of ethylene and acetylene is catalysed by the oxides of aluminium, tungsten, mercury, and by other catalysts. The reaction of acetylene with hydrogen sulphide or water yields heterocycles. For instance, furan can be obtained in the presence of aluminium oxide. This reaction proceeds at 425°, but is thermodynamically possible up to 800°; the formation of thiophen is possible up to 250°. Aluminium oxides (bauxites) catalyse the condensation of acetylene with ammonia; at 300° the oxides of aluminium, chromium, and iron catalyse the formation of pyrrole, as well as pyridine, from acetylene and ammonia.

Bakhadur showed that the action of sunlight on solutions of paraformaldehyde containing potassium nitrate and iron chloride produces valine, lysine, serine, and other amino-acids[8]. It is possible therefore that iron ions served as catalysts in photochemical processes. The same author observed that colloidal molybdenum oxide could catalyse the formation of amino-acids by the action of electric light upon a mixture of water and paraformaldehyde. Air was the source of nitrogen in these experiments.

The present author's work with Barshchevskii[9] has demonstrated that zinc oxide contaminated with copper, lead, and other heavy metals, is an active photocatalyst in processes involving hydrogen transfer†. Oparin expressed the opinion that rocks and minerals[3] could act as catalysts in polymerisations of acetylene — one of the first products formed during the cooling of the earth (from water and carbides).

In 1955 Akabori put forward the hypothesis that the precursors of proteins could have been formed by a reaction between formaldehyde, ammonia, and hydrogen cyanide, yielding aminoacetonitrile, followed by polymerisation and hydrolysis of the latter compound on the surface of clays. In subsequent reactions side-chains would be introduced into the polyglycine molecule formed. Akabori[11] showed that heating of aminoacetonitrile with acid clay yielded a product with positive biuret reaction; on the other hand, treatment of polyglycine deposited on kaolinite by formaldehyde or acetaldehyde in the presence of a basic catalyst (pyridine) resulted in the formation of serine and threonine groups. The author thinks that the methylene groups in polyglycine adsorbed on kaolinite are more reactive in the condensation with aldehyde than they are if no carrier is used. In Bernal's opinion, life could originate on the surface of clays as a result of an accumulation there of organic compounds[12]. In a reducing atmosphere, silicates, sulphides, and oxides could catalyse polymerisations and a series of other reactions, connected with the conversion of hydrocarbons. Interesting model experiments in this field were carried out by Frost, who in his theory on the origin of petroleum ascribed a major role in the formation of this product to the catalytic action of clays[13].

It should be remembered that ions of copper, manganese, iron, and other metals are capable of catalysing hydrogen transfer from donors, which thereby undergo oxidation, to acceptors, which include, apart from oxygen, reversibly reducible compounds such as some dyes. Processes of this type did not develop until later, and led to the formation of metalloflavoprotein systems. The present author has recently established that hydrogen transfer from cysteine and ascorbic acid to various dyes is catalysed by copper ions[14]; it is likely that hydrogen transfer in a reducing atmosphere was also catalysed by metal ions.

A characteristic feature of biocatalysis is the formation of energy-rich phosphorus compounds and their subsequent utilisation in synthesis. As one of the forerunners of the highly developed mechanisms in the living organisms, Calvin considered the orthophosphate-pyrophosphate system containing iron[1]. He emphasised the fact that the hydrolysis of pyrophosphates was generally a very slow process, and that organisms gradually developed catalytic systems for accelerating it and for making effective use of the energy liberated. The participation of metal ions in oxidative phosphorylations has been proved. The conversion of ferrous orthophosphate to ferric pyrophosphate sets free electrons which can be transferred to oxygen; this process combines the oxidation of the ferrous ion (which is exergonic) with the conversion of orthophosphate to pyrophosphate (which is endergonic). In Calvin's opinion, the effectiveness of this process increases if iron forms a compound with an organic molecule which makes its action specific. Organisms containing these efficient complexes have a better chance of survival than those which do not contain iron in the catalytically active form.

To sum up this short outline of the function of catalysts in the early stages of chemical evolution, we conclude that the initial accumulation of simple compounds was achieved mainly through the effect of non-catalytic factors. Catalysis played only a limited part in some photochemical reactions, in the formation of hydrocarbons and heterocycles, in the

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† According to the data of Shub, Tyurikov, and Veselovskii, the photoexcitation of iron oxide, which is a semiconductor, enables it to initiate the decomposition of hydrogen peroxide[10].

formation and polymerisation of hydroxynitriles, in the transformations of amino-acids, etc. But in subsequent periods the importance of its role in the evolution of organic compounds began to increase at a fantastic rate.

A large number of the new species had catalytic properties; metal ions in the oceans acted as catalysts for an ever-increasing number of different chemical processes; even relatively simple organic compounds possessed catalytic functions. Amines can catalyse the decomposition (decarboxylation) of keto-acids, and, as shown by Langenbeck[15], the activity of some of them can be very high; the present author has shown amines and amino-alcohols to be capable of catalysing the oxidation of polyphenols[16].

It is well known that amino-acids can be dehydrogenated in the presence of hydrogen acceptors (oxygen or various dyes) under the action of isatin and its derivatives[17]; acetamide accelerates the conversion of cyanogen to oxamide; cyanide ions catalyse the condensation of benzaldehyde to benzoin; many transformations involving the addition or the loss of a proton are catalysed by acids and bases. With the development of an oxidative atmosphere oxidations, catalysed by metal ions of variable valency, became increasingly important, etc.

A number of schemes, some soundly, some less soundly based, have been and are being suggested for the formation of compounds which played an important role in biological evolution. Thus, the formation of carbohydrates was undoubtedly influenced by the ability of aldehydes to polymerise and condense in the presence of catalysts — *e.g.* the hydroxides of calcium and barium oxides, or calcium carbonate. Euler and Euler[18] established that glycolic aldehyde and pentoses can be formed from formaldehyde in the presence of calcium carbonate. Hexoses were formed by the condensation of glyceric aldehyde, with the intermediate formation of dihydroxyacetone, in the presence of barium or calcium hydroxides. In all probability processes of this sort took place in the non-biogenic stage. According to Bernal[19], lipoids did not appear till much later; Oparin, however, thinks that they might have been formed before the appearence of life[3].

Amino-acids could have resulted from a number of various reactions. In addition to the work of Bakhadur mentioned above, Fox *et al.*[20] also showed that amino--acids can be formed from malic acid and urea in weakly alkaline media in the presence of calcium salts.

From the moment the "selection" mechanism came into action, the evolution of catalysts in nature began to follow two essentially different paths. Metals, oxides, sulphides, and aluminosilicates formed stable crystal lattices, in which, in the course of time, the stabilisation of new catalytic forms took place, partly through the elimination of defects, partly through the development of more regular structures, and partly through the lowering of the catalytic activity.

The difference between the catalytic activity of the new catalysts and that of the "old" inorganic ones is well known. Natural inorganic catalysts, consisting of oxides, salts, sulphides, etc. evolved into compounds with weakened catalytic activity. This could result in the partial exclusion of such catalysts from the processes which previously they accelerated. They were replaced by another type of catalysts, which we shall call the *biochemical* type.

Some 2 milliard years separate the beginning of the accumulation of organic compounds from the appearance of the first forms of life. This phase of the chemical history of the earth's surface is at once one about which we are most uncertain, and at the same time the most important for an understanding of the progress of biochemical evolution. In that time organic compounds were not accumulating at an accelerating rate — they were formed and decomposed, taking part in the self-reproduction processes characteristic of aperiodic structures.

It is remarkable that the period of the "chemical preparation" — a period of powerful and diverse transformations, about which we can only form cautious hypotheses -- should come to a halt when biochemical evolution began. The development of organisms had on the whole little effect on the basic features of the structure of proteins and enzymes. When Prolone analysed the haemoglobin from the Crossopterygian fish, he found nothing unusual in its amino-acid composition, and indeed it proved to be close to the haemoglobin composition of the vertebrates. Synge thinks that chemical evolution occurred in the past and that the only organisms which survived were those which attained a "standard" chemical composition[21].

Actually, small variations in the amino-acid composition of proteins, which retain a basic structural plan, can apparently give rise to different species of organisms. In this paper we cannot discuss this interesting problem, since we are mainly concerned with the basic structural plan of the most widely distributed biocatalysts.

We conclude that during the period discussed above certain factors led to a selection of the systems which were subsequently to become the structural elements of an infinite variety of living creatures. The majority of the other systems which involved organic reactions had disappeared. At present, the number of organic reactions occurring in nature without the presence of biocatalysts is so small, that it was completely natural for the pioneers in organic chemistry to make an error in so terming this science.

II. PROPERTIES OF PROCESSES ACCELERATED BY BIOCATALYSTS

It can be assumed, as a result of careful analysis, that all the many different metabolic processes occurring in the presence of biocatalysts consist in fact of but a small number of reactions, each involving different substrates, but each with completely distinct general characteristics. The most general characteristic of biochemical processes is that they involve transfer reactions. The group of the so-called transferring enzymes can transfer phosphoric acid radicals, acetyl, methyl, and mercapto groups, as well as the large radicals such as the glycine one (which can be transferred from any peptide to an amino acid). In this way glycyltryptophan is obtained from glycylglycine and tryptophan, glycylphenylalanine from glycylglycine and phenylalanine, etc.

The diversity of the products of protein biosynthesis is undoubtedly connected with enzymes of that type. There are grounds for the assumption that the capacity to catalyse transfer reactions is a characteristic of the hydrolytic enzymes; for instance the transfer of amino-acid radicals is catalysed by papain and chymotrypsin, which are typical hydrolases. It is impossible to find analogues of these biocatalysts in the field of ordinary catalysis, but there is no doubt that transferring enzymes played a large part in the adaptation, selection, and perfection of the enzyme systems;

it was through their activity that different materials were formed for the synthesis of proteins and sugars, and, in the long run, of enzymes themselves.

The transferring enzymes played an important part in the biosynthesis of sugars, particularly in the interconversion of polyfructosides and sucrose. In artichoke tubers there is an enzyme which catalyses the transfer of fructose radicals from inulin to sucrose and free fructose[22].

Hydrogen transfer has an unusual place among the transfer processes. It seems that the mechanism of hydrogen transfer consists generally in the transfer of an electron along a chain of donors and acceptors, whereby the molecule, which finally becomes negatively charged, acquires a hydrogen ion from its surroundings: Kluyver[23] has suggested the name transhydrogenation for this reaction. There are data, however, which support the theory of direct transfer of hydrogen atoms[24]. The significance of hydrogen transfer is so great, that Kluyver[23] considers the transfer reactions to occupy a dominant position amongst the fundamental processes which "constitute biochemistry". These processes can be represented by the following equations:

$$AH \rightarrow A + BHB,$$

$$AHB \rightarrow ABH,$$

$$AHB \rightarrow A + BH,$$

$$AH + B \rightarrow ABH.$$

The role of proteins in the processes connected with electron transfer was partly explained in the work of Geissman and Blyumenfel'd[25] which showed that electrons can be transferred from one polypeptide chain to the other along hydrogen "bridges".

All the catalytic processes, both now and in the early stages of biochemical evolution, can clearly be divided into two classes. The first consists of all the transformations which utilise the differences in the chemical potentials existing in nature to synthesise compounds which contain energy-rich bonds. The second class consists of those processes in which this energy is used for the formation of highly organised self-reproducing entities, namely living beings.

Given a constant potential difference, the chosen route of the energy transfer is the one corresponding to the smallest changes in each intermediate stage. Thus, the difference in the energy levels tends to be broken down into small intermediate steps, each transition requiring a specialised catalyst. The large number of intermediate steps involved in the course of fermentation, for instance, or in the similar process of respiration, is clearly demonstrated by the Embden–Meyerhof scheme.

The most important way in which energy may be captured for the synthesis of proteins is by the oxidation of glucose. This involves a series of catalytic reactions such as the phosphorylation of glucose. Adenosine triphosphate (ATP), containing energy-rich bonds, is obtained in further transformations, and its energy is utilised for synthetic purposes. The coupling of the energy of a series of reactions is extremely complicated, and is carried out in a large number of steps. Our knowledge of some of these steps is very limited.

Pyruvic acid, obtained by the oxidation of glucose, is involved in a complicated cycle of tricarboxylic acids – the Krebs cycle. Hydrogen split off from pyruvic acid begins a long journey along a chain of catalysts, till it finally reacts with oxygen or some other final acceptor. The chain begins when the substrate transfers a hydrogen atom to nicotinamide-adenine dinucleotide or nicotinamide-adenine dinucleotide phosphate, which is a dehydrogenase coenzyme. The reduced form of the coenzyme then passes hydrogen on to the flavoprotein, and is thereby regenerated. The reduced flavoprotein reacts with cytochrome, by passing an electron to it and thus reducing the cytochrome iron to the divalent state. Hydrogen passes into solution as an ion. Cytochrome reduces cytochrome oxidase, by the transfer of an electron, and finally, cytochrome oxidase transfers the electron to an atom of oxygen, forming an oxygen ion, which reacts with hydrogen ions to give water.

In his study of the transport of hydrogen from the metabolite to oxygen, Lipmann[26] pointed out that three phosphate bonds were formed in the process, averaging 12 kcal per bond, which is equivalent to 0.25 V for a two-electron system. The difference between the potential of oxygen and that of the "average" hydrogen donor is about 1.2 V. Consequently, it can provide energy for four phosphate bonds. The transfer of hydrogen from the metabolite to oxygen is carried out by a series of catalytic mechanisms, involving in succession nicotinamide-adenine dinucleotide and nicotinamide-adenine dinucleotide phosphate, flavoproteins, and cytochromes. At potential differences of 0.1, 0.5, and 0.9 V (referred to the hydrogen electrode at pH 7) catalysts transform the 0.25 V energy units into energy-rich phosphate bonds. Lipmann stressed further that these energy-transforming systems, which are used for the transfer of electrons (taken from hydrogen) hardly depend at all on the nature of the hydrogen donor. He thinks that energy-rich phosphate bonds can be formed in the most diverse oxidative processes. According to the principles of biochemical evolution, the energy transformation mechanism selected should have been one consistent with the largest number of individual steps; the advantage of phosphorus compounds in this respect is obvious.

The basic biosynthesis of amino-acids, elucidated in the well-known work of Braunstein, is also closely connected with transfer reactions[27]. The carbon skeleton of amino-acids is built from phosphoglyceric and pyruvic acids and from other products of the sugar biosynthesis. The amino group enters the molecule either as a result of hydrogenative amination, or during an earlier stage of its genesis, remaining in it while it becomes more complicated. Braunstein points out that proline, hydroxyproline, ornithine, and arginine can be prepared from glutamic acid; cysteine, tryptophan, and alanine from serine, etc.

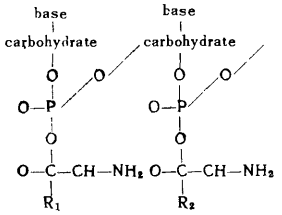
The biosynthesis of amino-acids is catalysed by the pyridoxal group of enzymes. According to Braunstein, only ketoglutaric acid itself can be subjected to direct reductive amination; all the other amino-acids are obtained by transamination, which is sometimes combined with a rearrangement of the carbon skeleton of the acid. Thus, glutamic acid is the first organic product of nitrogen assimilation.

We shall now consider the most important group of enzyme-catalysed synthetic reactions.

A great deal of work has been devoted so far to the biosynthesis of proteins, which has recently become the central problem in biochemistry. Borsook[28] introduced the concept according to which the synthesis of proteins took place in three stages; first, activation of the amino-acid carboxyl groups; second, transfer of the amino-acids to the nucleic acid which serves as a "templet" for their arrangement in a predetermined sequence, and where they combine *via* peptide bonds; and finally, removal of the completed protein molecules from the templet. After this the protein molecule curls up into the characteristic "spiral". Borsook thinks that the carboxyl group is activated during its interaction with adenosine triphosphate. The latter, by splitting off one phosphate group, is converted to the diphosphate, liberating the free energy required for the synthesis.

The mechanism of peptide formation consists, apparently, in the reaction of the enzyme with the amino-acid, *e.g.* with glutamic acid, and ATP, yielding a ternary complex in which glutamic acid is not phosphorylated; this complex subsequently reacts with ammonia, to give glutamine, ADP, phosphate, and the enzyme. Magnesium ions catalyse this synthesis. According to Borsook it is the activated amino-acids (through interaction with ATP), not the peptides, which are transferred to the templet. He bases his opinion on the work of Work and collaborators[29], where it was shown that the synthesis of casein is achieved directly from amino-acids.

The activated amino-acid is transferred to the templet by means of an activating enzyme or nucleotide, whose exact nature we do not know. The fixation of the amino-acid on the nucleic acid templet can be represented by the following scheme:



In the opinion of Haurowitz[30], the first step in the synthesis of proteins is the formation of a species-specific peptide model, which subsequently curls up into a three-dimensional globular molecule. The function of ribonucleic acid is to stretch this protein model, and to keep it in the stretched condition. Hammarsten[31] thinks that protein synthesis is of secondary importance compared with that of ribonucleic acid (RNA). According to Brachet[32], nucleoproteins or RNA provide a specific framework upon which enzyme systems are formed. The framework also serves for the formation of RNA itself, so that this is a case of autocatalysis as regards RNA.

The templet hypothesis seems to be soundly based, and it will certainly play an important role in the study of biochemical evolution. Indeed we must try to visualise a whole series of transformations leading from the very imperfect mechanisms of the amino-acid interactions, either on clays or by irradiation in a homogeneous medium, to the highly specialised reproduction of protein molecules on templets consisting of phosphorylated ribonucleic acid. Such mechanisms, though in much simpler form, probably existed and were used to form the precursors of proteins through the precursors of RNA; they changed continuously as long as the factors causing the change existed.

The synthesis of proteins proceeds extremely slowly — at a rate a hundred, and even a thousand, times slower than that of the usual enzymic reactions, for it involves the formation of the catalysts required for the reproduction of the protein molecule in finest detail.

Thus the characteristic features of the processes accelerated and controlled by biocatalysts are the following: (1) the coupling of the catabolic reactions (decomposition of food) with the synthetic processes (this is accomplished by means of compounds with high-energy bonds); (2) the breaking up of the general process into separate stages with small potential differences between each stage; (3) the change of the structure by means of the transfer electrons, hydrogen atoms and larger entities; (4) the reproduction, by means of the templet mechanism of the protein and enzyme molecules, *i.e.* those structures which can secure all the required stages, and, finally, (5) coupling of reactions in which the differences in the chemical potentials of the reactants are employed, irrespective of their nature.

Data regarding the metabolism of bacteria (see Stephenson[33]) suggest that whenever there is a potential difference between various compounds, an organism can be found which is capable of using this difference for its development and reproduction. In this respect the unusual universality of the biocatalyst systems is not only evidence of the formative action of the selection factors, but also an indication of the development of low-entropy structures capable of increasing the entropy of the surroundings. We shall come back to this point later. It is fully understood that the two groups of catalytic reactions must be coupled and must have a control mechanism.

III. CHARACTERISTIC STRUCTURES OF THE MOST IMPORTANT BIOCATALYSTS AND POSSIBLE WAYS OF THEIR FORMATION

To understand the nature of the biochemical evolution of catalysts, we have to look at the present stage of their development, and examine the results of the operation of selection factors over 2 thousand million years. The fear that we might have to deal with a host of types of catalysis adopted by life on earth, is readily proved to be groundless. The remarkable and very significant unity of the biochemical structure of living organisms is well established.

The prominent biochemist Florkin[34], who studied the problems of biochemical evolution, analysed the dry residues of different organisms; some of his data are collected in Table 1. The resemblance does not by any means end at the quantitative composition. Synge, in his report to the Symposium in Moscow in 1957, emphasised that the proteins, which are present in considerable quantities in all the living organisms studied, are – significantly — a compact chemical group. We encounter precisely the same amino-acids in the proteins of fungi, higher plants, algae, viruses, heterotrophic bacteria, and apparently, autotrophes. Precisely the same enzyme systems are invariably found in the most diverse organisms — and at different stages of development[35].

The means for carrying out different operations — oxidation by oxygen, hydrogen transfers, energy storage, etc. — are present in the same form in bacteria, plants, viruses, and vertebrates. The resemblance of the enzyme mechanisms in different forms of life is so great that the individual differences appear at first sight to be unimportant.

The formation of proteins, or of the hypothetical protein precursors, occupies a very special place in the biochemical evolution of catalysts. In Oparin's words, "proteins

TABLE 1.

Organism	Proteins, %	Fats, %	Carbohydrates, %
Sea urchin larva	63.7	19.5	5.4
Oyster	51.2	11.1	28.2
Silkworm egg	56.0	19.2	7.0
Silkworm larva	55.5	13.3	1.8

TABLE 2.

Enzyme	Groups essential for catalytic activity
Pancreatic amylase	amino
β-Amylase in barley	phenolic, disulphide
Chymotrypsin	ditto
Lysozyme	amino, carboxyl, guanidine, amido, hydroxyl, disulphide
Papain	phenolic, mercapto
Pepsin	phenolic
Phosphatase	amino
Ribonuclease	•
Trypsin	indolyl, amido

have vast chemical potentialities"[3]. In fact proteins combine within themselves the properties which make them an indispensable component of all the most important biocatalytic systems.

The structure of proteins has been widely discussed in the literature and is not considered in the present review. Attention is drawn only to those properties of proteins which are of immediate importance to catalysis, and from that standpoint some physicochemical properties which are common to proteins in general are commented on.

Proteins are themselves able to catalyse a multitude of reactions. It has been established that the macromolecule as a whole is not required for the manifestation of the catalytic function, but only some particular groups in it, which may be regarded as analogous to the "active centres" in heterogeneous catalysis[36]. Porter generalised the results of a number of workers on the nature of these groups which are indispensable for the manifestation of the biological activity of proteins. His data are given in Table 2.

Sanger[37] showed that insulins of different origin, although differing in their structure, can nonetheless possess identical physiological properties; this fact suggests that a definite structure is required in only a small part of the molecule. Sumner[38] showed in the case of urease that even denaturation, which is accompanied by deep-seated structural changes and by an irreversible fall in solubility, does not involve the complete loss of activity. The present author studied the very pronounced catalytic effect of proteins (casein and albumin) on the oxidation of indigo-carmine with hydrogen peroxide, and found that denaturation of the proteins did not completely annihilate their catalytic functions[39].

The first proteins could have been formed, by the mechanism described by Akabori and Bernal, from simple nitrogen compounds on the surface of the clay particles or on rocks with similar properties. Their high molecular weight, capacity for hydration, and high viscosity facilitated their concentration in a limited space and the formation of phase boundaries.

Hydrolytic processes undoubtedly caused partial destruction of the polypeptide chains, but the amino-acids formed by hydrolysis could be used again under different conditions as material for synthesis; this led to a greater diversity of products. It can be supposed that various proteins were the first types of biocatalysts, in which the active group consisted of relatively simple combinations of atoms in the peptide chain.

Protoproteins probably did not possess very diverse catalytic functions, but the most active ones underwent selection in the process of evolution. The most important property, which subsequently made the proteins carriers of enzymic functions is "internal coupling". This means that their molecules contain aggregations of atoms along which energy can be transferred over long distances (see section IV).

The semiconducting properties of proteins determined the development of the protein molecule as a whole. If the chemical reaction proceeding at one point of a molecule has no effect whatever upon its other parts, then this molecule can be regarded as consisting essentially of two autonomous parts, and the properties of one (*e.g.* mass) need not affect the functions of the other. But the situation is different with proteins, whose huge mass seems to be indispensable for the performance of biological functions.

If the protein is treated as a "unified" system, we can explain both its fundamental role in the cell, and the fact that in the course of evolution it did not undergo disaggregation, but, on the contrary, became more complex.

The other property of proteins which makes them the basis of an enormous number of biocatalysts is their capacity to increase sharply the catalytic activity and the selectivity of metal ions, metal complexes, and certain organic compounds with catalytic properties.

Regardless of the presence in proteins of definite catalytic functions, the characteristic feature of the majority of biocatalysts is their "dual" structure. In addition to protein, the enzyme also contains a non-protein part, frequently called the coenzyme or the prosthetic group, which is more or less closely united with the protein. In some cases the stability of the bond between the two parts is so small that the enzyme is virtually completely dissociated into the protein "carrier" and the prosthetic group. In the presence of the enzyme, the substrate is subjected to the action of protein and the prosthetic group alike. All three unite to form an intermediate complex.

Prosthetic groups were the next structural elements to be formed during a long period which elapsed from the appearance of first organic compounds to the origin of life.

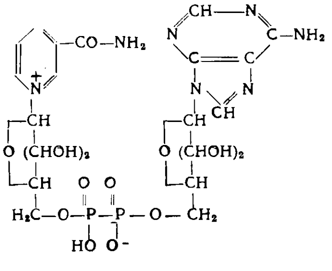
There is no doubt that metal ions played and are still playing a prominent role in the formation and functioning of even those enzymes whose prosthetic groups are believed not to contain a metal. New discoveries are made every year concerning the dependence of the activity of enzymes on the presence in them of small quantities of this or that metal. Nitrate reductase contains molybdenum; carbonic anhydrase – zinc; flavoproteins require copper for their functioning. Pyridoxal enzymes seem to need iron and copper, etc.[40]

Metal ions manifest their catalytic activity in many instances. At one extreme is the case where it is uncertain whether the metal is combined with the enzyme or with its substrate; at the other, the case where the metal is firmly united with the protoporphyrin nucleus, and both are fixed on to the protein. For this reason, the role of the metals in the genesis of complex prosthetic groups can hardly be underestimated. Even in the early stages of biological evolution, metal ions acted as centres of attraction for groups of atoms in organic molecules which were capable of complex formation. This resulted in the mutual approach of different molecules, followed by a change in their electronic state, various redox processes involving the central ion, and finally, the synthesis of new types of highly active biocatalysts in which the metal ion remained in a stable complex. We shall discuss later the various types of metal-ion functions. For the moment we shall consider the structural properties of the most important prosthetic groups.

In the early stages of the development of life the atmosphere was reducing and the biocatalysts controlling hydrogen transfer undoubtedly played an important part. The anaerobic dehydrogenases are an ancient type of biocatalyst.

The oxidative atmosphere, formed about 800 million years ago, brought in new possibilities for the synthesis of catalysts. The difference between the chemical potentials of oxygen and oxidisable compounds, on the one hand, and the products of oxidation on the other, was utilised by different mechanisms of aerobic dehydrogenation and electron transfer; the most efficient of these mechanisms involved the protein-porphyrin complexes.

The metalloporphyrin complexes containing iron, vanadium, or copper, were included in the transfer processes, forming the prosthetic groups of oxidases. They were present in catalases, which decompose hydrogen peroxide, in haemoglobin and haemocyanin, which bind oxygen reversibly, in polyphenol oxidases, in cytochromes, and probably also in a series of other biocatalysts. Whereas the mechanism of catalase action is still controversial, the function of cytochromes (*a*, *b*, and *c*) has been established beyond doubt, namely to transfer electrons along a chain of hydrogen-transfer reactions. These complexes have also played a decisive part in the development of photosynthesis.

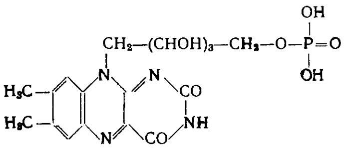


The prosthetic group of anaerobic dehydrogenases is the complicated compound nicotinamide-adenine dinucleotide (Coenzyme I). These dehydrogenases transfer hydrogen to acceptors other than oxygen. They are characterised by their great activity and the ease with which they dissociate into the prosthetic group and the protein carrier. The nature of the protein is the determining factor in the specificity of dehydrogenases. The structure of the prosthetic groups is shown above.

Nicotinamide-adenine dinucleotide and nicotinamide-adenine dinucleotide phosphate (Coenzyme II) is the prosthetic group of a series of dehydrogenases, differing from NAD in having an additional phosphate radical.

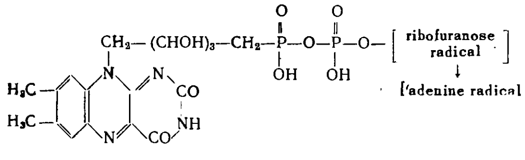
In aerobic respiration the hydrogen removed from the substrate by means of dehydrogenases is transferred to flavin enzymes, the cytochrome system, or "the respiratory pigments". The substrates of these dehydrogenases are lactic, malic, succinic, and glutamic acids, as well as glucose, glucose monophosphate, etc.

The prosthetic group of the flavin enzymes – aerobic dehydrogenases – consists of riboflavin:



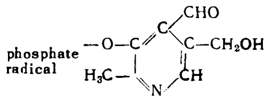
The flavin enzymes can transfer hydrogen directly to oxygen. The reversible oxidation and reduction of the enzyme is accompanied by a change in colour; the oxidised form is yellow, and the hydrogenated one is colourless. The well-known yellow respiratory enzyme belongs to this group; one of its substrates is hexose monophosphate, which plays an extremely important role in metabolism.

The oxidation of amino-acids is catalysed by a dehydrogenase whose prosthetic group is flavin adenine dinucleotide:



Different dehydrogenases, adapted to particular substrates involved in metabolism, are remarkably uniform in the structure of their prosthetic group, in spite of their own relatively complicated structure. The same applies to porphyrin catalysts which control oxidations and electron transfers. There is a growing belief that "adaptation" to specific substrates is invariably carried out by the protein.

The prosthetic group of transaminases, which catalyse the transfer of the amino group, is pyridoxal phosphate:



Amino-acids form a complex with this compound, which subsequently decomposes into a keto-acid and a product differing from pyridoxal in having a CH_2NH_2 group instead of CHO. This phosphopyridoxamine form of transaminases reacts with the keto-acid to give a complex which decomposes into the regenerated initial enzyme-pyridoxal transaminase- and the amino-acid, with the amino group in a different position.

Ideas about the possible chemical pathways for the formation of one or other biocatalyst have a bearing on the evolutionary theory of the origin of life. Equally interesting is the question why precisely these, and not other catalysts, came to be used so universally by different organisms to solve their metabolic problems.

It seems that the first catalytic mechanisms were concerned with hydrogen transfer and hydrolytic processes. Metalloporphyrins, so important for oxidations involving oxygen, were included in biocatalysis later, and it is quite possible that they were added to proteins by virtue of their being the most effective complex catalysts. In fact, whereas the structural elements of dehydrogenases have a definite resemblance to desoxyribonucleic acid, and the prosthetic groups of protein catalysts are often simply parts of the amino-acid molecules constituting the given protein, metalloporphyrins, as well as chlorophyll, are characterised by great specificity of their structure and are altogether different from polypeptides. The same seems to apply to complex specific biocatalysts of the cobalamin type, which appeared later, at a period when living forms became more complicated.

The evolution from the iron ion to the iron-porphyrin complex took place, according to Calvin, during the period lasting about two thousand million years, which he called chemical evolution. In this author's opinion the synthesis of porphyrin proceeded as follows: the action of radiation on water and carbon dioxide produced formic and oxalic acids; C_2 compounds yielded C_4 compounds, in particular succinic acid, on irradiation; amino-acids were formed by the action of ultra-violet light on nitrate solutions containing formaldehyde and iron salts (this has now been established experimentally); glycine obtained in the previous stage reacted with succinic acid to give porphyrin rings[1].

The formation of haemoproteins marked the beginning of biological evolution. Granik[41] studied the biosynthesis of chlorophyll and came to the conclusion that the similarity of chlorophyll to haem was a result of the fact that they followed identical synthetic pathways up to the protoporphyrin stage; they subsequently divided into the "iron" and "magnesium" branches. He believes that the chain of biosynthetic reactions was a repetition of the different stages in the evolutionary development of the pigment systems.

According to Krasnovskii porphyrins were probably the earliest photosensitisers. Porphyrins were present in the oldest autotrophes; they existed in a reducing atmosphere and contained the reduced form of porphyrins. Owing to the peculiarities of their spectra, the free porphyrins cannot fully utilise the visible part of sunlight[42]. Further evolution led to the formation of chlorophyll; the introduction of magnesium into the porphyrin molecule increased the activity of the latter and led to the combination of the complex with the histidine of the protein carrier. Krasnovskii thinks that the complexes of proteins with carotenoids are more recent photoreceptors than porphyrins.

The syntheses of products such as porphyrins, purines, polypeptides, and nucleic acids proceed along very complicated paths. Buchanan and Wilson[43] showed that the biosynthesis of purines and pyrimidines proceeds *via* a series of intermediates such as oxaloacetic, ureidosuccinic, and orotic acids; formic acid, CO_2, and glycine can be incorporated into the purine part of inosinic acid.

It does not, of course, necessarily follow that the synthesis of those precursors of organic bases which are required for the formation of the simplest analogues of nucleic acids took precisely that course. But the relative simplicity of these compounds, and the possibility of the formation of similar products by the action of radiation on simple inorganic compounds, suggest that the first forms of RNA, DNA, and the associated protoproteins might have originated in this way on the earth's surface.

According to Shemin the starting materials for the synthesis of purines were glycine and succinic acid. Ammonia, glycine, and the formyl radical appear to be necessary for the formation of purine and pyrimidine compounds[44]. However, as Oparin correctly pointed out, these complicated processes, which consist of a series of consecutive transformations, take place only if the separate stages are arranged in the proper sequence with regard to time and space[3].

This is even truer for the synthesis of nucleic acids, which, according to Roka, proceeds through the following stages[45]. Polyphosphoric acid, whose formation presumably took place in the early stages of the development of life, reacts with glyceric aldehyde to yield polyphosphoglyceric aldehyde. This complex molecule reacts in succession with acetaldehyde, ammonia, oxaloacetic acid, glycine, and the formyl radical, and forms desoxyribonucleic acid. The acccumulation in one place of all these products depends on a particular combination of specific conditions.

The formation of polypeptides from amino-acids requires free energy (from 400 to 3000 cal mole^{-1}). It is supposed that the reaction proceeds using adenosine triphosphate as a source of energy. Akabori, on the other hand, proved experimentally that the polypeptides could be formed through the polycondensation of aminonitriles, catalysed by clay particles.

Thus, any hypothesis about the origin of the compounds which are characteristic of biological systems must allow for some sort of organisation, whether it be a mechanism of the coupling of exergonic and endergonic processes, an adsorbent possessing catalytic properties, or, as in Oparin's opinion, a coacervate drop.

Taking into account all these considerations, the following approximate stages in the evolution of biocatalysts can be postulated.

(1) The formation of amino-acids on the surface of clay or in homogeneous media under the influence of radiation or by catalytic reactions at interfaces.

(2) The formation of polypeptide chains, occurring in conjunction with reactions involving rupture of high-energy bonds — possibly simple compounds of the iron phosphate type. Alternatively, this stage might have given rise to a special mechanism whereby amino-acids underwent activation and combined into a protoprotein, the formation of a templet for the reproduction of definite amino-acid combinations having followed gradually.

The question remains open whether the templet was pure protein, or a phosphorylated combination of bases with carbohydrates, *i.e.* a prototype of RNA. But either way, the synthesis of first templets from polyphosphates and, probably, aldehydes, could lead to their successful functioning only within the framework of a specific organisation. This first organisation consisted simply in the formation of colloidal particles and the development of boundary surfaces.

There is no doubt that structures of the coacervate types played a most important role in the functioning of these first, inefficient catalysts. It is probable that, owing to selection, only those mechanisms were preserved which were capable of best utilising the existing differences in chemical potentials and of reproducing themselves. Dehydrogenases and the transferring enzymes of the pyridoxal type could possibly have been the earliest biocatalysts.

(3) The selection of catalysts which were activated by proteins was an important stage in the development of enzymes. The proteins with a wide range of catalytic functions were in a privileged position. Thus, proteins evolved containing, in Baldwin's words, "built-in" prosthetic groups, closely bound to the protein molecule. At the same time proteins combined with low-molecular compounds which had catalytic properties, and increased these properties through this combination.

The study of a number of models of prosthetic groups shows that groups which would be activated on any selected protein are rare. The strength of the attachment to protein is not a decisive factor. In many cases the combination protein (prosthetic group) — substrate arises in the presence of metal ions, which play the role of a "coupling link" in a catalytic reaction.

(4) The development of the oxygen atmosphere introduced both a new source of energy and a number of new types of enzymes, with a very different structure from that of dehydrogenases. At the same time photosynthesis began to develop. The same porphyrin complexes served for the formation of oxidases and of chlorophyll.

For reasons which we shall discuss later, porphyrins were the metal complexes selected from a large number of others. This was the end of the development of a series of catalysts which have since been used for the transfer of hydrogen from the substance undergoing oxidation to atmospheric oxygen.

(5) With increasing complexity of the structure of catalysts and their carriers each new reaction, joining the number of those required to reproduce a given structure, either destroyed that structure, or became subjected to its controlling influence. The latter case is observed with the surviving structures. Along with the development of the controlling mechanisms the structure also developed and the "feedback" mechanism, which has now achieved a high degree of perfection, was established.

IV. METAL IONS AND BIOCATALYSIS. MODEL STRUCTURES

The role of metal ions, especially those of transition metals, was very important in the evolution of biocatalysts. There is now evidence that metal ions can catalyse hydrogenation by molecular hydrogen, decarboxylation, decomposition of bicarbonates, and hydrolytic reactions. Catalytic properties are not confined to the transition-metal ions, for the ions of potassium and sodium, like those of hydrogen, can accelerate condensations in homogeneous media[46]. Metal ions act as activators for a number of enzymes, *e.g.* amino-peptidases (manganese and magnesium ions). They can form very active complexes which are a part of prosthetic groups of some enzymes.

The characteristic features of the functioning of metal ions and the probable stages in the development of metal-containing biocatalytic systems can be understood either by the study of the function of metals in specimens available at present, or by the assessment of results obtained from biocatalyst models. It appears that all the modes of the functioning of metal ions in biological systems through the different stages of development have retained some of their importance to the present day. By studying the effects of the catalytic properties of ions, we might therefore be able to interpret correctly their role in the evolution of biocatalysts.

We begin our systematic discussion of these properties with cases in which the ion merely initiates a chain process. The most widely distributed, and the least specific effect is the initiation of chain processes by ions of variable valency (iron, copper, cobalt, etc.). The problem of the distribution in biological systems of catalytic processes involving chain reactions, *i.e.* those involving free radicals, is very complicated. The action of a number of catalysts, of catalase in particular, is based on the formation of intermediate products, and not on the development of chains. However, according to Mikhlin[47], the question of a chain mechanism is still open in the case of lipoxidases.

The generation of free radicals has undoubtedly played an important role in the early stages of the development of biocatalysts (see above, section I). The term "orientation" is most appropriate for describing a very weak ion-substrate interaction when the presence of a definite compound cannot be proved and the catalytic effect of the ion is not very specific. It is true that a detailed study of the "orientation" effect would probably reveal unstable intermediate compounds, but the acceleration, for instance, of the oxidation of indigo-carmine with hydrogen peroxide at the benzene-water interface, in the presence of manganese ions in a weakly acid medium (observed by the present author), is difficult to account for in terms of definite intermediate compounds.

In plant cells calcium can be totally or partially replaced by strontium, molybdenum by tungsten or vanadium, potassium by rubidium, etc. This fact is undoubtedly connected with the activating action of metal ions on different enzymes. The non-specific effect of ions on enzyme activity, described in Calvin and Martel's monograph[46], may well be based on such phenomena.

A closer ion — substrate interaction has a different effect. This is the case with innumerable redox processes in which the ion changes its valency and is used as an electron carrier. The oxidations of ascorbic acid, cysteine, glutathione, etc., in the presence of copper ions are some examples of a large number of reactions catalysed by metals[46]. This category probably also includes the interesting phenomenon of the catalytic action of copper ions on hydrogen transfers. Dehydrogenases, till recently believed not to contain a metal, do in fact require the presence of transition metal-ions for activation.

Mahler points out that flavoproteins, which can be oxidised by cytochromes and which contain metals have been recently discovered. He thinks that the function of the metal in catalysis by flavoproteins is to increase the stability of the intermediate semiquinone; on the other hand, the metal serves to unit the flavin molecule with two acceptor molecules into one complex, and to make possible an intramolecular electron transfer. The presence of the metal ion, which acts as a "coupling" between the donor and the acceptor, imparts to the reacting system the necessary internal "flexibility". Flavoproteins contain copper, iron, or molybdenum (or other metals), depending on the nature of the enzyme[48].

The present author undertook the study of the transfer of hydrogen from ascorbic acid to methylene blue. This reaction proceeds very quickly in the presence of light; it proceeds also in the dark, but much more slowly. In order to find out the possible catalytic role in this reaction of small amounts of metal salts, solution of methylene blue was treated with a small quantity of a substance capable of forming stable, sparingly soluble complexes with the ions of heavy metals. Ethylenediamine tetraacetic acid is especially suitable; it is used as an additive to oxidising agents [oxidisable substances? (Ed. of Translation)] for the elimination of traces of metals which could catalyse oxidations. Another such compound is cupferron, which also forms stable complexes with no catalytic property. The experiments showed that the addition of EDTA or cupferron to methylene blue sharply inhibits the discoloration of the dye by ascorbic acid; the effect is observed in the presence of light and in the dark alike. It follows therefore that the transfer of hydrogen from ascorbic acid to methylene blue is catalysed by metal traces present in the dye. An attempt was made to accelerate the reaction of methylene blue with ascorbic acid by adding to the solution salts of different metals, such as aluminium, sodium, magnesium, copper, iron, cobalt, nickel, titanium, and chromium. A noticeable acceleration of the reaction was observed only in the presence of copper. Thus, copper catalyses hydrogen transfer not only in metalloflavoproteins, but also in far simpler systems, and is responsible for effects usually ascribed to the direct reaction between oxidising and reducing agents [49].

Metals with only one valency can function as catalysts by strongly polarising the molecule with which they are united. In this connection we should mention the action of aluminium ions, investigated by Kornberg and his collaborators [50]. The reaction is accomplished in the zone surrounding the ion, whose radius depends on the nature of the reactants.

Goudot thinks that in such cases electron transfers also occur. She studied different enzyme–metal–substrate systems [51,52] and discovered the following properties, depending on the nature of the ion and the ligand. The redox potential of the cation which polarises the molecule of the substrate must be sufficiently high for the substrate to be able to undergo oxidation; the number of donating groups should correspond to the number of valency electrons which the metal ion is capable of accepting. This explains the failure of the attempts to decarboxylate oxaloacetic acid by means of the free magnesium ion. This ion can form octahedral complexes with three molecules of the acid, but cannot accept more than two electrons, which rules out a catalytic reaction between the divalent metal ion and three molecules of the substrate: for the electron transfer to take place the charges of the reacting groups in complex-forming agents should not all be equal. For instance, the aluminium ion does not catalyse the decarboxylation of acetoacetic acid, as all the six reactive groups in three molecules of the chelating agent have essentially equal negative charges.

The next type of active compound containing a metal ion are complexes in which an increased activity of the ion is obtained by its combination with certain ligands, which are not substrates in the reaction.

The study of the catalytic activity of relatively simple complexes opens up interesting prospects. The number of stable compounds which contain a metal and are attached to enzymes as prosthetic groups, is in fact extremely limited, and it is especially interesting that the very same molecular structure, namely the protoporphyrin ring, serves as a base for a number of completely different biocatalysts. At the same time the number of catalytic metal complexes is extremely large.

It is hardly likely that all other complexes proved to be unsatisfactory simply because they were not sufficiently active. We shall show later that some of them have a very high activity, approaching that of the enzymes. It is clear, therefore, that the catalysts selected in the course of evolution possessed a special combination of properties, all of which were required for the functioning of the chemical system of the cell.

The copper complexes, studied for a number of years in the author's laboratory, are especially suitable for modelling the prosthetic groups of enzymes — particularly those of catalase. The activity of such "copper models" is so great that it is almost a million times higher than that of the simple copper ion. The author studied the catalase activity of copper complexes with amino-acids, amides, amines, diamines, di- and tri-peptides, biuret, triuret, heterocyclic compounds, some proteins, etc. [53,54,55]. The study of these models revealed a series of general principles. First, for the appearance of very high activity four nitrogen atoms are required, co-ordinately bound to the copper ion. The introduction of oxygen atoms into the co-ordination sphere causes a sharp decrease of activity. Thus, chelation, whereby two polar groups of the ligand are co-ordinated to the metal, results, as a rule, in an increase of activity. The nature of the ligand is very important. The complexes with ammonia, biuret, trimethylene diamine, and propylene diamine are especially active.

The active complexes are easily decomposed by concentrated peroxide solutions. To study their activity 0.05–0.1 M solutions of peroxide should be used and a slight excess of free amine maintained in solution. In the presence of a large amine excess, the activity drops owing to the formation of complexes with co-ordination number 6. In such complexes there is no "reaction zone" round the ion where a molecule of peroxide or an HO_2^- anion could enter. The usual free-radical acceptors, *e.g.* methyl methacrylate, have no effect on a reaction catalysed by complex ions; this is the essential difference between the catalytic action of complexes and that of simple ions, which function according to a radical-chain mechanism. The present author believes that in the former case the catalytic reaction proceeds *via* a number of intermediates.

Goudot studied the question why some of the ligands used by the author gave especially active copper complexes. Using the method of molecular orbitals she calculated the charges carried by the atoms in ligands. Her ideas about the reaction mechanism generally agree with the author's — the reaction occurs within an intermediate complex, which consists of the copper complex and two molecules of peroxide (or one molecule and an HO_2^- ion). The metal ion is an intermediary in the electron transfer. Goudot thinks that when the diamagnetic copper ion forms complexes by sp^2 hybridisation (like iron in catalase), it has little chance of attracting electrons to its only unfilled orbital. The ligand–metal complex must be formed by dsp^2 hybridisation, leaving one of the p orbitals free, so that the metal ion may react with the first molecule of the substrate. For the reaction with the second molecule to take place, the ligand has to delocalise an electron pair from the metal ion.

Ligands should be "donors" and contain a considerable number of π electrons (this is the case with biuret, which forms a very active complex). When the electrons are delocalised in the ligand, the ionisation potential of the atoms which react with the ion should increase[56]. The overlapping of wave functions probably occurs also in cases where the complex is activated further as a result of adsorption. The other important feature of the functioning of catalase copper models is the constancy of the activation energy of the reaction. Despite the enormous acceleration of the decomposition of peroxide by complexes, the activation energy remains practically unchanged[57]. Consequently, the acceleration proceeds at the expense of the entropy factor. Porphyrin complexes, and haemin in particular, have another significant feature, in being capable of undergoing further activation. Langenbeck[15] showed that heamin activity can be increased by combining it with imidazole and pyridine. Whereas haemin itself is not a fully specific catalyst (it catalyses the decomposition of hydrogen peroxide as well as oxidations by hydrogen peroxide), the compound of haemin with sodium imidazolesulphonate accelerates only the latter reaction, and 12 times faster than does haemin. Thus, the addition of new ligands both increases the activity of, and renders more specific, catalysts of the metal-complex type. This, according to Langenbeck, accounts for the extraordinary effect of the protein carrier on the properties of the prosthetic group.

Formation of complexes is not the only means of activation in the synthesis of biocatalysts. Activation and increased selectivity are achieved, as a rule, by fixation of the prosthetic group (*e.g.* metalloporphyrin complex) on the protein carrier. In his brilliant experiments Langenbeck showed that the actual structure of the prosthetic group of an enzyme can be determined by studying models. Attempts are being made to use the same method for studying the role of the carrier. Lautsch and his collaborators[58] showed that by fixing different porphyrin compounds on polymers, it is possible not only to increase their activity but also to obtain changes in their absorption spectra similar to those observed in the fixation of porphyrins on proteins.

Iron complexes (haemin) are greatly activated when adsorbed on charcoal. It is notable that the order in which different charcoals increase the activity of haemin is the same as for the iron ion[59]. Thus, adsorption activation, characteristic of ions, is retained in complexes. The above properties of the iron porphyrin complexes have together placed them in an exceptional position relative to other complexes. Copper ions are not activated on charcoal and the selection of activating carriers for this ion is very difficult. Finally, all the attempts to activate the "copper models" of catalase by adsorption gave precisely the opposite result — the loss of catalytic activity. Consequently, the instability of the active copper complexes towards peroxides, their failure to be activated on adsorption, the need to keep an excess of the ligand in solution during the catalysis, all render the copper compounds unsuitable for the formation of enzymes of the catalase type.

Let us now consider the models of oxidases. The present author has studied the oxidation of ascorbic acid and pyrogallol by copper compounds. Of all the complexes studied, only copper-histidine and copper-insulin complexes were more active than copper ions themselves. Even greater activity was obtained by the adsorption of the copper-histidine complex on insulin[60].

Karpusova and the author[61] made a detailed study of the oxidation of pyrogallol by oxygen. Copper complexes were found to be very active catalysts; complexes with monoethanolamine, ethylene diamine, and propylene diamine were the most active of all. The activation energy in this reaction depends a good deal on the nature of the ligand, although here too the entropy factor plays a decisive role. The ligands themselves have a catalytic activity in this reaction; but the activity is increased on combination with the copper ion. Especially interesting is the fact that in this reaction copper ammine complexes can be activated by fixation on proteins.

Table 3 summarises the different types of the catalytic action of metal ions which could have been, or are at present, important in biological systems.

What properties are required of a compound for it to be used in the formation of a biological catalyst? With due caution we can lay down the following physicochemical properties as criteria of the biochemical value of a catalyst:

1. Activity.
2. Capacity for activation, namely the ability to change greatly their activity by slight changes in structure.
3. Capacity for adsorption activation — which is only the extreme case of the property cited under 2. Adsorption activation is the change in activity caused by weak interactions involving the catalyst molecule.
4. Ability to lower the activation energy of the reaction catalysed, particularly when adsorbed on a specific carrier.
5. Ability to preserve the interaction between its separate structural elements — "internal coupling" — after increase in structural complexity.

The catalytic complexes should have a planar structure co-ordination number 4, and, in redox processes, a chelate structure, where the ligand is attached to the central metal ion through nitrogen atoms. Only those which were capable of activation by adsorption, and which lowered the activation energy of the reaction they catalysed, were selected in the course of biochemical evolution. The requirement

TABLE 3.

Type of ionic effect	Example
Initiation of the chain reaction	oxidation of benzaldehyde in the presence of cobalt ions
A weak orientation effect (the "coupling" effect)	acceleration by manganese ions of the oxidation of indigo-carmine by hydrogen peroxide in benzene emulsion. The possible activation of leucineamino-peptidase by manganese and magnesium ions
Redox processes	oxidation catalysis in the presence of copper, iron, etc., ions
Formation of unstable complexes between the ion and the substrate	hydrogen transfer catalysed by copper ions
Polarisation effect	decarboxylation of keto-acids in the presence of aluminium ions
Catalysis by metal–ligand complexes	decomposition of hydrogen peroxide by copper ammine complexes. Catalysis by porphyrin complexes
Catalysis by means of complexes fixed on carriers	oxidation of pyrogallol by the copper--ethanolamine complex on albumin carrier
Catalysis by complexes fixed on specific proteins	the action of enzymes of the catalase type

that the complex should be capable of adsorption activation and that it should function not at the expense of the entropy factor but by lowering the activation energy, is probably equivalent to the requirement that this complex should be energy-coupled with the activating carrier. It seems that this coupling can be established through a conduction band, or, to use the author's early terminology[62], by means of "conducting channels".

Szent-Györgyi[63] stressed the importance of internal coupling in biological structures. In his opinion, the available experimental material leaves no doubt as to the existence of energy migrations within the protein molecule. He does not attempt to explain the mechanism of this energy transfer. In the preface to Szent-Györgyi's book, Terenin refers to the plausibility of energy transfers along the triplet and singlet levels of the protein. Szent-Györgyi thinks that "the protein molecule constitutes a single integrated system, and that the energy imparted to it belongs to the system as a whole" (ref. 63, p. 26).

In this connection we may observe that the inclusion in biologically active compounds of chains along which interaction of atomic groups is relatively difficult, brings in new and more stringent selection factors. This is particularly true of chains such as $-CH_2-CH_2-CH_2$. Shorygin and Alaune[64], in their work on the optical properties of molecules in relation to the interaction of atomic groups, concluded that CH_2 bridges "uncoupled" phenyl, amino, and $C=C$ groups. The presence of such insulating chains in ATP, for instance, is the cause of the coiling up of the molecule, the purpose of which is to allow the purine and the phosphate ends to come into very close contact and so make energy transfer from the phosphate to the purine end possible. This remarkable property is exhibited in the presence of the magnesium ion, which seems to act as a bridge for the transfer of electrons. Therefore, metal ions serve to overcome the difficulties which stand in the way of the internal energy integration of the parts of the biological system which are separated by insulating chains. Of especial interest in this connection are the cases in biological systems where it is possible to destroy large regions of a complicated macromolecule without essentially changing its catalytic function. Thus, a considerable part of the urease protein can be destroyed almost without detriment to its enzymic activity. The papain molecule consists of 180 amino-acid radicals. In this report to the VIIIth Mendeleev Congress, Engelhardt[65] underlined the importance of the fact that in spite of the elimination of 120 amino-acid residues from this enzyme, 99% of its initial enzymic activity is preserved.

These phenomena are difficult to explain, but one of the possible interpretations lies in the assumption of weak energy-coupling between the active group and the remote parts. It is possible that in the course of evolution the biologically active compounds retained certain "rudimentary" parts, which once had a role but were later separated from evolutionary areas by a specific energy-insulating barrier.

V. SUCCESSIVE STAGES AND CHARACTERISTICS OF MOLECULAR ORGANISATION

When Bernal asked him which of the two was formed first, proteins or nucleic acids[3], Oparin considered the question meaningless. It seems that the two components of this reproductive combination developed side by side, although unfortunately we are unable to determine their original form, or follow with confidence the course of their evolution. The initial synthesis is of amino-acids, for example, occurring in homogeneous media under the influence of radiation, did not require a complicated specialised organisation. On the other hand, polypeptides and protoproteins did require it.

Bernal himself divided the process of the origination of life into seven stages: the first stage was characterised by the absence of all interactions, when micromolecular processes developed throughout the hydrosphere. In the second stage there was a fixation of "subvital" units on mineral aggregates; in the third stage coacervates appeared; the fourth stage was marked by the formation of nucleoprotein systems, capable of some sort of metabolism; the fifth and sixth stages are connected with the appearance of lipoprotein membranes and the origin of the cell, containing mitochondria; in the seventh stage the nucleus appeared[66]. This does not include the following processes; the selection of coacervate systems, which contained compounds capable of increasing the catalytic activity by adsorption; the development of new bonds by means of electron transfers; the organisation of the spatial structure of the component parts of the conjugated system, which was to secure the utilisation of high-energy bonds and the corresponding transfer of atomic groups; the appearance of patterns and of the apparatus for self-reproduction.

It is extremely difficult to establish how the increasingly more complicated forms of organisation arose, and why they arose in one particular way and not in any other. At present we still do not know the general principles underlying our hazy ideas about biochemical evolution.

It is obvious, however, that every reaction causes certain changes in the environment, which are not recorded in its equation: changes in temperature, diffusion, radiation, etc.; the appearance of phase boundaries; detonation effects; etc. In a given reaction these effects either facilitate the progress of a particular process, or hinder it. The former type of process has a better chance of survival since it sets up the "organisation" necessary for it. When the organisation itself has a catalytic effect on that reaction, we are dealing with self-reproduction and with what is known in cybernetics as the "feedback" effect.

This is the term used to describe the effect of a given process on the environment, which causes that environment to change the course of the process. Common examples of feedback action in mechanical apparatus are centrifugal regulators; in chemical systems it can be exemplified by the burning of a fuel generating a stream of air, which intensifies combustion.

Intensification or weakening by feedback action are called positive and negative feedback, respectively. A characteristic feature of feedback action in physicochemical systems, and, consequently, in biological objects, is the extreme diversity of the forms it can take. Indeed, a process in a given environment can affect its own development in many ways. The formation of catalysts for self-reproduction is also a particular case of feedback action in biochemical systems. Obviously, such a system must be very stable, a necessary condition for its stability being the presence of feedback in the broadest sense.

Consequently, the forms of organisation selected in the course of evolution were those which ensured the most efficient feedback and control. It seems that the simplest organisations were various phase boundaries where adsorption occurred, bringing specific regularities into the relative disposition and concentration of molecules. Adsorption finally led to catalytic effects. As already mentioned, even adsorption at the water-hydrocarbon interface was the cause of the acceleration of some reactions. Aluminosilicates had far greater potentialities in this respect. Of all the polymerisation products formed on the surface of these adsorbents, the only compounds which underwent further development were those which, being catalysts themselves, ensured a certain amount of feedback.

These forms were probably based on the functioning of conduction bands in protoproteins. The compounds formed started by being catalysts only, and were preserved because their catalytic ability acted as a protection against the chemical influences which could destroy the existing structure.

In 1941 Lipmann[67] showed that the energy liberated in the transfer of hydrogen in cells was not lost or transformed into heat because of coupled phosphorylation, which yielded energy-rich bonds, *i.e.* increased the chemical activity of certain compounds. Here biocatalyst systems obviate the increase in entropy and the disorganisation of the structure, and help to maintain the organisation. The first stage of evolution was probably concluded by the selection of catalysts.

Coacervate drops, so important according to Oparin, were apparently the most suitable and promising form of the preservation of the selection and development of catalysts in the stage of incipient organisation. Oparin's opinion is corroborated by examples of the striking properties of coacervates, particularly their capacity for selective adsorption[3]. Thus, some coacervate drops were able to absorb selectively the active compounds such as porphyrins from the surrounding solution. Porphyrins reacted with iron increasing its catalytic activity. Oparin pointed out further that if this increase enhanced the biological stability of the drops, they enjoyed considerable advantage in the course of selection over other analogous systems.

Since effective catalysis consists of a series of steps, involving small changes in the chemical potential and low activation energy, it follows that some mechanism for the transfer of electrons and, probably, hydrogen atoms along donor-acceptor chains must have existed. Consequently, the catalysts must have developed not only a suitable apparatus, but also the proper spatial arrangement. Hence the idea of the specific "geometry" of biocatalysis.

Twenty years ago Talmud suggested the general features of a model for "metabolism". He considered that the protein molecule, in the form of a globule, must have a series of openings whose dimensions correspond approximately to those of the benzene ring. Through such openings simple amino-acids could enter the interior of the globule and, having combined there into larger protein fragments, were unable to escape. This theory also implies that the interior of the globule favoured condensations whereas the surrounding medium contained an enzyme able to decompose polypeptides. Talmud's experiments showed that proteins could entrain glycine ethyl ester from the solution; at a slightly higher temperature the ester was transformed into diketopiperazine and the portion of the compound retained by protein remained in solution[68].

The studies of Cramer and his collaborators[69] on interstitial compounds (where the "guest" molecule is occluded in the cavity, or crystal, of another which is a "host") showed that occlusion can lead to considerable changes in the molecular state of the "guest", namely shifts in redox potentials, colour changes, catalytic effects, etc.; it can therefore be concluded that processes occurring inside a macromolecule have played a part in the evolution of biocatalysts, and that they should be considered as a complex example of phase-boundary effects.

Nevertheless, this mechanism alone is insufficient to explain the development of protein structures; the forms of organisation which allow for the coupling of energy must also be taken into account. These forms have to secure the utilisation of high-energy bonds, or, as in the synthesis of protein-like substances, act as the original templet of the RNA type, able to orient amino-acids or to lengthen the appropriate templet. Embryonic forms of such organisation may have existed in complex coacervates.

Roka's idea of a "primary templet" based on polyphosphates, was not confirmed experimentally. Energy coupling under suitable spatial conditions could mean the transition to the synthetic stage in the functioning of first catalysts. Naturally, those synthetic products which owing to their composition or form were able to destroy the system of catalysts (in a coacervate or in a complex of the clathrate compound type), did just that. Therefore the extremely slow-acting selection was completed only in cases where the synthetic system reinforced and reproduced itself.

Vorob'ev and Shapot[70] carried out interesting model experiments involving the reaction of globulins with macromolecular DNA and RNA. They obtained synthetic complexes, very similar in properties to protoplasmatic structures, which consisted of nucleoproteins and were accordingly destroyed by desoxyribonuclease activated by magnesium ions. The product obtained by the combination of globulins with DNA had an elasticity which is typical of protoplasmatic structures. The authors attribute great significance to such formations and believe that compounds of this type constitute the physicochemical basis of the protoplasmatic structure. In fact, the synthesis of complicated proteins requires not only RNA, but also a very highly developed organisation. It is now believed that the formation of energy-rich compounds is carried out in mitochondria, which have a specific fine structure and contain a series of enzymes, located in specific positions relative to one another. The synthesis of proteins takes place in other cytoplasmatic particles — the microsomes.

The results of Khesin and of Gale and Folkes throw some light on the "level" of organisation required for the synthesis of proteins and enzymes. Khesin[71] isolated the secretory granules from the pancreatic cells, and showed that they were the sites of the synthesis of amylase. Gale and Folkes[72] disintegrated bacterial cells by the action of ultrasonic waves; after careful elimination of intact cells they added to the suspension a mixture of the essential amino-acids, nucleic acids, and hexose diphosphate and adenosine triphosphate as a source of energy. Protein synthesis and increased enzymic activity were observed in the suspension. Of especial interest is the fact that, in experiments on the synthesis of enzymes, RNA can be substituted by a mixture of purine and pyrimidine bases, which are its components.

Oparin finds it difficult to accept that in the early stages of biochemical evolution a compound as complicated as ribonucleic acid could be formed at one stroke. It is however highly probable that less complex compounds, capable of self-reproduction, could have been formed in mixtures consisting of amino-acids and organic bases, coupled with an energy source.

VI. GENERAL PRINCIPLES

To grasp the full significance of the development of the complex organic structures which preceded the formation of the first living organisms, one has to bear in mind that this development took place in open systems. Oparin emphasised the fact that the continued subsistence of protoplasm and the stability of its form are based on continuous motion, and not on invariability or rest[3]. Protoplasm is not, therefore, a static but a dynamic system.

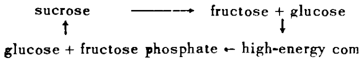
The thermodynamics of open systems has received considerable attention lately. Prigogine, an eminent worker in this field, divided bounded systems into open, closed, and isolated[73]. The first group comprises those systems which exchange both their mass and energy with their environment; in closed systems there is only energy exchange, while isolated systems exchange neither. Processes taking place in open systems differ essentially from those with which we usually deal in ordinary thermodynamics. Such systems, when containing a catalyst, are capable of changing the position of the equilibrium. Pasynskii points out that in an open system processes can take place in which the entropy falls at the expense of the entropy increase in the surroundings with which they are thermodynamically coupled[74]. This significant fact is illustrated clearly by the properties of any living organism, whose total activity consists in growth involving a local decrease of entropy, and in processes involving an increase in entropy, *i.e.* the transformation of compounds with high overall potential into products with a lower potential.

Pringl[75] remarked that all living beings are characterised by coupled chemical reactions in an open system, resulting in a fall of entropy at the expense of entropy increase in the environment. He regards this fact as of fundamental importance. He compares this localised drop in the entropy of living organisms with processes involving "autocatalytic" synthesis. In the opinion of Oparin, this last term only means the dynamic continuity of the evolution of all life. According to Pringl, the first open systems did not have definite boundaries, but represented localised increases in the concentrations of the reacting compounds in the first oceans. The Japanese scientist Sugita thinks that the fluctuations of molecular clusters, which eventually resulted in the formation of coacervates, were also a result of the development of irreversible processes in open systems[76].

Although, according to Frank[77], the capacity of all living matter for self-reproduction must be inherent in complex organic molecules, satisfactory models for the study of these phenomena are not available. A question of major significance is whether the development of self-reproducing systems is a *sine qua non* under specific conditions. Classical thermodynamics does not require this stipulation, but at the same time it is not contradicted by biological facts.

The point is that thermodynamics does not explain the different methods whereby a system achieves equilibrium. and, after all, so far as biochemical evolution is concerned, we cannot speak of equilibrium in the same sense as we do in the case of an isolated system. However, when we consider particular cases in biological specimens, we tend to look for features which are typical of spontaneous transformations, and assess the feasibility of any process by the sign of the corresponding thermodynamic function. We thus find that the concept involving consideration of an individual process is very inexact. In addition to spontaneous transformations accompanied by an increase in entropy, and in complete agreement with thermodynamic laws, numerous "active reactions"[78] occur; for example, when a compound is transported against the concentration gradient, when constant concentration ratios of the products of synthesis and decomposition, which are absolutely incompatible with equilibrium, arise, etc. Careful analysis of such cases always reveals a coupling mechanism whereby the energy required for its functioning is drawn from the energy-rich bonds, but the bonds themselves are obtained, for instance as in the oxidation of glucose, by means which obey the laws of thermodynamics.

Afanas'eva[79] analysed the causes of concentration ratios which do not obey thermodynamic laws, and suggested the following cycle to incorporate different pathways for the synthesis and for the decomposition. This difference is achieved at the expense of high-energy bonds, which are formed in other cycles:



At constant concentration of compound E, the ratio of sucrose concentration to the sum of the concentrations of its decomposition products is kept constant, and only at E = 0 is sucrose fully decomposed into glucose and fructose.

"Active reactions" are dealt with fully in the literature[77], and in all cases a coupling mechanism is postulated, which does not violate the laws of thermodynamics, but which is not envisaged by them. Are we right in concluding that the appearance of coupling mechanisms is another general principle which should be added to the other postulates of thermodynamics in order to make it fully effective as regards biological systems?

By following the evolution of biocatalysts, we get the impression that a relatively small number of structures which are typical of the living specimens of all known species is used for building up the immense multitude of mechanisms which are required for the development of the vast number of higher forms of life. When one considers, for instance, that the composition of the biocatalysts of the Crossopterygian fish is not very different from that of man, the difference between the two species must be ascribed to the different degree of complexity of their respective coupling mechanisms, which, in man with his capacity for creation, have produced a system with extremely low entropy. Consequently, evolution concentrated on the development and refinement of these mechanisms. From the viewpoint of cybernetics, such mechanisms are, simply, systems with feedback action.

There seems to be no reason for rejecting the view that the development of such coupled catalytic mechanisms represents a general principle which should naturally belong to thermodynamics, although it would mean overcoming the difficulties associated with the search for a strict formulation. This principle is of a statistical character inasmuch as of all the possible ways of equalising the existing potential differences, the ones finally selected are those which are associated with the development of self-reproducing structures. This means that in only one experiment the appearance of such a structure is extremely improbable. Even if an immense number of experiments is carried out simultaneously under different conditions, the probability still remains very small. But in experiments repeated over a long time, only that path of equalisation of potential differences which results in the formation of self-reproducing structures is the most likely one, as the chance of all the others being repeated several times is small. This path, which has led to the formation of the cell, involved the smallest activation barriers and was so organised that the exergonic reactions had no opportunity to disrupt the structure or to increase its entropy; "protection against entropy" was effected by means of high-energy bonds, transfer of groups, and apparently, by the transfer of excitation energy to considerable distances along "channels" conduction.

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HYDROPEROXIDES OF ALKYLARENES AND THEIR DERIVATIVES

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CONTENTS

INTRODUCTION

The main course of petrochemical synthesis is the oxidation of hydrocarbons[1,2]. Most petrochemical products can be obtained by direct oxidation of petroleum hydrocarbons, of products of the petroleum-processing industry, or of by-product and natural gases. At the present time higher paraffin hydrocarbons are transformed industrially into aliphatic alcohols and acids by catalytic liquid-phase oxidation[3]. During recent years investigators have shown exceptional interest in the liquid-phase autoxidation of hydrocarbons to hydroperoxides by means of atmospheric oxygen. The interest in autoxidation is explained by the fact that similar processes occur widely in nature and are employed commercially for the synthesis of products of great economic importance.

Many hydroperoxides are quite stable compounds, and have been isolated in a pure form and characterised. In the USSR important investigations on the liquid-phase oxidation of hydrocarbons to hydroperoxides have been carried out by Ivanov[4-9], Sergeev[10-15], Yurzhenko[16-21], Erofeev *et al.*[22,23] and others[24-26]. These investigations have provided methods for preparing concentrated hydroperoxides, analysing them qualitatively and quantitatively in solution, isolating them in a pure form, and converting them into products of economic value.

Organic peroxides and hydroperoxides have formed the subject of several monographs[4,27,28] and reviews[29-31], and have been included in special sections of textbooks of organic chemistry[32]. In the periodical literature many original papers are published annually on the autoxidation of hydrocarbons. For 1958 alone the Chemistry Section of the *Referativnyi Zhurnal* contained more than 60 abstracts of papers and patents. All this indicates the immense importance which is now attached to the autoxidation of hydrocarbons.

The present review deals only with the liquid-phase oxidation of aromatic hydrocarbons and their derivatives by molecular oxygen, *i.e.* the so-called autoxidation process. Such oxidation results in the formation of hydroperoxides. Depending on the catalyst, temperature, time, and rate of introduction of oxygen or air, these may be either the final or the intermediate products of oxidation.

LIQUID-PHASE AUTOXIDATION OF ALKYLARENES

The autoxidation of alkylarenes to hydroperoxides or so-called "Dioxes" (organic peroxy-compounds)[33] is becoming more and more an independent field in a state of broad and intensive development. Hydroperoxides of alkylbenzenes have already acquired great industrial importance both in their own right and as intermediates, *e.g.*

in the synthesis of phenols, aliphatic, and aliphatic-aromatic ketones and alcohols. Hydroperoxides of mono- and di--isopropylbenzenes are used as weed-killers[34], as additives to solvents for the cleaning of apparatus from polymers in the production of "cold rubber"[35], as additives to improve the inflammability of motor fuels[36-39], as oxidants in the bleaching of textiles, and as efficient initiators in the low-temperature copolymerisation of butadiene with styrene and other unsaturated compounds[40-48]. Special interest as polymerisation initiators attaches to the hydroperoxides of cyclohexylbenzene, *p*-isopropylcyclohexylbenzene, 1,1-diphenylethane, *p*-isopropyl-t-butylbenzene, and 1,3,5-tri-isopropylbenzene. It appears that in the future the scale of production of hydroperoxides will be determined solely by the demand for those products which will be manufactured from them, since their technology is comparatively simple, and the raw-material basis unlimited. The synthesis of alkylbenzenes, which are necessary for the manufacture of hydroperoxides, was carried out on an industrial scale, even during the pre-war period, by the catalytic alkylation of benzene and its homologues with olefines.

A survey of the investigations shows that, in the liquid--phase autoxidation of alkylarenes, oxygen always attacks the alkyl carbon atoms directly attached to the aromatic nucleus, independently of the size and structure of the groups. Oxidation is carried out with oxygen or air in the presence and in the absence of catalysts, under the action of ultra-violet radiation, at atmospheric and at high pressures, in the presence and the absence of solvents. The course of the liquid-phase oxidation depends on the rates of formation and decomposition of the hydroperoxides, but the rate is determined by the structure and purity of the hydrocarbons, the nature of the catalyst, the temperature, the time, and the velocity at which the oxygen or air is passed through.

As a rule, oxygen enters more readily at a tertiary C–H bond. Primary carbon–hydrogen bonds are the most resistant to oxidation. But, as will be seen, in many cases this rule is not observed. It has not yet proved possible to oxidise an aromatic carbon–hydrogen link to a hydroperoxide, but, judging from data in patents, benzene has already been oxidised to phenol with oxygen or oxygen-containing gases under pressure[49-55]. Alkylarenes are not oxidised to hydroperoxides if quaternary carbon atoms are present in the α-position. Thus only those alkylarenes in which hydrogen atoms are attached to the α-carbon atoms undergo autoxidation. Toluene, the xylenes, and mesitylene, which contain only primary α-carbon atoms, are oxidised very slowly. Ethylbenzene is somewhat more readily oxidised, t-butylbenzene is not oxidised at all by atmospheric oxygen to a hydroperoxide, and isopropylbenzene, s-butylbenzene, *p*-cymene, *p*-di-isopropylbenzene, *p*-di-s-butylbenzene, and cyclohexylbenzene, which contain tertiary α-carbon atoms, are very readily oxidised.

The ease of oxidation of monoalkylbenzenes usually increases with increase in the degree of branching and in the length of the alkyl groups, but steric hindrance must be taken into account here, as a result of which the isopropyl group, for example, is usually more easily oxidised than the more ramified and longer s-butyl group.

Successive introduction of identical alkyl groups increases the oxidisability of hydrocarbons to a greater extent the more symmetrical the structure of the polyalkylbenzenes. If the alkyl groups differ in structure, those containing tertiary α-carbon atoms are oxidised first of all (in the case of dialkylbenzenes and symmetrical trialkylbenzenes). With unsymmetrical trialkylbenzenes the attack of oxygen is directed firstly at the α-carbon atom of the most remote radical, *e.g.* in 1,2,4-tri-isopropylbenzene at the group in position 4. If two or three groups having tertiary α-carbon atoms are attached to the benzene nucleus, the attack of oxygen is usually directed to the α-carbon atom of the larger alkyl group. The introduction of a methyl group *para* to an alkyl radical containing a tertiary α-carbon atom lowers the oxidisability, as can be seen on comparing the rates of oxidation of isopropylbenzene and *p*-cymene, s-butylbenzene, and *p*-s-butyltoluene. The last-named compound approaches the methylbenzenes in rate of oxidation. Autoxidation is facilitated by the presence of a double bond in the vicinity of an α-carbon atom. The attack of oxygen is then directed to the C–H bond of the carbon atom in the α-position with respect to the double bond.

Several investigators[56] link the different rates of oxidation of hydrocarbons with the values of the energy of rupture of the C–H bond, which is in general agreement with the experimental results, as can be seen from the Table.

Hydrocarbons	Bond	Bond energy kcal
Benzene	C_6H_5—H	102
Methane	CH_3—H	101
Propane	n-C_3H_7—H	100
Propane	i-C_3H_7—H	94
Butane	n-C_4H_9—H	102
Isobutane	t-C_4H_9—H	89
Propene	CH_2=CH—CH_2—H	77
Toluene	$C_6H_5CH_2$—H	77.5
Ethylbenzene	$C_6H_5CH(CH_3)$—H	75
Isopropylbenzene	$C_6H_5C(CH_3)_2$—H	74

The extent of autoxidation and the maximum concentration of hydroperoxides of alkylarenes depend on the stability of the hydroperoxides, the purity of the original hydrocarbon, temperature, time, type of catalyst, and other factors. The stability of the hydroperoxides rises with increasing number of alkyl groups attached to the α-carbon atoms, tertiary hydroperoxides of alkylbenzenes being the most stable, and the primary compounds the least stable[26]. In the absence of catalysts at room or not very high temperatures (up to 65°) autoxidation hardly occurs at all or only very slowly; the production of a considerable amount of oxidation products requires the prolonged action of oxygen or air on the hydrocarbon. As a result, the final products are usually aldehydes and acids in the case of the oxidation of hydrocarbons containing primary alkyl groups, and ketones in the case of compounds containing secondary alkyl radicals. Under conditions of liquid-phase oxidation with molecular oxygen, tertiary alkyl groups are not oxidised at all, as already mentioned.

Catalysts accelerate autoxidation and shorten the induction period, but many of them also bring about decomposition of the hydroperoxides which have been formed, and promote further oxidation to ketones and tertiary alcohols[53]. Thus the stearates and acetates of cobalt possess the ability to initiate and terminate reaction chains, so that in the presence of a certain concentration of these salts the autoxidation process is initiated, but increasing the concentration reduces or slows down the oxidation[57]. The naphthenates of cobalt, chromium, manganese, nickel, and other metals also often cause the formation of non-radical oxidation products and contribute to a more far-reaching oxidation[58].

In the autoxidation of alkylarenes there is nearly always observed at first an induction period, the duration of which depends on the type of catalyst, the nature and purity of the hydrocarbon, and other factors. This is followed by a rapid accumulation of hydroperoxide, and after some slowing down in the rate of oxidation a maximum concentration of hydroperoxide is reached, which then begins to diminish owing to decomposition of the hydroperoxide into ketones and alcohols or acids (depending on the structure of the hydrocarbon). When oxidation is resumed after being interrupted for 10 – 12 h, an induction period is also observed at first, after which the rate gradually levels out, and the process proceeds normally[59].

The autoxidation of the following monoalkylbenzenes has been studied: toluene, ethylbenzene, n-propylbenzene, isopropylbenzene, n-butylbenzene, s-butylbenzene, and isobutylbenzene[10,14,60-63]. All these hydrocarbons, on vapour-phase oxidation with air in the presence of $V_2O_5 + MnO_2$ at 300° – 500°, form benzoic acid and maleic anhydride[60]. Alkylaromatic hydrocarbons containing primary and secondary α-carbon atoms often form as the main final products alcohols or ketones on oxidation with oxygen in the liquid phase, owing to the readiness with which the hydroperoxides of such hydrocarbons are cleaved[64-66].

Methyl-substituted arenes are oxidised very slowly by molecular oxygen to hydroperoxides, and under severe conditions are usually converted into higher oxidation products. Toluene, for example, is oxidised to benzaldehyde and benzoic acid under the prolonged action of oxygen in the absence of a catalyst[67-69] or in the presence of anthraquinone[70] or a copper, bismuth, iron, vanadium, or silver salt[71].

The autoxidation of toluene to a hydroperoxide has been achieved by several investigators[14,72-75], and has been studied in special detail by Sergeev and Fedorova[10] in the presence of manganese resinate as catalyst and isopropylbenzene peroxide as initiator. These workers found that, after air had been passing through for 44 h, the content of hydroperoxide in the toluene solution had reached 0.6%, and then began to diminish. They were able to isolate *via* the sodium salt a preparation containing 68.8% of benzyl hydroperoxide.

When ethylbenzene is oxidised with atmospheric oxygen in the presence of an oxide of copper or iron, 75 – 80% of acetophenone and 20 – 25% of α-phenylethyl alcohol are formed[65,66,76]. Oxides and hydroxides of iron, manganese, and cobalt, iron benzoate[77], ferric chloride, copper nitrate[78,79], and other substances[80] can also be used as catalysts for this oxidation. In the absence of catalysts, the prolonged action of oxygen at room temperature[67,68] or at 110°[81] oxidises ethylbenzene to acetophenone. Under milder conditions Hock[72] was able to oxidise ethylbenzene to a hydroperoxide, which was isolated in the free state *via* the sodium salt. Ethylbenzene is oxidised by oxygen to a hydroperoxide in the presence of esters of β-keto acids or of the hydroperoxide of isopropylbenzene and NaOH[82]. In a similar way, the prolonged action of oxygen on n-propylbenzene converts the latter into propiophenone[81].

Alkylbenzenes containing tertiary α-carbon atoms are very readily oxidised to hydroperoxides in the presence of metal oxides, hydroxides, and salts of organic acids[33,83-85]. As an example of such hydrocarbons, the oxidation of isopropylbenzene has been especially well studied. Among the products of organic synthesis few compounds can be found which have attracted such attention from research workers. This is explained primarily by the availability of isopropylbenzene and the ease of conversion of its hydroperoxide into phenol and acetone, 2-phenylpropan-2-ol and α-methylstyrene or acetophenone. The importance of these products is well known[86-88].

In 1926, Stephens[81] first studied the oxidation of isopropylbenzene, and showed that the action of oxygen on it at 80° – 104° for 3 – 5 weeks yielded acetophenone and formic acid. Later several patents were taken out for the oxidation of isopropylbenzene to acetophenone and 2-phenylpropan-2-ol[76,77,89,90]. The catalysts recommended were calcium hydroxide; chromic oxide and calcium carbonate; ferric, manganese, cobalt, copper, and silver oxides and hydroxides; and iron benzoate.

In 1944, Hock and Lang[91] first prepared isopropylbenzene hydroperoxide, in 7.5% yield, by the oxidation of isopropylbenzene with atmospheric oxygen under the influence of ultra-violet radiation. Udris, Sergeev, Nemtsov, and Kruzhalov[92,93] made a detailed study of the oxidation of isopropylbenzene to the hydroperoxide in the presence of manganese resinate. This hydroperoxide is now manufactured in many countries of the world for the production of phenol and acetone. In the USSR the first large-scale plant for the production of phenol and acetone *via* isopropylbenzene hydroperoxide was put into operation in 1946[86]. In Canada the first plant with an annual production of 6000 tons of phenol, 3500 – 4000 tons of acetone, and 5000 tons of α-methylstyrene[94,95] started work in 1953. Several enterprises of this type are operating in the USA with a total output exceeding 40 000 tons of phenol and ~ 25 000 tons of acetone per year[96-99]. Similar works exist in England, Poland[100,101], France[102,103], Western Germany, Belgium, Japan, and other countries[104].

The process for obtaining phenol and acetone consists in alkylating benzene with propene, oxidising the isopropylbenzene to the hydroperoxide with atmospheric oxygen, and splitting the hydroperoxide into phenol and acetone[86,105,106]. Autoxidation is carried out in homogeneous liquid phase at 85° – 130° in the presence of catalysts and various additives, or in alkaline emulsion. The recommended oxidation initiators are naphthenates, linoleates, and acetates of manganese, cobalt, and lead[84,107,108] and salts of alkali and alkaline-earth metals with strong acids[109]. In several patents the liquid-phase oxidation of isopropylbenzene in the presence of finely ground sodium carbonate or bicarbonate suspended in the reaction mixture is proposed[110,111]. Hydroperoxyisopropylbenzene is obtained by this procedure in 83% of the theoretical yield. Oxidation of isopropylbenzene with atmospheric oxygen in the presence of sodium bicarbonate at 75° yields up to 57.6% of hydroperoxide in the reaction mass[112], but in the presence of powdered calcium carbonate or barium carbonate the yield may reach 94% based on the isopropylbenzene. When the reaction is carried out in the presence of carbonates there is no induction period[113]. The gradual decrease in activity of the calcium carbonate may be overcome by periodic addition of sodium carbonate. Calcium carbonate can be employed up to relatively high temperatures while maintaining a high rate of oxidation.

Kolmakov *et al.*[114] have shown that the autoxidation of isopropylbenzene in the presence of azobis(isobutyronitrile), NaOH or sodium carbonate, in contrast to the industrial process using manganese resinate, occurs at a higher velocity, gives a higher concentration of hydroperoxide, and is less sensitive to inhibition of the reaction by formic acid. For the initiation of oxidation the following are recommended as well as the catalysts mentioned: oxides, hydroxides, and salts of metals of variable valency (*e.g.* manganese or cobalt), hydroxides of the alkali and alkaline-earth metals and their salts with formic, stearic, oxalic, benzoic, and other organic acids, as well as gaseous ammonia [115-128]. Aliphatic alcohols accelerate the oxidation[129], and esters of β-keto acids (*e.g.* ethyl acetoacetate and benzoylacetate) proved to be suitable for this purpose[63,130].

The metals copper and silver are active catalysts for the autoxidation of isopropylbenzene[131], and are supposed to act as stabilisers for the hydroperoxide. It is therefore sometimes recommended that, to prevent decomposition of the hydroperoxide at temperatures above 50°, the internal surface of the reaction vessel should be covered with copper, silver, gold, or their alloys[132]. According to other patents, copper causes decomposition of the hydroperoxide, and the use of copper reaction vessels is not recommended[109]. Metallic catalysts were suggested for the oxidation of alkylbenzenes as early as 1931 [78].

Several patents cover the oxidation of isopropylbenzene in aqueous alkaline emulsion[62,64,105,133-142,148]. The rate of oxidation is then 3–7% of hydroperoxide per hour. The reaction is affected by the pH of the medium, the temperature, the relative volumes of the phases, and the intensity of agitation. For optimum conditions the medium should have a pH of 7–11. When the autoxidation of isopropylbenzene is initiated with barium peroxide (1%), the peroxide, the hydroperoxide, or other products are formed depending on the conditions [143].

In many patents hydroperoxycumene, either by itself[144,145], with alkaline additions[82,146-150] or with copper and silver salts[128], is recommended as initiator for the oxidation of isopropylbenzene. The use of hydroperoxides as oxidation initiators shortens or eliminates the induction period: hence it accelerates autoxidation and diminishes the formation of by-products.

The induction period is shortened and the yield of by-products diminished when hydrocarbons of general formula $ArCHR_2$ are treated with ozonised oxygen or air containing ozone in the presence of substances which combine with acidic products[151-155].

Preliminary purification of isopropylbenzene and other similar hydrocarbons from impurities which inhibit oxidation is regarded as of very great importance for increasing the velocity and the extent of oxidation[72,141,156,157]. Before oxidation, commercial isopropylbenzene is usually treated with concentrated sulphuric acid (permanganate, hypochlorite), caustic soda, heated over metallic sodium, and distilled. Several patents[158] suggest treating the hydrocarbon with alkylation catalysts before oxidation. Particularly good results are achieved by treating isopropylbenzene with sulphuric acid and carrying out autoxidation in a Pyrex glass reaction vessel. For this purpose porous alumina[159,160] or an aqueous solution of mercuric acetate[161,162] can also be employed. Autoxidation of isopropylbenzene with oxygen or gases containing oxygen occurs also in the absence of catalysts[163]. Homologues of cumene are capable of undergoing liquid-phase oxidation under the influence of ultra-violet radiation or in the presence of alkali-metal peroxides; formates, oxalates, and benzoates of the alkali and alkaline-earth metals; formaldehyde; organic hydroperoxides; and compounds which can be used as alkylation catalysts (*e.g.* fluorosulphonic acid, aluminium chloride, and BF_3-HF) [74,164-169].

During recent years a great deal of attention has been paid in research and patent specifications to the liquid-phase oxidation of s-butylbenzene, which, like isopropylbenzene, can be obtained among the readily available hydrocarbons of the petroleum-processing industry, and is readily converted, *via* the hydroperoxide, into phenol and butan-2-one. The latter is of great practical interest as a selective solvent.

s-Butylbenzene, like cumene, is oxidised by oxygen comparatively rapidly after an induction period[170], the concentration of α-hydroperoxy-α-ethyl-α-methyltoluene reaches a maximum, and then begins to fall owing to its decomposition. The induction period is smaller in the presence of hydroperoxy-s-butylbenzene, and completely disappears with large quantities of the latter.

The liquid-phase oxidation of s-butylbenzene is carried out in the presence of manganese resinate[62], calcium hydroxide[125], hydroperoxides[144], and other initiators which can be used for the oxidation of cumene[171]. The addition of barium peroxide is recommended[172-174] as it increases the yield of s-butylbenzene hydroperoxide. In the opinion of the investigators, BaO_2 is not a catalyst, but takes part in suppressing side reactions, *e.g.* in the formation of acetophenone.

Oxidation of s-butylbenzene to the hydroperoxide under the influence of ultra-violet radiation was first accomplished by Ivanov *et al.*[175] In the absence of catalysts and initiators, s-butylbenzene is oxidised by air considerably more slowly than is isopropylbenzene (Fig. 1), in spite of their similarity in structure[176]. The reaction is less sensitive to various additives, and occurs very slowly at 100°–110°. The rate of oxidation increases with rise in temperature, and the length of the induction period decreases. Addition of manganese resinate (0.25 mg litre^{-1})

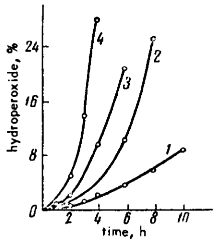


Fig. 1. Oxidation of s-butylbenzene (*1,3*) and cumene (*2,4*), at 120° (*1,2*) and 140° (*3,4*) in the absence of catalysts or initiators.

accelerates the oxidation of s-butylbenzene. As the amount of manganese resinate increases, the rate of oxidation increases, but the maximum achievable concentration of hydroperoxide in the reaction mass decreases (Fig. 2). Also with rise in temperature over the range 110°–150° the rate of oxidation increases, but the concentration of hydroperoxide in the reaction mixture decreases (Fig. 3).

This reaction has been studied in detail by Sergeev *et al.*[177] according to whom the optimum conditions for the oxidation of s-butylbenzene to a hydroperoxide content of 14–15% in the reaction mixture are a temperature of 110°–112° and a time of 8 h with 5 mg of manganese resinate per mole of the hydrocarbon. Addition of a minute amount of hydroperoxide considerably accelerates the autoxidation. The side-products of the oxidation are acetophenone, α-ethyl-α-methylbenzyl alcohol, and benzoic acid. Ethyl acetate and acetaldehyde have also been detected.

Investigation of the effects of various liquid, gaseous, and solid additions[176] on the rate of oxidation of s-butylbenzene has shown that cumene, barium carbonate, sodium sulphate, ammonia (0.1% added to the air), and barium sulphate (2%) have practically no effect on the rate of oxidation. Phenol, the sulphates of nickel, manganese, and copper, hydrogen sulphide, and oxides of chromium, nickel, and copper retard the accumulation of the hydroperoxide. α-Ethyl-α-methylbenzyl alcohol, chlorine, and hydrogen chloride have an inhibiting effect. Sulphur dioxide has a particularly strong effect in diminishing the rate of oxidation, which practically ceases with a content of 0.001% of SO_2 in the air.

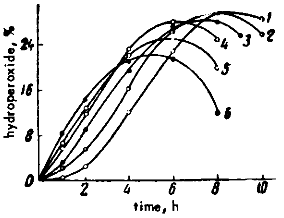


Fig. 2. Oxidation of s-butylbenzene at 140° in the presence of manganese resinate (mg $litre^{-1}$):
1) 0.0; 2) 0.25; 3) 9.0; 4) 18; 5) 36; 6) 62.

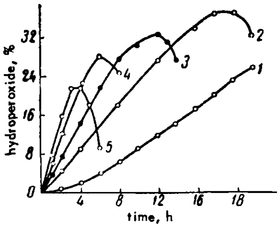


Fig. 3. Oxidation of s-butylbenzene in the presence of manganese resinate (18 mg $litre^{-1}$) at different temperatures:
1) 110°; 2) 120°; 3) 130°; 4) 140°; 5) 150°.

s-Butylbenzene is comparatively readily oxidised to the hydroperoxide in aqueous alkaline emulsion[178]. Oxidation of s-butylbenzene in the presence of sodium stearate, cobalt naphthenate, and sodium carbonate in aqueous solution yields α-ethyl-α-methylbenzyl alcohol and acetophenone[142].

The autoxidation of n-butylbenzene and isobutylbenzene with atmospheric oxygen to the corresponding hydroperoxides has been studied in the presence of ultra-violet radiation[64] and of various initiators[62,82,122].

Cyclohexylbenzene is comparatively slowly oxidised by molecular oxygen to hydroperoxide, but with appropriate choice of conditions a concentration of up to 23% of the latter in the reaction mass can be achieved. Suitable oxidation initiators are manganese resinate, formates, oxalates, and benzoates of the alkali and alkaline-earth metals, hydroperoxides, esters of β-keto acids, and formaldehyde[4,61,63,94,144,179-183].

LIQUID-PHASE OXIDATION OF DIALKYLBENZENES

Until very recently little information, and that mainly in the patent literature[85,115,169,183,184], was available on the liquid-phase oxidation of dialkylbenzenes to hydroperoxides. Dialkylbenzenes are oxidised by molecular oxygen in the presence of the same catalysts as with monoalkylbenzenes. Depending on the conditions, either monohydroperoxides or higher oxidation products are formed. Up to the present the dihydroperoxides of *p*-di-isopropylbenzene, *p*-isopropyl-s-butylbenzene, *p*-di-s-butylbenzene, and *p*-di-s-pentylbenzene have been isolated.

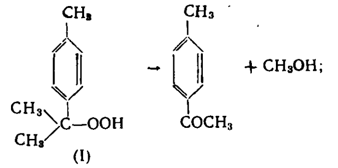
All the xylene isomers, on prolonged oxidation with oxygen either in the presence or in the absence of catalysts, are usually converted into the corresponding aldehydes or mono- and di-carboxylic acids[67-70,185-187]. A detailed review of the oxidation of xylenes has been given in a lecture by Toland and Nimer[188]. The monohydroperoxide of *p*-xylene was obtained by Hock and Lang[72] by shaking up *p*-xylene with oxygen and irradiating with light from a mercury source. This hydroperoxide can be prepared in 82% of theoretical yield by treating *p*-xylene with oxygen in the presence of di-t-butyl peroxide[74]. According to Lorand and Edwards' results[169] oxidation of *p*-xylene with molecular oxygen in the presence of di-t-butyl peroxide yields, in addition to *p*-methylbenzyl hydroperoxide, the following side-products: tolualdehyde, toluic acid, *p*-methylbenzyl alcohol, and 4,4′-dimethylbenzil and its polymeric homologues.

Sergeev and his coworkers[61] have studied the oxidation of *p*- and *m*-xylenes with air in the presence of manganese resinate and cumene hydroperoxide at 110°, and have shown that the monohydroperoxides which are then formed are very unstable and readily decompose during the oxidation. He was able to isolate preparations containing 67% of *p*-methylbenzyl hydroperoxide and 72% of the *meta*-isomer. Tolualdehydes and toluic acids were separated as by-products.

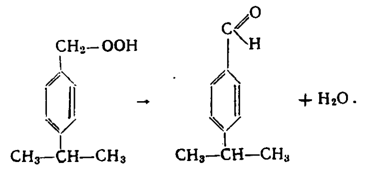
On oxidation in the presence of oxides of chromium and cobalt, *o*-, *m*-, and *p*-diethylbenzenes form the ethylacetophenones in yields of 14–19, 32–42, and 25–30% respectively[190,191]. The absence of the diacetylbenzenes among the oxidation products suggested that the acetyl group in the ethylacetophenones exerts an inhibiting action and prevents further oxidation. Sergeev and Sladkov[12] showed that, in the case of the oxidation of *p*-isopropylacetophenone, an acetyl group in the *para* position may even accelerate the oxidation of the isopropyl to a hydroperoxy group. Zavgorodnii[59] confirmed this view in the case of the oxidation of *p*-s-butylacetophenone. Later Sergeev and Sladkov[192] oxidised *p*-diethylbenzene with air in the presence of nickel benzoate and obtained *p*-ethyl-α-methyl-α-hydroperoxytoluene, separating it from the alkaline layer by treatment with CO_2. *p*-Ethylacetophenone was found among the by-products of the oxidation.

Research on the autoxidation of *p*-cymene is extensive. The liquid-phase oxidation of this hydrocarbon shows a failure of the rule that attack by molecular oxygen always occurs as a tertiary α-carbon atom.

The oxidation of *p*-cymene has been studied under various conditions, and some authors have assumed from the products isolated that oxidation occurs at the primary carbon atom of the methyl group[193,194] and others that the attack of oxygen is directed to the tertiary carbon atom of the isopropyl group[22,195]. In fact, the oxidation of *p*-cymene involves attack by oxygen on both the primary and the tertiary α-carbon atom with the formation of hydroperoxides of the two types (I) and (II) [61,67-69,81,196], which during the oxidation are partly decomposed into *p*-methylacetophenone and 4-aldocumene:



(I)



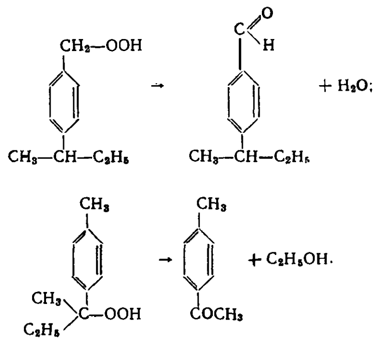
(II)

Serif *et al.*[197] studied the comparative ability of the methyl and isopropyl groups of *p*-cymene to undergo liquid-phase oxidation by Armstrong's emulsion method[133] and Helberger's photochemical method[194], and found that when *p*-cymene is oxidised in aqueous emulsion at 85° the isopropyl group is oxidised four times as readily as the methyl group. The same products are obtained at 60°, but under these conditions the hydroperoxides, formed initially, undergo less profound changes. Photochemical oxidation at 60° takes place at a lower rate than emulsion oxidation, and is not accompanied by cleavage of the primary oxidation products, so that the final products are only 4-methyl-α,α-dimethylhydroperoxytoluene and 4-(α-hydroperoxymethyl)cumene. The comparative capacity for oxidation of the tertiary α-carbon atom of the isopropyl group and of the primary methyl group in *p*-cymene is the same as with emulsion oxidation, *i.e.* 3.5 : 1. Thus the method affects the rate but not the direction of oxidation.

The substances recommended as initiators for the liquid-phase oxidation of *p*-cymene are hydroperoxy-*p*-cymene[144,198,199], di-t-butyl peroxide[74], benzoyl peroxide[200,201], esters of β-keto acids[63], magnesium naphthenate[155], sodium stearate, manganese acetate and NaOH[198], sodium carbonate[202], and others[119]. In all cases oxidation products of both the isopropyl and the methyl group are formed.

Yamamoto and Hata[203] obtained a 63% yield of *p*-cymene hydroperoxides, representing a mixture of the 7-, 8-, and 9-hydroperoxides, by the autoxidation of an emulsion of the hydrocarbon in the presence of benzoyl peroxide. *o*-Cymene is oxidised to hydroperoxides by molecular oxygen in the presence of manganese resinate at only half the rate observed with *p*-cymene[22].

p-s-Butyltoluene, like *p*-cymene, is oxidised by molecular oxygen in the presence of manganese resinate to form 4-methyl-α-ethyl-α-methyl-α-hydroperoxytoluene and 4-(s-butyl)-α-hydroperoxytoluene[61,196]. *p*-s-Butylbenzaldehyde and *p*-methylacetophenone were also detected among the oxidation products. They are formed by decomposition of the primary and tertiary hydroperoxides:



During recent years many investigations and patent specifications have been published on the liquid-phase oxidation of di-isopropylbenzenes, especially the *para*-isomer, which is obtained in considerable quantities as a by-product in the manufacture of cumene, and can be used *via* the mono- and di-hydroperoxides for the synthesis of *p*-isopropylphenol and quinol.

A survey of the investigations shows that *p*-di-isopropylbenzene is very readily oxidised by molecular oxygen to the mono- and di-hydroperoxides, especially if it has first been treated with sulphuric acid or finely ground, porous alumina[161]. The oxidation of di-isopropylbenzenes is carried out in the presence of alkali and alkaline-earth metal salts of formic, acetic, oxalic, benzoic, and stearic acids[122,126,204], metal oxides and hydroxides[62,119], manganese resinate either alone or with alkaline additions[205-207], esters of β-keto acids[63,109], barium peroxide[155], gaseous ammonia[208], and organic peroxides and hydroperoxides[82,144,209-213]. High pressures or periodic ozonisation of the oxygen which is passed through has an extremely favourable effect on the reaction[78]. A mixture of mono- and di-hydroperoxides is usually formed.

Our investigations have shown[206,207] that, in the presence of manganese resinate without added alkali, the liquid-phase oxidation with air of *p*-di-isopropylbenzene yields a maximum concentration of 25% of hydroperoxide, even if the hydrocarbon has been carefully purified from impurities by treatment with sulphuric acid. Alkalis, *e.g.* NaOH, KOH, $Ca(OH)_2$, and Na_2CO_3, are not very effective by themselves and have almost identical effects, but when added to manganese resinate in amounts of 0.5–1.0 g per mole of the hydrocarbon, they accelerate the oxidation process and enable a higher concentration of hydroperoxide to be obtained. Oxidation is particularly vigorous if *p*-di-isopropylbenzene is first oxidised in the presence of alkali to a hydroperoxide content of 2–3% in the reaction mixture, and then manganese resinate is added and the passage of air continued. The *p*-di-isopropylbenzene prepared in this way can be oxidised in the presence of manganese resinate to a content of 78% of hydroperoxide in the solution.

A mixture of manganese resinate and cobalt acetate containing added calcium hydroxide initiates the oxidation more vigorously than do manganese resinate and cobalt acetate taken separately with this same addition. Addition of sodium stearate to a mixture of manganese resinate, cobalt acetate, and calcium hydroxide accelerates the oxidation and enables a 71% yield of the hydroperoxide to be obtained in 17 h, whereas when these initiators are employed in the absence of sodium stearate, the amount of oxidation is 33% of hydroperoxide in 16 h. *p*-Di-isopropylbenzene is comparatively easily oxidised to mono- and di-hydroperoxides in the presence of NaOH and hydroperoxides in an inert solvent, *e.g.* t-butylbenzene or a halogenobenzene[214].

Dihydroxyperoxy-*p*-di-isopropylbenzene is precipitated after its concentration in the solution exceeds 40%. This suggests that autoxidation of *p*-di-isopropylbenzene first yields a monohydroperoxide, but when the latter has reached a considerable concentration the oxygen begins to attack the second isopropyl group, ending with the formation of the dihydroperoxide. The effect of temperature on the rate of oxidation of *p*-di-isopropylbenzene is illustrated in Fig. 4.

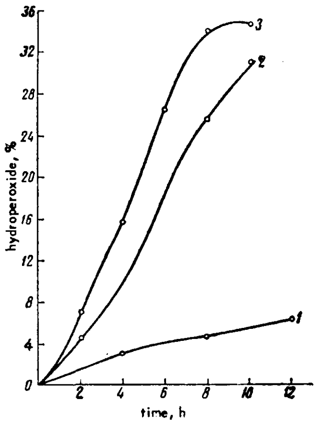


Fig. 4. Rate of oxidation of *p*-di-isopropylbenzene in the presence of manganese resinate and calcium hydroxide at temperatures of:
1) 85°; 2) 110°; 3) 130°.

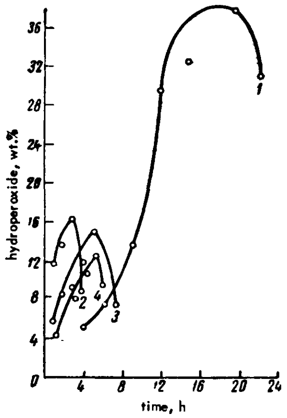


Fig. 5. Rate of oxidation of *p*-ethylisopropylbenzene at 85°:
1) manganese resinate, cobalt acetate, calcium hydroxide, and caustic soda;
2) manganese resinate, cobalt acetate, calcium hydroxide, and sodium stearate; 3) manganese resinate, cobalt acetate, and calcium hydroxide;
4) cobalt acetate and calcium hydroxide.

Oxidation of *p*-di-isopropylbenzene occurs readily in aqueous alkaline emulsion[183,215]. *m*-Di-isopropylbenzene is oxidised by atmospheric oxygen in the presence of alkali to a mixture of mono- and di-hydroperoxides[216,217], decomposition of which yields, in addition to resorcinol, *m*-isopropylphenol and *m*-isopropenylphenol.

Eventova *et al.*[218,219] found that the resistance to liquid-phase oxidation with oxygen at 175° falls in the series: *o*-, *m*-, and *p*-di-isopropylbenzenes, the *para*-isomer being oxidised three times as rapidly as the *ortho*-isomer. Among the oxidation products were found phthalic acids, phenol, acetophenone, formic acid, acetic acid, *m*-acetylbenzoic acid, resorcinol, and *m*-diacetylbenzene. It was confirmed that, in this case too, the action of the oxygen is directed at the tertiary α-carbon atom with the formation of hydroperoxides.

We have studied the liquid-phase oxidation of *p*-ethylisopropylbenzene. The initiator used was manganese resinate with addition of calcium hydroxide, caustic soda, sodium stearate, and cobalt acetate[207]. Under the conditions studied this hydrocarbon was found to oxidise very slowly (influence of the ethyl group in the *para*-position). The hydroperoxide formed is unstable and usually starts to decompose after 3–6 h. The main product of acid cleavage is *p*-isopropylphenol. Hence it follows that the attack of molecular oxygen is directed in the first place at the secondary α-carbon atom, in spite of the presence in the molecule of the tertiary α-carbon atom in the isopropyl group. The effect of manganese resinate on the rate of oxidation in the presence of various additives is shown in Fig. 5.

p-t-Butylcumene is oxidised by atmospheric oxygen to the corresponding monohydroperoxide. The liquid-phase oxidation of this hydrocarbon has been studied in detail by Sergeev and Kruzhalov[220]. It has been shown that one mole of the well-purified hydrocarbon requires 2.5 mg manganese resinate or 0.02–0.03 g caustic soda for the oxidation to occur at a rate of 5–7% hydroperoxide per hour. The extent of oxidation or the percentage conversion of the hydrocarbon into the hydroperoxide reaches 30 wt.% and more. In several experiments the concentration of hydroperoxide in the reaction mixture reached 42–45 wt.%. Hydroperoxy-*p*-t-butylcumene has limited solubility in the reaction mixture, so that, on standing, up to 50% of it separates as crystals. It can be isolated in this form by washing the oxidation products with n-pentane[221].

In the presence of peroxides and hydroperoxides *p*-s-butylcumene is oxidised in the liquid phase to its mono- and di-hydroperoxides. According to Tsutsumi and Odaira's results[222] the α-carbon atom of the isopropyl group is the one more readily attached by oxygen. According to our own results[223,224], *p*-s-butylcumene, in the presence of manganese resinate alone or with $Ca(OH)_2$, NaOH, Na_2CO_3, BaO_2, or sodium stearate, at 95°, 115°, or 120°, is very easily oxidised by air even without any special additional purification. Addition of calcium hydroxide to the manganese resinate allows the oxidation to be carried out during the first 5 h at a rate of 10% of hydroperoxide per hour, and to obtain after 10 h a maximum concentration of 71% of hydroperoxide. If sodium carbonate is added instead of calcium hydroxide to the manganese resinate, oxidation occurs still more rapidly. The maximum concentration of hydroperoxide is reached in 6 h and amounts to 71.1%. Thus additions of alkali not only accelerate the oxidation of *p*-s-butylcumene but also increase its extent.

Cleavage of hydroperoxy-*p*-s-butylcumene with sulphuric acid yields acetone, ethyl methyl ketone, quinol, and a mixture of *p*-isopropylphenol and *p*-s-butylphenol. The presence of these products shows that the oxidation of *p*-s-butylcumene involves the formation of 4-(s-butyl)-α,α-dimethyl-α-hydroperoxytoluene and 4-(α-methyl-α-ethyl-α-hydroperoxy)cumene and the dihydroperoxide.

p-Cyclohexylisopropylbenzene, previously purified by washing with sulphuric acid, is comparatively readily oxidised by air in the presence of manganese resinate alone or with added alkali at 95°–120°. The attack by oxygen is then directed mainly at the tertiary carbon atom of the isopropyl radical and results in the formation of hydroperoxy-*p*-cyclohexylisopropylbenzene. The tertiary carbon atom of the cyclohexyl radical is oxidised with greater difficulty under these conditions, and therefore 4-(hydroperoxycyclohexyl)cumene is formed in negligible yield[225]. In this case, too, autoxidation involves the formation of a maximum concentration of hydroperoxide, which on prolonged oxidation completely disappears from the reaction mixture. The effect of added alkali on the autoxidation is clear from Fig. 6.

In the presence of manganese resinate alone, *p*-cyclohexylisopropylbenzene is oxidised to a lesser extent than when alkali is also present. Sodium carbonate and calcium hydroxide have roughly the same effect.

The course of the oxidation of *p*-cyclohexylisopropylbenzene in the presence of manganese resinate, calcium hydroxide, cobalt acetate, and sodium stearate is unusual. The maximum content of hydroperoxide in the solution is 6% and is reached in 6 h; then it begins to diminish, and after 10 h the hydroperoxide disappears from the reaction mass and cannot be detected after the lapse of tens of hours. The products of the reaction are *p*-cyclohexylacetophenone and *p*-cyclohexylphenol.

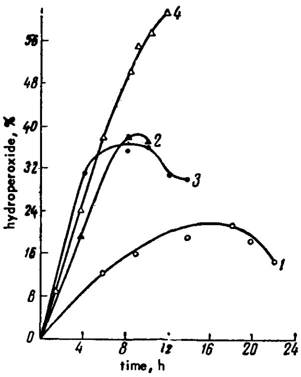
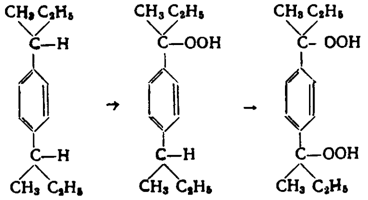


Fig. 6. Effect of added alkali on autoxidation of *p*-cyclohexylisopropylbenzene at 118°–120° with an air flow of 30 litres h^{-1}: 1) manganese resinate; 2) manganese resinate and sodium carbonate; 3) manganese resinate and calcium hydroxide; 4) manganese resinate, sodium carbonate, and barium peroxide.

A thorough study has been made of the liquid-phase oxidation of *p*-di-s-butylbenzene, which is obtained as a by-product of the manufacture of s-butylbenzene and has not yet found any industrial use. The oxidation of *p*-di-s-butylbenzene has been investigated mainly by the Japanese chemists Tsutsumi, Odaira, and Torii[142,215] and Yamada and Matsumoto[226,227]. They showed that this hydrocarbon is oxidised by oxygen, in either the presence or the absence of catalysts, to form mono- or di-hydroperoxides or higher oxidation products. One secondary butyl group is especially easily oxidised. In the presence of water, sodium carbonate, and sodium stearate at 80° and 30 atm, *p*-di-s-butylbenzene is oxidised with the formation of α,α′-dihydroxy-*p*-di-s-butylbenzene, *p*-diacetylbenzene, and *p*-s-butylacetophenone. In the presence of the same catalysts and benzoyl peroxide or the hydroperoxide of the original hydrocarbon at 95°, the mono- and di-hydroperoxides are formed with a maximum concentration of 39.5%. Fedorova and Sergeev made a detailed study of the liquid-phase oxidation of *p*-di-s-butylbenzene[61,228] and showed that, in the presence of manganese resinate, the hydrocarbon is oxidised at a mean rate of 3.0–3.5% hydroperoxide per hour, the maximum concentration of hydroperoxide reaching 48.5%. They estimated the rate of formation of mono- and di-hydroperoxides of *p*-di-s-butylbenzene by periodically determining the available oxygen in the reaction mass and analysing the products of sulphuric-acid cleavage. Zavgorodnii[59] studied the oxidation of *p*-di-s-butylbenzene, both the by-product of the experimental production of s-butylbenzene and the synthetic material, purified with sulphuric acid, and the unpurified material, containing 3–4% of the *ortho*-isomer. Oxidation was carried out in the presence of manganese resinate and added alkali at 95°–120° and a rate of flow of air of 25–120 litres h^{-1} per mole of hydrocarbon. Conditions were found under which *p*-di-s-butylbenzene could be oxidised to a hydroperoxide concentration of 62.2% (arbitrarily based on the monohydroperoxide) or practically entirely converted into mono- and di-acetylbenzenes. *p*-Diacetylbenzene is formed in 57% yield of the theoretical in a single oxidation. On the basis of these results the author assumes that the oxidation of *p*-di-s-butylbenzene takes place in stages. The monohydroperoxide is formed initially, and no dihydroperoxide is present among the reaction products. When a definite concentration of the monohydroperoxide is reached, the oxygen attacks the *α*-carbon atom of the second s-butyl group, resulting in formation of the dihydroperoxide. On prolonged passage of air the hydroperoxides are split into ketones. The oxidation can be represented by the scheme:



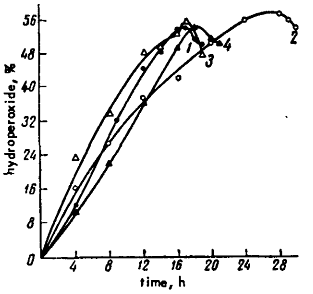


Fig. 7. Effect of added alkali on autoxidation of *p*-di-s-butylbenzene at 118°–120° with an air flow of 30 litres h^{-1}:

1) manganese resinate; 2) manganese resinate and calcium hydroxide; 3) manganese resinate and sodium carbonate; 4) manganese resinate and cobalt acetate.

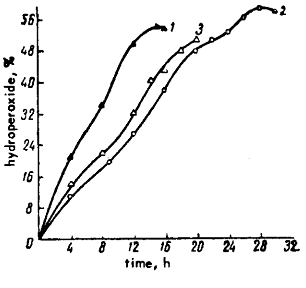


Fig. 8. Autoxidation of *p*-di-s-butylbenzene in the presence of manganese resinate and sodium carbonate at 110°–120° and air flows of litres h^{-1}:

1) 5; 2) 30; 3) 60.

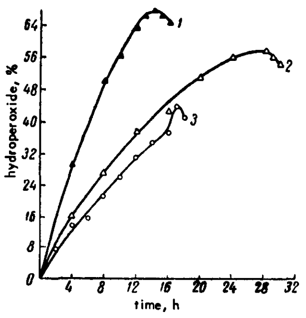


Fig. 9. Autoxidation of *p*-di-s-butylbenzene from different sources in the presence of manganese resinate and calcium hydroxide at 118°–120°:

1) pure synthetic; 2) containing 3–4% of the *ortho*-isomer; 3) isolated from the polybutylbenzene residues from experimental production.

The effects of added alkali, the rate of flow of air, and the purity of the hydrocarbon on the velocity and character of the oxidation of *p*-di-s-butylbenzene are shown in Figs. 7–9.

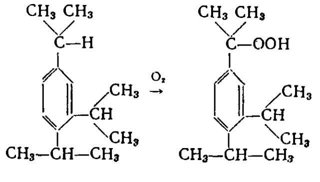
LIQUID-PHASE OXIDATION OF TRIALKYLBENZENES

The oxidation of trialkylbenzenes to hydroperoxides has hardly been studied at all. According to the literature, the prolonged action of oxygen on 1,2,4-trimethylbenzene and mesitylene yields the corresponding dimethylbenzoic acids[67,69]. Recently Sergeev and coworkers[61] have been able to oxidise mesitylene in the presence of manganese resinate to the monohydroperoxide, the maximum concentration of which after 40 h was 4.13%. This hydroperoxide is very unstable, and readily decomposes during oxidation, so that the oxidation products include also *α*-aldomesitylene and *α*-carboxymesitylene.

Among other trialkylbenzenes the oxidation has been studied of 1,3,5-tri-isopropylbenzene to the mono-, di-, and tri-hydroperoxides[229-232]. The main aim of the investigations, as was emphasised by Proft at the annual meeting of the Chemical Society of the GDR,[233] was to oxidise the hydrocarbon to the trihydroperoxide and cleave the latter to phloroglucinol, *i.e.* to accomplish the synthesis of this interesting but inaccessible trihydric phenol.

Oxidation of 1,3,5-tri-isopropylbenzene by a current of oxygen in ultra-violet radiation, or at 110° in the presence of a small amount of concentrated caustic soda solution, does not yield the desired results, owing to rapid decomposition of the reaction products (in the former case after absorption of 12% of the required amount of oxygen, and in the latter after absorption of 17%). The maximum yield (30%) of hydroperoxy-1,3,5-tri-isopropylbenzene was obtained by oxidising the hydrocarbon in a faintly alkaline emulsion at 85°. The use of NaOH, KOH, $Ca(OH)_2$, or hydroperoxides is recommended to eliminate the induction period. In order to obtain the monohydroperoxide, oxidation is continued to the extent of 30% conversion; for the di- and tri-hydroperoxides up to 80–90% conversion is required (calculated on the monohydroperoxide).

We have studied[231] the liquid-phase oxidation of 1,2,4- and 1,3,5-tri-isopropylbenzenes. The former is oxidised by atmospheric oxygen in the presence of manganese resinate and sodium carbonate to a maximum hydroperoxide concentration in the solution of 53%. Only the isopropyl group standing alone then undergoes autoxidation, the two groups mutually *ortho* blocking one another and remaining practically unoxidised. As a result, only the monohydroperoxide is formed:



1,3,5-Tri-isopropylbenzene in the presence of manganese resinate and sodium carbonate is oxidised extremely rapidly by atmospheric oxygen, the mean initial velocity being 20–30% of hydroperoxide per hour. Volkov[234] has shown that the oxidation takes place with the successive formation of a mixture of the mono-, di-, and tri-hydroperoxides of 1,3,5-tri-isopropylbenzene. Tri-isopropylbenzene peroxide is also obtained as a by-product.

There are indications, although only in the patent literature[232], that *meta*-substituted phenols can be obtained by oxidising 1,3,5-triethylbenzene, 1,2-di-isopropyltoluene, 1,3,5-tri-s-butylbenzene, 1,3,5-tri-n-pentylbenzene, 1,3,5-tricyclopentylbenzene, and 3,5-dichlorocumene, instead of 1,3,5-tri-isopropylbenzene. The resulting hydroperoxides are employed to obtain the corresponding alcohols and acetylphenols, and are also used as components of explosives and initiators for free-radical polymerisation.

LIQUID-PHASE OXIDATION OF POLYNUCLEAR ARENES

A. Oxidation of Hydrocarbons Containing Separated Benzene Nuclei

Descriptions have been published of the liquid-phase oxidation of diphenylmethane[91,142], di-*p*-tolylmethane[235], 1,1-diphenylethane[16,20,236-240], 1-phenyl-1-*p*-tolylethane, 1-*p*-ethylphenyl-1-phenylethane, 1-*p*-isopropylphenyl-1-phenylethane, 1-phenyl-1-*p*-t-butylphenylethane, 1,1-di-*p*-tolylethane, 1,1-diphenylpropane[21,241], 1,1-diphenylbutane, 1,1-diphenylpentane, 1,1-diphenylhexane, tribenzylmethane, tris(β-phenylethyl)methane, 1,2-diphenylethane, 1,3-diphenylpropane, 1,4-diphenylbutane, 1,5-diphenylpentane, and 1,6-diphenylhexane[240,242]. The same catalysts are recommended for these oxidations as for those of alkylbenzenes. The simplest of these hydrocarbons, diphenylmethane, is oxidised comparatively slowly, a yield of up to 12% of diphenylmethanol being obtained in the presence of water, sodium carbonate, and sodium stearate.

The oxidation of 1,1-diphenylethane has been most thoroughly studied, probably owing to the ease with which the hydroperoxide of this hydrocarbon can be isolated and its excellent initiating properties for the low-temperature copolymerisation of butadiene with styrene. When oxygen is passed at a rate of 6–8 ml min^{-1} through 1,1-diphenylethane at 65°–70°, the hydroperoxide concentration reaches 28.5%. The hydroperoxide can be isolated in the form of crystals or it can be decomposed, without being isolated, with sulphuric acid into phenol and acetophenone[237].

Eventova *et al.*[239] have found that the rate of oxidation of 1,1-diphenylethane at 175° is 28.9% after 3 h. Higher oxidation products were obtained (the hydroperoxide decomposes above 120°), but it was considered that under these conditions also the oxidation proceeds *via* formation of the hydroperoxide.

Yurzhenko and Puchin[236] worked out a technical method for oxidising 1,1-diphenylethane to the hydroperoxide in the presence of diphenylethane hydroperoxide and NaOH. After 25–30 h, the concentration of the hydroperoxide was 32–35%. When the reaction mixture was allowed to stand for 2–3 days, up to 64% of hydroperoxide came down in the precipitate, and could be readily separated. The oxidation of 1,1-diphenylpropane occurs similarly *via* the formation of a hydroperoxide having the structure $(C_6H_5)_2.C(OOH).C_2H_5$.[239]

The other 1-alkylphenyl-1-phenylethanes mentioned above are oxidised to the corresponding hydroperoxides in a similar way by oxygen in the presence of NaOH, although considerably more slowly than are t-alkylbenzenes (0.25–0.35% of hydroperoxide per hour). The hydroperoxides can readily be separated and purified by chromatography on Al_2O_3. In the case of the liquid-phase oxidation of 1,1-diphenylbutane, 1,1-diphenylpentane, and 1,1-diphenylhexane the tendency for hydrocarbons of this type to undergo oxidation increases with increase in the number of carbon atoms in the chain, independently of whether it is odd or even, but hydrocarbons of this series are less resistant to oxidation than are hydrocarbons of the 1,6-diphenylhexane series[240].

Triphenylmethane is oxidised by oxygen to the hydroperoxide, which can be obtained also from triphenylmethyl chloride and hydrogen peroxide[243-245].

Methylcyclohexylphenylmethane (I), dicyclohexylphenylmethane (II), cyclohexadienyldiphenylmethane (III), and cyclohexylcyclohexylidenephenylmethane (IV) are oxidised to hydroperoxides[246]. The rate of oxidation increases in the order II, I, IV, III. Examination of the reduction and acid cleavage products of the hydroperoxides showed that oxidation occurs not only at the central methane carbon linked to the cyclohexyl and phenyl radicals but also at the first and second carbon atoms of the cyclohexyl radical; as a result, a mixture of hydroperoxides having a concentration in the solution of ⩾ 7% is formed.

In the liquid-phase oxidation of tribenzylmethane and tris(β-phenylethyl)methane at 175°, the oxygen attacks the α-carbon atoms directly linked to the benzene nucleus[247,248] in spite of the presence of a tertiary carbon atom in the aliphatic chain. This results in the formation of α,α′-dihydroperoxides, which split into benzoic, acetic, and formic acids. The same rule is observed in the liquid-phase oxidation of 1,2-diphenylethane, 1,3-diphenylpropane, 1,4-diphenylbutane, 1,5-diphenylpentane, and 1,6-diphenylhexane. In this series of diphenylalkanes the tendency to oxidation increases with molecular weight. Hydrocarbons containing an odd number of carbon atoms in the aliphatic chain are more resistant to oxidation than are those containing an even number.

Kuznetsov and Ivanov[242] constructed a circulatory-flow apparatus for investigating the kinetics of the oxidation of hydrocarbons by molecular oxygen, established optimum conditions for the oxidation of diphenyl- and dicyclohexyl-alkanes, and showed that the rate of oxidation decreases with increase in the velocity of circulation of oxygen above 24–25 ml min^{-1} and in temperature above 140°–160°.

B. Oxidation of Hydrocarbons Containing Fused Benzene Nuclei

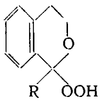
The oxidation to hydroperoxides of several alkylnaphthalenes, alkylhydronaphthalenes, alkylbiphenyls [*sic* (Ed. of Translation)], and other aromatic hydrocarbons containing fused benzene rings has now been studied. 2-Methylnaphthalene in the presence of organic peroxides — in particular of di-t-butyl peroxide — is oxidised to a hydroperoxide which on acid cleavage is converted into 2-naphthol and formaldehyde[74]. 2-Isopropylnaphthalene, on liquid-phase oxidation with oxygen or gases containing oxygen in the presence of hydroperoxides, alkali-metal carbonates or bicarbonates, cobalt linoleate, or peroxides, form a hydroperoxide with the peroxy-group attached to the α-carbon atom of the isopropyl group[84,249-251]. In a mixture of 1- and 2-isopropylnaphthalenes, the latter isomer is oxidised considerably more readily than the former[252]. 1,4-Dihydronaphthalene[37,253] and 1,2-dihydro-1-methylnaphthalene[254] are oxidised in the liquid phase to the corresponding hydroperoxides. Tetralin is readily oxidised to the hydroperoxide[4,255-257]. Chizhevskaya and Idel'chik[258] suggested a faster method for obtaining hydroperoxytetralin by oxidising the hydrocarbon in the presence of 0.01% of manganese stearate or cobalt stearate. Oxidation of tetralin proceeds well at 60°–80° under normal or high pressures with simultaneous illumination of the reaction mixture by red and yellow light in the presence of chlorophyll, which has a sensitising action[259]. In the oxidation by atmospheric oxygen of commercial tetralin, containing 0.1% of magnesium stearate, in tubes made of brass, copper, Monel, stainless steel, and iron at 70°–75° in a thermostat, the respective yields of 1-hydroperoxy-1,2,3,4-tetrahydronaphthalene obtained after 50 h were 37.5, 36.0, 35.2, 29.4, and 21.1%. In a silver-plated tube the yield of hydroperoxide amounts to 35.6%[260]. 1,2,3,4-Tetrahydro-1-methylnaphthalene[255,261,262], 1-ethyltetralin, 1,4-dimethyltetralin, and 1,4-diethyltetralin[263] are readily oxidised to the hydroperoxides in the presence of various catalysts, *e.g.* sodium carbonate. Decalin is oxidised in the liquid phase to the 9-hydroperoxide[264,265]. A mixture of *cis*- and *trans*-decahydronaphthalenes (90% of the *cis*-isomer), on oxidation with atmospheric oxygen in the presence of cobalt, manganese, and zinc oleates, gives products containing 80% of a solid hydroperoxide[266].

In the presence of peroxides and hydroperoxides, alkylbiphenyls are comparatively readily oxidised to hydroperoxides by molecular oxygen. For example, 4-isopropylbiphenyl in the presence of di-t-butyl peroxide and $NaHCO_3$ at 148°–153° on oxidation had a hydroperoxide content of 32.8% after 1 h, and 34.6% after 2 h. The hydroperoxide of 3-isopropylbiphenyl was obtained in a similar manner. In the presence of sulphuric acid the former is split into 4-phenylphenol, and the latter into 3-phenylphenol[267]. A mixture of 3- and 4-isopropylbiphenyls, on oxidation with air in the presence of calcium hydroxide at 165°–170°, is converted after 24 h to the extent of 35.8% into "α-diphenylylacetophenone" and 11.9% into 4-biphenylyldimethylmethanol[268]. 4-s-Butylbiphenyl, in the presence of manganese resinate and hydroperoxycumene is oxidised by air to a hydroperoxide, whose concentration reaches 22% after 32 h.[269]

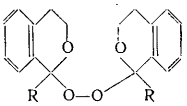
Aromatic hydrocarbons and several of their derivatives having more highly fused ring systems are capable of autoxidation to form the corresponding hydroperoxides. The oxidation to hydroperoxides has been described of indane[27,270], 1,3,3-trimethylindane[271,272], perhydroindane[27,262], fluorene[261], 1,2,3,4,10,11-hexahydrofluorene[273], octahydroanthracene[274], tetrahydroacenaphthylene or tetraphene[275], isochroman and di-isochroman[276,277], alkylisochromans[278], and symmetrical and unsymmetrical hexahydropyrenes[279]. 1,2,3,4,10,11-Hexahydrofluorene on liquid-phase oxidation gives a 76% yield of the 11-hydroperoxide. Autoxidation of tetraphene at 60°–80° in a glass flask yields di-11-tetraphenyl† peroxide and small quantities of 5-tetraphenone, which is probably a product of the spontaneous dehydration of the intermediate 5-hydroperoxytetraphene. When oxygen is blown through tetraphene in a quartz vessel at 40°, 11-hydroperoxytetrahydroacenaphthylene is obtained.

Isochroman, 1-methylisochroman, 1-isopropylisochroman, and 1-benzylisochroman are readily oxidised in the light to the corresponding hydroperoxides[276]. The hydroperoxides of isochroman and 1-methylisochroman are converted under the action of H_2SO_4 into dimeric peroxides (B):

(A)



(B)



The analogous peroxides of 1-ethylisochroman and 1-cyclohexylisochroman, as well as the peroxide of bis-5,6-benzoisochroman-1-yl, are obtained by direct autoxidation of the corresponding isochromans without separation of the intermediate products.

Symmetrical and unsymmetrical hexahydropyrenes, 1,2,3,4,5,8,9,10,11,16-decahydropyrene, and hexadecahydropyrene undergo autoxidation[279].

Steroid compounds containing isolated double bonds are readily converted into hydroperoxides in the presence of photosensitisers[280,281]. Thus irradiation of cholesterol and haematoporphyrin with a mercury lamp in a current of oxygen gives a 49.2% yield of 5α-hydroperoxycholesterol[281]. Photo-oxidation of Δ^5-cholesten-3-one in the presence of dichlorotetraiodofluorescein in $C_6H_6-CH_3OH$ mixture by irradiation with a sodium lamp results in the formation of the carcinogenic 6β-hydroperoxy-Δ^5-cholesten-3-one in 9.3% yield. This suggests a link between carcinogenic hydroperoxysteroids and cancerous diseases caused by ultra-violet radiation. Ergosterol on ultra-violet irradiation in the presence of 1,8-dihydroxyanthraquinone gives a 33% yield of hydroperoxide[281]. Hydroperoxides of pregnenolone have been obtained.

LIQUID-PHASE OXIDATION OF SUBSTITUTED ALKYLBENZENES

(*a*) Oxidation of alkylhalogenobenzenes. We have studied the liquid-phase oxidation of *p*-fluoroisopropylbenzene and *p*-cyclohexylfluorobenzene to the corresponding hydroperoxides by atmospheric oxygen in the presence of manganese resinate, cobalt acetate, and

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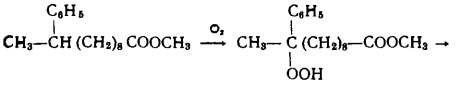
† For numbering of rings see Treibs and Thörmer, ref. 275, p. 95 (Ed. of Translation).

NaOH.[282] The halogenated alkylbenzenes are oxidised more slowly and form lower maximum concentrations of hydroperoxides than the alkylbenzenes themselves. Thus oxidation of *p*-fluoroisopropylbenzene in the presence of caustic soda yielded a maximum concentration of 23.2% of the hydroperoxide. Oxidation of *p*-cyclohexylfluorobenzene in the presence of NaOH, cobalt acetate, and manganese resinate gave a maximum hydroperoxide concentration of 12%. *p*-Chloroisopropylbenzene in the presence of hydroperoxycumene and NaOH is oxidised to the hydroperoxide[283]. In a similar manner 4-chloro-, 2-chloro-, 4-methyl-, 3-chloro-4-isopropyl-, and 2,4-dichloro-isopropylbenzene are oxidised to the corresponding hydroperoxides.

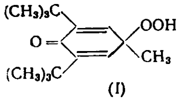
(*b*) Oxidation of oxygen-containing aromatic compounds. Among oxygen-containing compounds the oxidation to hydroperoxides has been studied of *p*-methylacetophenone[13], *p*-isopropylacetophenone[12,15], *m*-isopropylacetophenone[284], *p*-s-butylacetophenone[59], the methyl and ethyl esters of phenylacetic[14], toluic[285], isopropylbenzoic, and 10-phenylundecanoic acids[286,287], several alcohols[288,289], and alkylphenols[290,291].

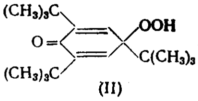
p-Methylacetophenone in the presence of nickel benzoate is oxidised by atmospheric oxygen to give 2% of the hydroperoxide after 20 h, but this is very unstable, so that the end-product is *p*-acetylbenzoic acid in 70% yield after 56 h. Methyl and ethyl phenylacetates on similar oxidation are converted into the esters of phenylglyoxylic acid[14]. The dimethyl and diethyl esters of *cis*-3,6-diphenyl-Δ^4-cyclohexene-1,2-dicarboxylic acid are oxidised to the respective 5-hydroperoxides[292]. *p*-Isopropylacetophenone in the presence of nickel benzoate is oxidised to the corresponding hydroperoxide, which also, like the hydroperoxide of *m*-isopropylacetophenone, is cleaved by sulphuric acid into ketophenols employed in the synthesis of drugs. Methyl 10-phenylundecanoate in the presence of the sodium salt of cumene hydroperoxide is oxidised according to the scheme:

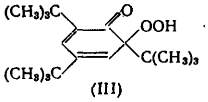


$$CH_3{-}\overset{\displaystyle C_6H_5}{\overset{|}{C}H}(CH_2)_8COOCH_3 \xrightarrow{O_2} CH_3{-}\underset{\displaystyle OOH}{\underset{|}{\overset{\displaystyle C_6H_5}{\overset{|}{C}}}}(CH_2)_8{-}COOCH_3 \rightarrow$$
$$\rightarrow CH_3{-}CO(CH_2)_8COOCH_3 + C_6H_5OH.$$

Phenols are known to inhibit autoxidation. Trialkylphenols, added in the autoxidation of isopropylbenzene, are themselves partly oxidised to derivatives of alkyl 4-hydroxyaryl ketones and 1,2-di-*p*-hydroxyphenylethane[293]. Bicke and Gersmann[290] showed that 4-methyl-2,6-di-t-butylphenol and 2,4,6-tri-t-butylphenol in alkaline medium in an atmosphere of oxygen form hydroperoxides in 75% yield, the first compound forming a single hydroperoxide (I), and the second yielding two hydroperoxides (II and III):


(I),


(II),


(III)

(*c*) Oxidation of alkylnitrobenzenes. *o*-Ethylnitrobenzene[294] in the presence of $K_2Cr_2O_7$, $KMnO_4$, and HNO_3 is usually oxidised to *o*-nitrobenzoic acid. *p*-Isopropylnitrobenzene in the presence of nickel benzoate at 100° is oxidised by air to the hydroperoxide, the concentration of which reaches 38.5% after 55 h. The pure hydroperoxide on standing for a long time in the light gradually darkens, and on heating to 150°–160° it decomposes with a flash and the separation of soot[11,295]; when oxygen is blown through *p*-isopropylnitrobenzene in the presence of caustic soda at 130°, the yield of hydroperoxide reaches 89.6% after 15 h. Oxidation can be carried out in the presence of hydroperoxycumene[296].

The following hydroperoxides were obtained in an analogous manner: 4,3-$CH_3(NO_2)C_6H_3.C(CH_3)_2.OOH$, *p*-$NO_2.C_6H_4.C(CH_3)_2.OOH$, etc.[297]

p-Nitrotoluene on oxidation with air under pressure in the presence of manganese and cobalt naphthenates forms *p*-nitrobenzoic acid in 55–75% yield[298].

Arylmagnesium halides, *e.g.* *p*-bromophenylmagnesium bromide, phenylmagnesium bromide, and mesitylmagnesium bromide, are oxidised by oxygen at low temperatures forming the hydroperoxides in yields of 9.3, 5.2, and 3% respectively[299].

ISOLATION AND SEPARATION OF HYDROPEROXIDES

The most varied methods are used for isolating hydroperoxides from the reaction mixture in a pure or highly concentrated form. However, the most widely employed method is to convert them into the sodium salts. It is possible in this way to isolate even the relatively unstable hydroperoxides of toluene, the xylenes, and mesitylene in a quite concentrated form.

Steam distillation is often employed to concentrate the hydroperoxides. A considerable proportion of the unoxidised original hydrocarbon usually distils over with the steam, and a more concentrated hydroperoxide remains in the flask[142,300].

Stable hydroperoxides are isolated by distillation under reduced pressure. Thus distillation of cyclohexylbenzene hydroperoxide at 0.1 mm yielded a preparation containing 90.53% of the hydroperoxide[48]. Extractive distillation of mixtures[301,302] and treatment with hydrogen peroxide in the presence of mineral acids are employed[303].

Mixtures of hydroperoxides are usually separated by first treating the oxidation products with alkaline solutions of various concentrations, then selectively extracting the hydroperoxides from the latter with volatile, water-immiscible solvents such as CH_2Cl_2, $CHCl_3$, $C_2H_4Cl_2$, $(C_2H_5)_2O$, etc. In this way it was possible to separate the primary and tertiary hydroperoxides of the cymenes[304] and of *p*- and *m*-di-isopropylbenzenes[305].

Hydroperoxides are often isolated and purified by chromatography, which is specially suitable for the isolation of crystalline hydroperoxides, *e.g.* hydroperoxy-1,1-diphenylethane[241].

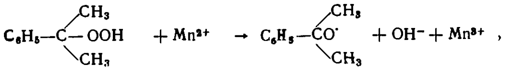
When a hydroperoxide is crystalline and may be precipitated (*e.g.* the dihydroperoxides of *p*- and *m*-di-isopropylbenzenes and of *p*-di-s-butylbenzene), it is filtered off from the cooled reaction mixture and well washed with petroleum ether[220,306]. If it is desired to extract the dihydroperoxide completely the filtrate is treated at a low temperature with benzene or petroleum ether, after which the precipitated dihydroperoxide is again separated, the residue treated with caustic alkali and the hydroperoxide isolated *via* the sodium salt[213].

MECHANISM OF LIQUID-PHASE OXIDATION OF ALKYLARENES

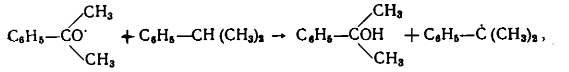
The question of the mechanism and the velocity of the liquid-phase oxidation of hydrocarbons in general, and in particular of alkylarenes with molecular oxygen, has been extensively studied and the results described in review papers[56,86,307]. However, we still do not have a definite solution for all stages of the mechanism, possibly owing to the extraordinary complexity of this reaction[308].

Attempts have been made to find a relationship between the structure of alkylarenes and their reactivity towards oxygen, and to establish the laws governing the oxidative reactivity of hydrocarbons[67,68,73,309-312]. Since individual investigators have used hydrocarbons of varying purity in their work, and have judged the reactivity from data on the oxidation products or from the oxygen absorbed, the conclusions have often been inconsistent. This is indeed understandable, since the rate of oxidation is greatly affected by the purity of the oxidisable species, and the oxygen is not only used up in forming the primary oxidation products, the hydroperoxides, but must also take part in many secondary reactions.

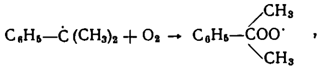
Underlying the mechanism of the liquid-phase oxidation of alkylarenes is Bakh's peroxide theory[313], later developed by Semenov[314] as a free-radical chain mechanism. A characteristic feature of the autoxidation reaction is its great sensitivity to various impurities capable of reacting with active free radicals and thus terminating the reaction chains. The mechanism of the oxidation of one of the most thoroughly studied hydrocarbons, isopropylbenzene, in the presence of manganese salts[88,114,315,316] can be represented by the equations:


(1)

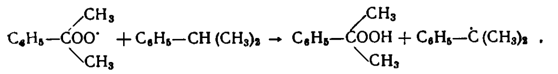
$$C_6H_5-C(CH_3)_2-OOH + Mn^{2+} \rightarrow C_6H_5-C(CH_3)_2-O^{\cdot} + OH^- + Mn^{3+}, \quad (1)$$


(2)

$$C_6H_5-C(CH_3)_2-O^{\cdot} + C_6H_5-CH(CH_3)_2 \rightarrow C_6H_5-C(CH_3)_2-OH + C_6H_5-\dot{C}(CH_3)_2, \quad (2)$$


(3)

$$C_6H_5-\dot{C}(CH_3)_2 + O_2 \rightarrow C_6H_5-C(CH_3)_2-OO^{\cdot}, \quad (3)$$


(4)

$$C_6H_5-C(CH_3)_2-OO^{\cdot} + C_6H_5-CH(CH_3)_2 \rightarrow C_6H_5-C(CH_3)_2-OOH + C_6H_5-\dot{C}(CH_3)_2. \quad (4)$$

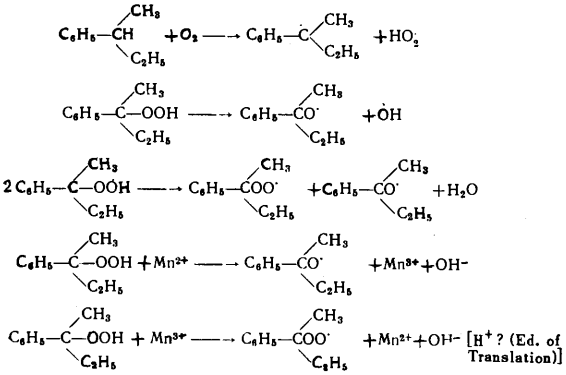
It is evident from these schemes that the principal stable product of the initial oxidation is hydroperoxyisopropylbenzene[317]. A by-product is α,α-dimethylbenzyl alcohol, which lowers the rate of oxidation. The chain reaction is maintained by the phenylisopropyl radical, formed according to Eqn. (2). The role of the catalysts, the manganese salts, consists in splitting up the hydroperoxide which is formed.

Hock and Kropf[149] have shown that the oxidation of isopropylbenzene in the presence of PbO_2 and hydroperoxycumene can occur simultaneously by different mechanisms.

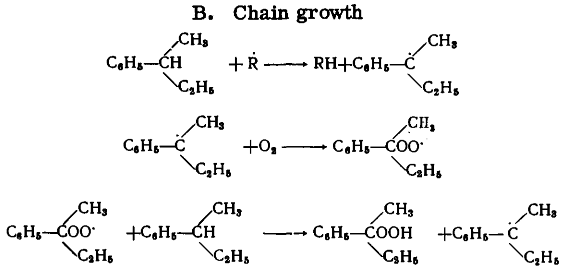
When NaOH is added to the reaction mixture, ions as well as radicals are formed, leading to an increase in the yield of α,α-dimethylbenzyl alcohol to 40%. On addition of Na_2O_2 the conversion of isopropylbenzene into acetophenone increases to 33%. The yield of the latter increases also on addition of ZnO, Al_2O_3, and MnO_2 (to 34–42%). The acidic oxides V_2O_5 and MoO_3 sharply diminish the percentage conversion of the isopropylbenzene.

A radical chain mechanism for the oxidation of s-butylbenzene, including chain initiation, growth, and termination, can be represented by reactions[176] such as:

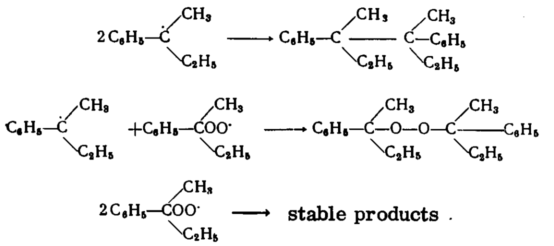
A. **Initiation of reaction chains**


$$C_6H_5-CH(CH_3)(C_2H_5) + O_2 \longrightarrow C_6H_5-\dot{C}(CH_3)(C_2H_5) + HO_2^{\cdot}$$
$$C_6H_5-C(CH_3)(C_2H_5)-OOH \longrightarrow C_6H_5-C(CH_3)(C_2H_5)-O^{\cdot} + \dot{O}H$$
$$2C_6H_5-C(CH_3)(C_2H_5)-OOH \longrightarrow C_6H_5-C(CH_3)(C_2H_5)-OO^{\cdot} + C_6H_5-C(CH_3)(C_2H_5)-O^{\cdot} + H_2O$$
$$C_6H_5-C(CH_3)(C_2H_5)-OOH + Mn^{2+} \longrightarrow C_6H_5-C(CH_3)(C_2H_5)-O^{\cdot} + Mn^{3+} + OH^-$$
$$C_6H_5-C(CH_3)(C_2H_5)-OOH + Mn^{3+} \longrightarrow C_6H_5-C(CH_3)(C_2H_5)-OO^{\cdot} + Mn^{2+} + OH^-$$
[H+ ? (Ed. of Translation)]

B. **Chain growth**


$$C_6H_5-CH(CH_3)(C_2H_5) + \dot{R} \longrightarrow RH + C_6H_5-\dot{C}(CH_3)(C_2H_5)$$
$$C_6H_5-\dot{C}(CH_3)(C_2H_5) + O_2 \longrightarrow C_6H_5-C(CH_3)(C_2H_5)-OO^{\cdot}$$
$$C_6H_5-C(CH_3)(C_2H_5)-OO^{\cdot} + C_6H_5-CH(CH_3)(C_2H_5) \longrightarrow C_6H_5-C(CH_3)(C_2H_5)-OOH + C_6H_5-\dot{C}(CH_3)(C_2H_5)$$

C. **Chain termination**


$$2C_6H_5-\dot{C}(CH_3)(C_2H_5) \longrightarrow C_6H_5-C(CH_3)(C_2H_5)-C(CH_3)(C_2H_5)-C_6H_5$$
$$C_6H_5-\dot{C}(CH_3)(C_2H_5) + C_6H_5-C(CH_3)(C_2H_5)-OO^{\cdot} \longrightarrow C_6H_5-C(CH_3)(C_2H_5)-O-O-C(CH_3)(C_2H_5)-C_6H_5$$
$$2C_6H_5-C(CH_3)(C_2H_5)-OO^{\cdot} \longrightarrow \text{stable products}.$$

Apart from recombination of free radicals, chain termination can occur by the combination of radicals with by-products of the conversion of the alkylbenzene itself as well as of impurities.

From the liquid-phase oxidation of *p*-xylene in the presence of di-t-butyl peroxide (source of free radicals) Lorand and Edwards[189] give the following scheme, which includes the simultaneous formation of 1,2-di-*p*-tolylethane by the linking together of methylbenzyl free radicals:

$$(CH_3)_3-COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO^{\cdot} \rightarrow 2CH_3COCH_3 + 2CH_3^{\cdot}$$

$$p\text{-}CH_3C_6H_4CH_3 + (CH_3)_3CO^{\cdot}\ (\text{or } CH_3^{\cdot}) \rightarrow CH_3C_6H_4CH_2^{\cdot} + (CH_3)_3COH\ (\text{or } CH_4)$$

$$CH_3C_6H_4CH_2^{\cdot} + O_2 \rightarrow CH_3C_6H_4CH_2OO^{\cdot}$$

$$CH_3C_6H_4CH_2OO^{\cdot} + p\text{-}CH_3C_6H_4CH_3 \rightarrow p\text{-}CH_3C_6H_4CH_2OOH + p\text{-}CH_3C_6H_4CH_2^{\cdot}$$

$$p\text{-}CH_3C_6H_4CH_2^{\cdot} + {}^{\cdot}CH_2C_6H_4CH_3\text{-}p \rightarrow p\text{-}CH_3C_6H_4CH_2CH_2C_6H_4CH_3.$$

Other by-products in this reaction are *p*-tolualdehyde, *p*-toluic acid, *p*-methylbenzyl alcohol, etc.

Erofeev and his coworkers[318] studied the kinetics of the oxidation of cumene mixed with $CH_3.COOH$, $(CH_3)_2CH.COOH$, and n-$C_{17}H_{35}$.COOH in the presence of cobalt acetate, and showed that additions of up to 1% of these acids increased the velocity of oxidation. As the concentration of the acids increased, the quantity of CO_2 increased at the same time, at least part of it being formed by decarboxylation of these acids; this is explained[318] by the occurrence of an associated decarboxylation with simultaneous autoxidation of the hydrocarbons according to the scheme:

$$C_6H_5C^{\cdot}(CH_3)_2 + O_2 \rightarrow C_6H_5C(CH_3)_2OO^{\cdot},$$
$$C_6H_5C(CH_3)_2OO^{\cdot} + RCOOH \rightarrow C_6H_5C(CH_3)_2OOH + RCOO^{\cdot},$$
$$RCOO^{\cdot} \rightarrow R^{\cdot} + CO_2,\quad R^{\cdot} + C_6H_5CH(CH_3)_2 \rightarrow C_6H_5C^{\cdot}(CH_3)_2 + RH,$$
$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot},\ ROO^{\cdot} + C_6H_5CH(CH_3)_2 \rightarrow C_6H_5C^{\cdot}(CH_3)_2 + RCOOH.$$

Razuvaev and his coworkers[319] studied the kinetics of the oxidation of cumene by atmospheric oxygen in the presence of manganese resinate and several other substances, and established that the reaction is autocatalytic. This is confirmed by the shortening of the induction period produced by previous addition of hydroperoxycumene (up to 0.2%) to the initial cumene. The induction period is still further shortened by adding the sodium salt of hydroperoxycumene, in conformity with numerous observations of the accelerating action of hydroxides and carbonates of the alkali and alkaline-earth metals. Introduction of small quantities of manganese resinate (up to 36 mg litre^{-1}) also shortens the induction period and increases the rate of formation of the hydroperoxide. Further increase in the concentration of manganese resinate produces a gradual fall in the rate of accumulation of hydroperoxide, owing to the ability of manganese resinate to accelerate not only the formation but also the decomposition of cumene hydroperoxide.

Many substances retard or inhibit the process of autoxidation. Among those which strongly inhibit the oxidation of isopropylbenzene are above all phenols, acids, alcohols, amines, and aromatic thiols. Their action is quite complicated, and probably consists in chain termination. In the opinion of many investigators, the first stage of inhibition is the removal of active hydrogen from the oxygen or the nitrogen of the inhibitor by means of a peroxy radical:

$$ArOH + RO^{\cdot}_2 \rightarrow ArO^{\cdot} + ROOH,$$
$$ArNHR + RO^{\cdot}_2 \rightarrow ArN^{\cdot}R + ROOH.$$

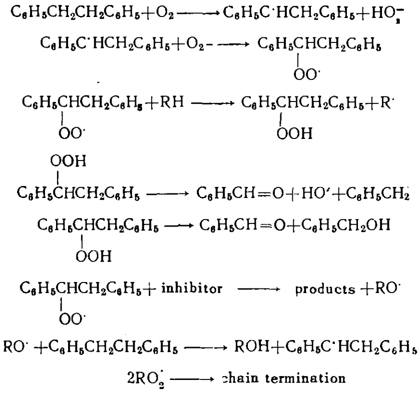
Boozer *et al.*[320,321] consider the first stage of inhibition to be complex formation between the inhibitor and a peroxy radical $RO_2^{\cdot}$ with subsequent cleavage of the complex. Phenol and formic acid exert an especially strong retarding effect on the oxidation; even at a concentration of 0.002 mole % they halve the reaction velocity[319]. Hey and Waters[293] investigated the autoxidation of isopropylbenzene in the presence of trialkylphenols, and established that about 2% of the latter is oxidised to derivatives of alkyl 4-hydroxyaryl ketones and 1,2-di-*p*-hydroxyphenylethane.

In the opinion of Barnard *et al.*[322] the inhibiting effect of mono- and di-sulphides on the autoxidation of squalene at 75° is due to the formation, in the course of the oxidation, of sulphoxides and thiosulphinates, the inhibiting action of which is considerably stronger than that of the original sulphides. The activity of sulphoxides of the type R.SO.R′ as antioxidants depends on the nature of the radicals R and R′, long alkyl substituents exhibiting the greater activity. The activity of thiosulphinates RSOSR′ is less dependent on the nature of R and R′, but dialkyl derivatives are more active than diaryl derivatives.

Ivanov and Vilyanskaya[323] have shown that the liquid-phase oxidation of petroleum hydrocarbons by molecular oxygen is completely inhibited, even in the presence of a source of free radicals, by retarding agents of the type of *p*-hydroxydiphenylamine and 4-methyl-2,6-di-t-butylphenol, for these substances react with R· to give inactive products. When oxidation is initiated by the radical $RO_2^{\cdot}$ of hydroperoxycumene + Co^{3+}, substances of the type of 4,4′-diaminodiphenyl sulphide are effective inhibitors, since they react both with $RO_2^{\cdot}$ and with hydroperoxides ROOH, whereas 4-methyl-2,6-di-t-butylphenol reacts with $RO_2^{\cdot}$, but not with the hydroperoxide, so that it merely retards the reaction without completely inhibiting it.

α,α-Dimethylbenzyl alcohol has a weaker effect than phenol or acids in inhibiting the oxidation of isopropylbenzene[319]. Di-isopropylbenzene, acetophenone, and cyclohexene have still feebler effects. Benzene, toluene, ethylbenzene, *p*-cymene, acetone, and chlorobenzene have hardly any effect on the reaction velocity even at a concentration of 4 mole %. Sulphur dioxide has the strongest retarding effect on the oxidation. A concentration of 0.001 vol.% completely stops the reaction. A smaller influence is exerted by Cl_2, HCl, and H_2S. The reaction is strongly poisoned by solid Fe_2O_3 and $FeCl_3$, and also $NiSO_4$ and $CuSO_4$. CuO and Cr_2O_3 accelerate the reaction in the initial stages, but then the content of hydroperoxycumene hardly rises at all.

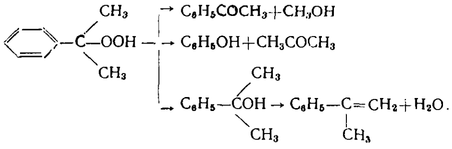
In the initial stages of the oxidation of 1,2-diphenylethane[324] at 110°, 130°, 140°, and 150°, only peroxides are detected among the reaction products. The curves for their formation are practically identical with those for the absorption of oxygen, which is a direct proof of the formation of the monohydroperoxide. Other compounds are formed by decomposition of this hydroperoxide and subsequent oxidation of the products formed. The following radical-chain mechanism is suggested for the oxidation of 1,2-diphenylethane:



$$C_6H_5CH_2CH_2C_6H_5 + O_2 \longrightarrow C_6H_5C^{\cdot}HCH_2C_6H_5 + HO_2^{\cdot}$$
$$C_6H_5C^{\cdot}HCH_2C_6H_5 + O_2 \longrightarrow C_6H_5\underset{\substack{|\\ OO^{\cdot}}}{C}HCH_2C_6H_5$$
$$C_6H_5\underset{\substack{|\\ OO^{\cdot}}}{C}HCH_2C_6H_5 + RH \longrightarrow C_6H_5\underset{\substack{|\\ OOH}}{C}HCH_2C_6H_5 + R^{\cdot}$$
$$C_6H_5\overset{\substack{OOH\\ |}}{C}HCH_2C_6H_5 \longrightarrow C_6H_5CH{=}O + HO^{\cdot} + C_6H_5CH_2^{\cdot}$$
$$C_6H_5\underset{\substack{|\\ OOH}}{C}HCH_2C_6H_5 \longrightarrow C_6H_5CH{=}O + C_6H_5CH_2OH$$
$$C_6H_5\underset{\substack{|\\ OO^{\cdot}}}{C}HCH_2C_6H_5 + \text{inhibitor} \longrightarrow \text{products} + RO^{\cdot}$$
$$RO^{\cdot} + C_6H_5CH_2CH_2C_6H_5 \longrightarrow ROH + C_6H_5C^{\cdot}HCH_2C_6H_5$$
$$2RO_2^{\cdot} \longrightarrow \text{chain termination}$$

MECHANISM AND KINETICS OF THE CLEAVAGE OF HYDROPEROXIDES

Depending on the catalyst and other conditions, hydroperoxides of alkylarenes can be cleaved to form phenols and aliphatic ketones, aliphatic aromatic ketones, alcohols, and their dehydration products, arylolefines. In the case of isopropylbenzene hydroperoxide such cleavage can be represented by the scheme:

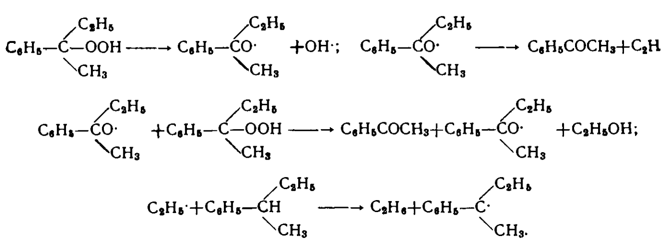


Acetophenone and methanol are formed by the thermal decomposition of hydroperoxycumene. Hydroperoxy-s-butylbenzene, on being heated in sealed tubes, begins to decompose at an appreciable rate at 132°–138°; vigorous decomposition occurs on heating to 145° and above. In this case, too, the principal decomposition product is acetophenone[177]. The decomposition of hydroperoxycumene in acid media, which was first observed by Udris *et al.*[98] in 1943, leads to the formation of phenol and acetone, but in alkaline media α,α-dimethylbenzyl alcohol is obtained.

Various opinions exist as to the mechanism of the decomposition of hydroperoxides. According to some investigators[325–329] it occurs by a unimolecular mechanism with rupture of an O–O bond. Other workers[170,307,330,331] cite data supporting a bimolecular decomposition of hydroperoxides with formation of water and of hydroxy- and peroxy-radicals, and several consider that decomposition occurs simultaneously by unimolecular and bimolecular reactions.

According to results obtained by Kharasch *et al.*[332] hydroperoxyisopropylbenzene reacts with strong acids by an ionic mechanism. With other reagents the hydroperoxide decomposes by a radical mechanism with formation of the $C_6H_5.C(CH_3)_2.O\cdot$ radical in the initial stages of the reaction.

Yamada[333] assumed the following mechanism for the decomposition of hydroperoxy-s-butylbenzene:



$$C_6H_5{-}C(C_2H_5)(CH_3){-}OOH \longrightarrow C_6H_5{-}C(C_2H_5)(CH_3)O\cdot + OH\cdot;\quad C_6H_5{-}C(C_2H_5)(CH_3)O\cdot \longrightarrow C_6H_5COCH_3 + C_2H_5\cdot;$$

$$C_6H_5{-}C(C_2H_5)(CH_3)O\cdot + C_6H_5{-}C(C_2H_5)(CH_3){-}OOH \longrightarrow C_6H_5COCH_3 + C_6H_5{-}C(C_2H_5)(CH_3)O\cdot + C_2H_5OH;$$

$$C_2H_5\cdot + C_6H_5{-}CH(C_2H_5)(CH_3) \longrightarrow C_2H_6 + C_6H_5{-}\dot{C}(C_2H_5)(CH_3).$$

Kucher and Yurzhenko[334] studied the rate of decomposition of hydroperoxyisopropylbenzene in aqueous solutions of Nekal [generic name for a group of wetting and emulsifying agents (Ed. of Translation)] and potassium laurate and stearate, and established that in acid medium the primary thermal decomposition of the hydroperoxide occurs at the peroxy bond O–O resulting in the formation of two radicals:

$$C_6H_5.C(CH_3)_2.O{-}OH \rightarrow C_6H_5.C(CH_3)_2.O\cdot + \cdot OH.$$

The first radical then reacts with a molecule of the hydroperoxide:

$$C_6H_5.C(CH_3)_2.O\cdot + C_6H_5.C(CH_3)_2.O{-}OH \rightarrow$$
$$\rightarrow C_6H_5.C(CH_3)_2.O\cdot + C_6H_5OH + CH_3.CO.CH_3.$$

This type of decomposition leads to recombination of free radicals, and is therefore inactive with respect to the initiation of emulsion polymerisation. The action of the emulsifiers on the decomposition of the hydroperoxide is, in the opinion of these workers, associated with their hydrophilic character, the surface activity of the soap being taken as a measure of this property. The more hydrophilic the soap, the more it protects the hydroperoxide molecule from decomposition, *i.e.* the more the latter is stabilised. Consequently, the more hydrophobic the emulsifier, the better it catalyses the decomposition of the hydroperoxide.

Shushunov *et al.* made a detailed study of the kinetics of the decomposition of hydroperoxy-isopropylbenzene and -s-butylbenzene and established that the rate of cleavage of the former into phenol and acetone is proportional to the concentration of the sulphuric acid, and obeys a first-order equation with respect to hydroperoxide concentrations below 0.02 M.[335] An autocatalytic effect is observed which is greater the higher the concentration of hydroperoxyisopropylbenzene: this is explained by the effect of the acetone formed, additions of which accelerate the reaction. Benzophenone and phenol do not affect the reaction velocity.

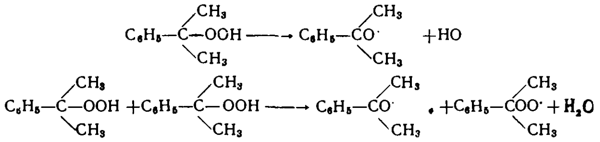
The sulphuric-acid catalysed decomposition of hydroperoxy-isopropylbenzene and -s-butylbenzene in dioxan is of the first order with respect to both the hydroperoxides and the catalyst[336]. Addition of glacial acetic acid has no effect, but addition of water strongly retards the acid-catalysed decomposition of these hydroperoxides. Acetic anhydride strongly accelerates the reaction. Additions of ethyl methyl ketone and phenol up to concentrations of 0.1–0.5 M have little effect on the rate of decomposition.

The rate of cleavage of hydroperoxyisopropylbenzene into acetophenone and α,α-dimethylbenzyl alcohol in the presence of Co^{2+}, Mn^{2+}, Cu^{2+}, Fe^{2+}, and Na^+ stearates in chlorobenzene is also proportional to the hydroperoxide and stearate concentrations[337]. The initial concentration of hydroperoxide does not affect the catalytic rate constant, which indicates the absence of any induced decomposition of the hydroperoxide. The catalytic activity falls in the sequence $Co^{2+} > Mn^{2+} > Cu^{2+} > Fe^{2+} > Na^+$. Zinc stearate possesses no catalytic activity. It is assumed that the catalyst facilitates the first stage of the reaction — decomposition of the hydroperoxide molecule with rupture of the O–O bond to form the radicals $C_6H_5.C(CH_3)_2.O\cdot$ and $\cdot OH$.

The rate of reaction of hydroperoxyisopropylbenzene with triethylenetetramine in the presence of ferric sulphate in aqueous solution at 20°–25° depends on the time for which the Fe^{3+} solutions have been kept, and is identical for Fe^{3+} and Fe^{2+} at equal concentrations[338]. The decomposition products include acetophenone and α,α-dimethylbenzyl alcohol.

Decomposition of hydroperoxyisopropylbenzene in a mixture of isopropyl alcohol and benzene leads to the formation of acetone, α,α-dimethylbenzyl alcohol, acetophenone, and α-methylstyrene. The velocity of this reaction depends on the composition of the solvent, the concentration of hydroperoxide, and the temperature. Sokolov and Shushunov[339] propose the following chain mechanism for the decomposition of hydroperoxycumene in the presence of isopropyl alcohol:

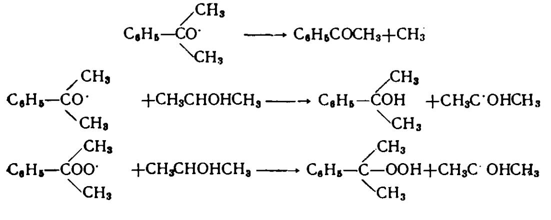
A. Chain initiation



$$C_6H_5{-}C(CH_3)_2{-}OOH \longrightarrow C_6H_5{-}C(CH_3)_2O\cdot + HO$$

$$C_6H_5{-}C(CH_3)_2{-}OOH + C_6H_5{-}C(CH_3)_2{-}OOH \longrightarrow C_6H_5{-}C(CH_3)_2O\cdot + C_6H_5{-}C(CH_3)_2OO\cdot + H_2O$$

B. Chain growth



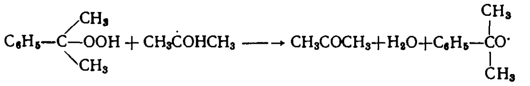
$$C_6H_5{-}C(CH_3)_2O\cdot \longrightarrow C_6H_5COCH_3 + CH_3$$

$$C_6H_5{-}C(CH_3)_2O\cdot + CH_3CHOHCH_3 \longrightarrow C_6H_5{-}C(CH_3)_2OH + CH_3\dot{C}OHCH_3$$

$$C_6H_5{-}C(CH_3)_2OO\cdot + CH_3CHOHCH_3 \longrightarrow C_6H_5{-}C(CH_3)_2{-}OOH + CH_3\dot{C}OHCH_3$$

$$CH_3CHOHCH_3 + CH_3^{\cdot} \longrightarrow CH_4 + CH_3\dot{C}OHCH_3$$

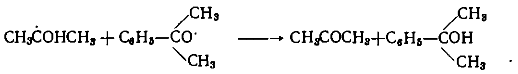
$$CH_3CHOHCH_3 + OH^{\cdot} \longrightarrow H_2O + CH_3\dot{C}OHCH_3$$



$$C_6H_5{-}C(CH_3)_2{-}OOH + CH_3\dot{C}OHCH_3 \longrightarrow CH_3COCH_3 + H_2O + C_6H_5{-}C(CH_3)_2O^{\cdot}$$

C. Chain termination

$$2CH_3\dot{C}OHCH_3 \longrightarrow CH_3COCH_3 + CH_3CHOHCH_3$$



$$CH_3\dot{C}OHCH_3 + C_6H_5{-}C(CH_3)_2O^{\cdot} \longrightarrow CH_3COCH_3 + C_6H_5{-}C(CH_3)_2OH$$

Since these workers employed dilute solutions, they assume that chain initiation occurred according to the first reaction, and that bimolecular decomposition, as in the second reaction, did not occur.

Studies have been made of the kinetics of the heterogeneous decomposition of hydroperoxycumene on nickel sulphate[340] and on the ion-exchange resin KU-2.[341] Previously dehydrated nickel sulphate has been shown to accelerate the decomposition of hydroperoxycumene into acetone and phenol. In separate experiments the yield of phenol reached 94–97% of theoretical. Small amounts of α,α-dimethylbenzyl alcohol and acetophenone (traces) are formed in the reaction. Heterogeneous decomposition of the hydroperoxide into heptane on nickel sulphate occurs at an appreciable rate at 50°. The reaction velocity increases with rise in temperature. The initial rate of such decomposition of hydroperoxyisopropylbenzene is directly proportional to the catalyst concentration. In contrast to the acid-catalysed decomposition[335] the process occurs without self-acceleration. Additions of phenol and acetone have no effect, but addition of α,α-dimethylbenzyl alcohol strongly retards the reaction.

The heterogeneous decomposition of hydroperoxyisopropylbenzene on the ion-exchange resin KU-2 in the solvents n-octane, chlorobenzene, and acetone is accompanied by the formation of acetone and phenol in almost quantitative yield. The reaction is of the first order with respect to hydroperoxyisopropylbenzene.

CLEAVAGE OF HYDROPEROXIDES INTO PHENOLS AND ALIPHATIC KETONES

Metal sulphates and chlorides as well as acid catalysts (as just noted) usually cleave hydroperoxides into phenols and aliphatic ketones. Substances which are very frequently employed are dilute sulphuric acid[183,342-350], a mixture of concentrated or dilute sulphuric acid with acetone[351-357] or other inert solvents[358], porous material (pumice, kieselguhr) moistened with 85% sulphuric acid[359], orthophosphoric and acetic acids[332,360], hydrochloric acid[361], perchloric acid[362], arylsulphonic acids and their acid chlorides[363-365], sulphates of metals of Groups I and II, in particular copper and calcium sulphates[366,367], ferric chloride[368], boron trifluoride[369], sulphur dioxide and trioxide[156,357,370], and other catalysts[371-373].

The sulphuric-acid cleavage of α-hydroperoxytoluene yields phenol and formaldehyde[181,374,375]. Treatment of hydroperoxy-*p*-xylene with concentrated sulphuric acid in methyl alcohol yields *p*-cresol in 55% yield[375]. Hydroperoxy-*p*-di-isopropylbenzene in acetone at 56°–75° is cleaved by sulphuric acid into *p*-isopropylphenol in 83% yield[74].

Hydroperoxides containing the peroxy-group at a secondary or tertiary α-carbon atom are split by acids into phenols and aldehydes or ketones. Thus hydroperoxyethylbenzene in the presence of electrophilic catalysts (H_2SO_4, BF_3 in the form of its compounds with ethers and with orthophosphoric acid) is cleaved to phenol and acetaldehyde[376-378].

Many methods have been published for cleaving hydroperoxyisopropylbenzene of various concentrations and for isolating the resulting products. In industry cleavage is usually effected with concentrated sulphuric acid. When the hydroperoxide is cleaved with sulphuric acid diluted with water or acetone, phenol can be obtained in yields up to 98% and acetone in about 75% yield[91,105,348,356,379-381].

In order to obtain phenol in good yield, Bewley[382] recommends decomposing the residue in the vat in the presence of an acid catalyst at a high temperature, with subsequent treatment with water at 50°–100°. Several patents[383-385] propose cleaving hydroperoxyisopropylbenzene into phenol and acetone with sulphuric or perchloric acid in the presence of phenol. Perchloric acid in acetic acid cleaves this hydroperoxide almost quantitatively[332]. As an improved method for obtaining phenol and acetone, another patent[355] recommends completely freezing the reaction mixture from HCl (after separating the hydrocarbon from the cleavage products) by washing with a small quantity of a 1–2% solution of citric, tartaric, salicylic, or phthalic acid.

Cleavage of hydroperoxyisopropylbenzene occurs quite smoothly if hydrogen peroxide or substances which produce it are first added to the crude hydroperoxide[346,386]. For the cleavage of hydroperoxycumene suitable catalysts are, as indicated above, sulphates of metals of Groups I and II[366,387], elements of Groups V and VI of the Periodic System[388], activated clays[148,389], and ion-exchange resins, *e.g.* the sulphonated resins KU-1 ‡ and KU-2 ‡[390].

A recommended method for isolating phenol from mixtures formed by the cleavage of hydroperoxycumene, which always contain acetophenone, α,α-dimethylbenzyl alcohol, and α-methylstyrene, though in small amounts, is to treat the products with alkaline aqueous solutions with subsequent fractional distillation[391,392] or simply to fractionate the cleaved mixture on efficient plate columns[393-395] and several other methods[396-404]. Thus one patent[371] recommends neutralising the cleavage products of hydroperoxyisopropylbenzene with an equimolecular amount of a 10–60% aqueous solution of sodium phenoxide, and in this way avoiding the possible formation of a gelatinous deposit, as occurs on neutralising with solid or aqueous solutions of caustic alkalis. Phenol can be isolated and purified by treating the mixture of cleavage products from hydroperoxycumene with hexane after addition of water[405]. Bowen[406] recommends, after removing acetone, α-methylstyrene, and acetophenone from the mixture, subjecting the remaining *p*-cumenylphenol to pyrolysis at 200°–400°, and

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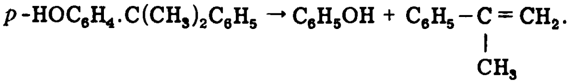
‡ KU-1 is a strongly acidic bifunctional cation exchange resin with SO_3H and OH as the active groups. It is obtained by polycondensation of *p*-phenolsulphonic acids with formaldehyde in acidic media. KU-2 is a monofunctional, strongly acidic, cation exchange resin with SO_3H as the only active group. It is obtained by treating swollen copolymer of styrene and divinylbenzene with chlorosulphonic acid, with subsequent saponification of the sulphochloride derivative (Ed. of Translation).

thereby increasing the yield of phenol and α-methylstyrene by means of the reaction

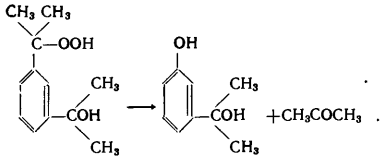


$$p\text{-}HOC_6H_4.C(CH_3)_2C_6H_5 \rightarrow C_6H_5OH + C_6H_5-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2.$$

The cleavage of hydroxyperoxy-s-butylbenzene takes place quietly and in good yield in the presence of arylsulphonyl chlorides[365], *e.g.* benzenesulphonyl chloride.

Mono- and di-hydroperoxides of dialkylbenzenes are cleaved in the presence of acid reagents into alkylphenols or dihydric phenols and aliphatic ketones. Thus acid cleavage of hydroperoxides of the cymenes (mainly 8-hydroperoxy-*p*-cymene) gives a good yield of cresols[228,369,407-409]. Monohydroperoxy-*p*-ethylisopropylbenzene on cleavage with sulphuric acid forms mainly *p*-isopropylphenol[207]. The monohydroperoxides of *p*- and *m*-di-isopropylbenzenes are converted by dilute sulphuric acid into *p*- and *m*-isopropylphenols respectively[183, 206, 343, 381, 410]. The dihydroperoxides of *p*-xylene and of *p*- and *m*-di-isopropylbenzenes are cleaved by sulphuric acid to quinol or resorcinol with yields of 90% and above[96,183,343,353,354,381,396,406,411-413]. The yield of monohydric and dihydric phenols can be increased by subjecting the residues in the vat, after removal of the main amounts of phenols, to thermal cleavage in the presence of inert organic solvents, *e.g.* tri-isopropylbenzene, alkylnaphthalenes[191,410].

m-α-Hydroxyisopropyl-α′,α′-dimethyl-α′-hydroperoxytoluene in dry benzene is cleaved in the presence of H_2SO_4 into *m*-α-hydroxyisopropylphenol[364,414]:



The mono- and di-hydroperoxides of *p*-isopropyl-s-butylbenzene are split by sulphuric acid into *p*-isopropyl- (mainly and *p*-s-butyl-phenol and quinol[233]; those of *p*-di-s-butylbenzene into *p*-s-butylphenol, quinol, and ethyl methyl ketone[59,222,224]; hydroperoxy-*p*-isopropyl- and -*p*-cyclohexyl-fluorobenzene are converted by sulphuric acid into *p*-fluorophenol[282]. A mixture of the mono-, di-, and tri-hydroperoxides of 1,3,5-tri-isopropylbenzene is split in the presence of sulphuric acid into monoisopropylresorcinol, di-isopropylresorcinol, and phloroglucinol[231]. Hydroperoxy-1,2,4-tri-isopropylbenzene is cleaved to 3,4-di-isopropylphenol[231]. Similarly, hydroperoxycyclohexylbenzene hydroperoxide is split by dilute sulphuric acid into phenol and cyclohexanol[350], and hydroperoxy-*p*-cyclohexylisopropylbenzene into *p*-cyclohexylphenol[225]. Hydroperoxy-*p*-s-butylbiphenyl is converted by acidic reagents into *p*-hydroxybiphenyl[269].

Hydroperoxides containing aliphatic carbon atoms linked to two or three aryl radicals are readily cleaved in acid medium by means of steam[415]. The process is carried out by continuously feeding in the hydroperoxide and the steam, and distilling off the resulting phenol with the steam. Acid cleavage of hydroperoxy-1,1-diphenylethane yields phenol and acetophenone[416]. 1,1-Di-*p*-tolylethane gives *p*-cresol and *p*-methylacetophenone; hydroperoxytriphenylmethane in acid medium is also decomposed into phenol and benzophenone[257].

Under mild conditions hydroperoxides in contact with strong acids may condense to form diperoxides[417].

A 28% yield of 2-naphthol is obtained by cleaving hydroperoxy-2-isopropylnaphthalene with sulphuric acid[349,375]. 1,4-Dihydroperoxy-1,4-diethyltetralin on cleavage in this way gives catechol, *o*-4-oxohexanoylphenol, and octane-3,6-dione[263]. Hydroperoxy-1,3,3-trimethylindan-1-yl is cleaved by sulphuric acid with the formation of 2,4,4,-trimethylchrom-2-en and 2,4,4-trimethylchroman-2-ol. When the hydroperoxide is heated with alkanesulphonic acids, *e.g.* $C_4H_9SO_3H$ in acetone, 2,4,4-trimethylchroman-2-yl peroxide is formed together with other products[271].

CLEAVAGE OF HYDROPEROXIDES INTO ALCOHOLS, ALDEHYDES, OR KETONES

Mono- and di-hydroperoxides of alkylbenzenes having the peroxy-group attached to a tertiary α-carbon atom are readily reduced by sulphides of the alkali and alkaline-earth metals, caustic soda or potash, or sodium bisulphite or thiosulphate to the corresponding mono- and di-carbinols. Thus, for example, hydroperoxyisopropylbenzene in an aqueous solution of sodium sulphide is converted into α,α-dimethylbenzyl alcohol[418] and mono- and di-hydroperoxy-*p*-di-isopropylbenzenes are reduced by sodium thiosulphate, caustic soda, or caustic potash into *p*-isopropylphenyldimethylmethanol and *p*-(α,α′-dihydroxydi-isopropyl)benzene respectively[183,206]. Hydroperoxyisopropylbenzene and other hydroperoxides are reduced in the presence of Raney nickel, platinum, or cobalt to dimethylphenylmethanol[419]. Monohydroperoxy-*p*-s-butylisopropylbenzene on reduction with $Na_2S_2O_3$ is converted into *p*-s-butylphenyldimethylmethanol, while the dihydroperoxide forms $p\text{-}(CH_3)_2C(OH).C_6H_4.C(CH_3)(C_2H_5).OH$. Hydroperoxy-*p*-t-butylisopropylbenzene in an alkaline solution of sodium sulphate is readily converted into *p*-t-butylphenyldimethylmethanol[220]. Monohydroperoxy-*p*-di-s-butylbenzene is reduced by zinc dust and 30% caustic soda solution to *p*-s-butylphenylethylmethylmethanol, the yield being 96% of theoretical, and the dihydroperoxide under similar conditions is converted into *p*-(α,α′-dihydroxy-s-butyl)benzene with a yield of 92% of theoretical[59]. Similarly, the mono-, di-, and tri-hydroperoxides of 1,3,5-tri-isopropylbenzene are quantitatively reduced by excess of sodium to the corresponding tertiary alcohols[231]. Monohydroperoxy-1,2,4-tri-isopropylbenzene is reduced by zinc dust and caustic soda to 1-α-hydroxyisopropyl-3,4-di-isopropylbenzene[231], and the hydroperoxides of tetralin and 1,3,3-trimethylindan-1-yl into the corresponding alcohols[271].

Primary hydroperoxides of alkylbenzenes in the presence of metal salts are usually cleaved to the corresponding aldehydes, but the secondary and tertiary hydroperoxides are converted into acetyl derivatives. This also occurs as a side-reaction during the autoxidation of alkylarenes to hydroperoxides, and therefore aldehydes or ketones are always present among the products of the sulphuric-acid cleavage of hydroperoxides. Their amount depends on the initiators employed for the autoxidation and on the extent of oxidation. As has been shown above, in individual cases the acetyl derivatives may be the principal or even the only products of the liquid-phase oxidation of alkylarenes. Ferrous sulphate solution is most often employed for the ketonic cleavage. For example, hydroperoxy-n-butylbenzene is split by ferrous sulphate at elevated temperatures into benzaldehyde[64], but hydroperoxy-s-butylbenzene gives acetophenone[175]. Hydroperoxyisopropylbenzene with ferric chloride is cleaved to acetophenone[4], but monohydroperoxy-*p*-di-s-butylbenzene is reduced to *p*-s-butylacetophenone. The dihydroperoxides of *p*-di-isopropylbenzene and *p*-di-s-butylbenzene are converted by ferrous sulphate solution into *p*-diacetylbenzene[183,222]. A mixture containing 53.7% of total mono- and di-hydroperoxides of *p*-di-s-butylbenzene on heating with aqueous 1 *N* $FeSO_4$ forms *p*-s-butylacetophenone and *p*-diacetylbenzene in yields of 58% and 60% respectively based on the hydroperoxide content[59].

1,4-Dihydroperoxy-1,4-diethyltetralin with $FeSO_4$ is converted into 1,4-naphthaquinone[263], but hydroperoxydecalin gives an 80% yield of 2-n-butylcyclohexanone.

Hydroperoxyisochroman on boiling with 2 *N* KOH is converted into isochroman-1-one in 66% yield, but with NaOH, Na_2SO_4, and H_2O it gives a 62% yield of *o*-2-hydroxyethylbenzaldehyde[276]. Hydroperoxy-*p*-isopropylnitrobenzene in the presence of $Cu(NO_3)_2.3H_2O$ decomposes into *p*-nitroacetophenone and dimethyl-*p*-nitrophenylmethanol[296].

FORMATION OF PEROXIDES

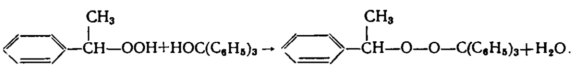
Alkyl and aryl hydroperoxides, in the presence of a small quantity (0.2%) of copper, cobalt, and manganese salts of glycollic and other acids, react with organic compounds containing reactive hydrogen atoms to form peroxides by replacement of the hydrogen by the peroxy-group[420]. In this way α-cumenyl-t-butyl peroxide and α-cumenylperoxycyclohexene have been obtained in 90% yield.

Alkyl and aryl hydroperoxides can be alkylated by ethers[421]. In the presence of a small amount of H_2SO_4 at 20° t-butyl hydroperoxide reacts with ethyl triphenylmethyl ether in $CH_3.COOH$ to form t-butyl triphenylmethyl peroxide:

$$(C_6H_5)_3C-O-C_2H_5 + C_4H_9OOH \rightarrow (C_6H_5)_3C-O-O-C_4H_9 + C_2H_5OH.$$

Similarly, hydroperoxycumene is alkylated by isopropyl triphenylmethyl ether to form the peroxide $C_6H_5.C(CH_3)_2.O.O.C(C_6H_5)_3$. t-Butyl hydroperoxide with bis(diphenylmethyl) ether gives the peroxide $C_4H_9.O.O.CH(C_6H_5)_2$.

Hydroperoxy-1-phenylethane is alkylated by triphenylmethanol to form 1-phenylethyl triphenylmethyl peroxide[422]:



Tertiary hydroperoxides of alkylarenes can react with alcohols with the formation of peroxides. Hydroperoxycumene with dimethylphenylmethanol in glacial acetic acid in the presence of a catalyst (H_2SO_4 or $HClO_4$) forms dicumenyl peroxide in 95% yield based on the hydroperoxycumene and 80% yield based on the dimethylphenylmethanol[423]. *p*-Isopropyl-s-butylbenzene hydroperoxide with dimethyl-*p*-s-butylphenylmethanol forms the peroxide $\{p\text{-s-}C_4H_9.C_6H_4.C(CH_3)_2.O\}_2$. Hydroperoxydiphenylmethane when heated with diphenylmethanol in the presence of *p*-$CH_3.C_6H_4.SO_3H$ and $CH_3.COOH$ to 80° for 1 h forms bis(diphenylmethyl) peroxide[424].

Alkyl and aryl hydroperoxides of general formula $R.C(CH_3)_2.OOH$ (R = CH_3 or C_6H_5) condense with orthoesters $RO.CR'(OC_2H_5)_2$ (R = C_2H_5, R′ = CH_3 or H) to form perorthoesters[425]:

$$R-C(OC_2H_5)_3 + R'C(CH_3)_2-OOH \rightarrow R'C(CH_3)_2-O-O-C(R)(OC_2H_5)_2 + C_2H_5OH,$$

where R = CH_3 or H; R′ = CH_3 or C_6H_5.

Oxidation of cumene with air in the presence of PbO_2 at 50° forms 27% of hydroperoxycumene, 21% of dimethylphenylmethanol, 7% of cumene peroxide, 2% of acetophenone, and 42% of isopropylbenzene. With phenol in the presence of 96% H_2SO_4 this mixture forms *p*-α-cumenylphenol in 87–99% yield based on the carbinol[426]. Hydroperoxyisopropylbenzene with tetraethyl-lead in glacial acetic acid at 30° gives acetophenone, dimethylphenylmethanol, and dicumenyl peroxide in amounts of 0.32, 0.54, and 0.03 mole respectively per mole of hydroperoxycumene[427]. In the presence of this hydroperoxide in benzene solution, diphenyl sulphides are oxidised to symmetrical diphenyl sulphoxides[428].

Hydroperoxides of ethylbenzene, isopropylbenzene, tetralin, and decalin tend to increase the yield of benzene hexachloride and its γ-isomer content in the chlorination of benzene in the liquid phase[429].

INITIATION OF POLYMERISATION BY HYDROPEROXIDES

Several hydroperoxides are now employed in industry as initiators, *e.g.* for the emulsion copolymerisation of butadiene with styrene, which occurs by a free-radical mechanism, and, like other similar reactions, requires the presence of an activating agent to start the chain.

The initiation of the polymerisation of unsaturated compounds by hydroperoxides of aliphatic and alkylarenes is based on their ability, under certain conditions, to decompose into free radicals, which initiate the chain as follows:

$$\begin{gathered}ROOH \rightarrow RO\cdot + HO\cdot \\ RO\cdot + RH \rightarrow R\cdot + ROH \\ RH + HO\cdot \rightarrow R\cdot + H_2O \\ R\cdot + O_2 \rightarrow ROO\cdot \\ RH + ROO\cdot \rightarrow ROOH + R \quad \text{etc.}\end{gathered}$$

Among the large group of hydroperoxides, tertiary hydroperoxides of alkylarenes are especially active initiators of polymerisation[4,29,430]. In the USSR hydroperoxyisopropylbenzene is employed for the copolymerisation of 1,3-butadiene with styrene to form rubbers. Americans use, in addition to this hydroperoxide and that of di-isopropylbenzene, hydroperoxy-*p*-menthane, etc. However, the problem of finding new, more active polymerisation initiators remains extremely urgent today.

Fedorova and Sergeev[48] tested as initiators for the low-temperature emulsion copolymerisation of butadiene with styrene, the tertiary hydroperoxides of *p*-cymene, *p*-s-butyltoluene, and cyclohexylbenzene, the monohydroperoxide and a mixture of the mono- and di-hydroperoxides of *p*-di-s-butylbenzene having a content of active oxygen of 9.54%. Hydroperoxy-*p*-isopropyl-t-butylbenzene was taken for comparison. In the presence of hydroperoxy-*p*-s-butyltoluene no polymerisation was observed during 4 h. Hydroperoxycyclohexylbenzene possesses the same activity as that of *p*-isopropyl-t-butylbenzene, but hydroperoxy-*p*-cymene exhibits rather less initiating activity.

As initiators for the low-temperature copolymerisation of butadiene with styrene we have tested, according to recipe SKS-30A[§], the hydroperoxides of cyclohexylbenzene, *p*-cyclohexylisopropylbenzene, *o*-chloro-*p*-di-isopropylbenzene, *p*-di-isopropylbenzene, and *p*-di-s-butylbenzene[431]. The initiating properties of these hydroperoxides were studied at the same time and under similar conditions as those of the peroxides of isopropylbenzene, di-isopropylbenzene, and unsymmetrical diphenylethane. The most active initiator among the hydroperoxides studied was that of *p*-cyclohexylisopropylbenzene in bottle copolymerisation at 10° for 3 h. With this catalyst the rubber content of the latex is 25 g, and the conversion of the hydrocarbons 100%, whereas in the presence of the hydroperoxide of unsymmetrical diphenylethane, which is regarded as the most active initiator, the rubber content of the latex is 24.2 g and the conversion of hydrocarbons 94.4%. It may be mentioned for comparison that, in the presence of hydroperoxyisopropylbenzene, which is used at the present time in industry, the rubber content of the latex under these conditions is 19 g, and the conversion 65.8%. Somewhat better results are obtained in the presence of the hydroperoxides of di-isopropylbenzene, cyclohexylbenzene, and *o*-chloro-*p*-di-isopropylbenzene. In the presence of these hydroperoxides the quantity of rubber in the latex is 22–23 g.

Results of the same order were obtained also in experiments on the autoclave copolymerisation according to recipe SKS-30A at a temperature of +5°.

The hydroperoxides of *p*-cyclohexylisopropylbenzene and of unsymmetrical diphenylethane are more active than that of isopropylbenzene by factors of 2 and 3 respectively. With these hydroperoxides the conversion of hydrocarbons after 4 h is 59%. The physical and mechanical properties of rubbers obtained according to recipe SKS-30A in the presence of the various hydroperoxides do not differ appreciably.

Cumenyl peroxide has been tested[432] as initiator for the copolymerisation of styrene with divinylbenzene and 2,4-dimethylstyrene. Perfluoropenta-1,4-diene, 1,1,3,3,5,5-hexafluoropenta-1,4-diene, 4,5-dichloro-1,1,2,3,3,4,5,5-octafluoropentene, and 1-ethoxyperfluorocyclobutene are polymerised neither by a radical mechanism in bulk or as an emulsion, nor by an ionic mechanism in solution. However, they all copolymerise with butadiene, styrene, and vinyl acetate in the presence of hydroperoxides. With butadiene in the presence of hydroperoxy-*p*-menthane at 5° rubberlike copolymers are formed[433]. Hydroperoxides of tri-isopropylbenzenes are active initiators for emulsion polymerisation[434]. They give the same conversion as hydroperoxy-*p*-isopropyl-t-butylbenzene, but lower than that of hydroperoxycyclohexylbenzene.

Hydroperoxyisopropylbenzene and dihydroperoxy-*p*-di-isopropylbenzene in the form of their sodium and potassium salts are good initiators for the polymerisation of ethylene and the copolymerisation of ethylene with styrene, α-methylstyrene, methyl vinyl ketone, vinylpyridine, and other unsaturated compounds[435]. The polymerisation of styrene in the presence of various hydroperoxides in benzene solution is unimolecular with respect to the initiator[¶], and is explained by reaction between the hydroperoxide and the styrene, leading to the formation of a free radical[436]. There are some indications that hydroperoxy-5-*p*-isopropylphenylpent-2-ene is an active initiator for the polymerisation of diene hydrocarbons to solid polymers[437]. A study has been made of the copolymerisation of methyl acrylate with di-t-butyl peroxide as initiator at a temperature of 60°–68°,[438] and of the polymerisation of vinyl, vinylidene, and diene compounds in the presence of hydroperoxyisopropylnaphthalene. This last hydroperoxide is recommended for the reclaiming of rubber, the process of flotation, and in kier-boiling, finishing, and other textile operations[252].

[§] Designation for synthetic rubber made from butadiene with 30% styrene by low-temperature (5°) polymerisation (Ed. of Translation).

[¶] The reader is advised to consult Schröder's[436] paper here (Ed. of Translation).

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IRREVERSIBLE POLAROGRAPHIC WAVES

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CONTENTS

I. INTRODUCTION

The fundamental basis of classical polarographic theory[1-4], which has contributed to the wide and varied use of the polarographic method, is the hypothesis that the magnitude of the current is determined only by the rate of diffusion of the reacting substances, and the electrochemical reaction proceeds sufficiently quickly for electrochemical equilibrium to be attained at the electrodes. For many so-called "reversible" polarographic waves, these assumptions are quite justified. In the interpretation of such waves by means of the Nernst equation[5], the standard electrode potential φ^0, and hence also the half-wave potential $\varphi_{\frac{1}{2}}$, depend simply on the standard free energy $\Delta G^0(-\Delta G^0 = nF\varphi^0)$[6,7].

For a series of inorganic, and the majority of organic, compounds the rate of electrode reaction is less than, or about the same as, the rate of supply of the depolariser to the electrode surface. During the passage of current the electrochemical equilibrium is disturbed. Polarographic waves obtained under these conditions are termed irreversible. Until recently, irreversible polarographic waves could be handled only by means of empirical expressions, but lately there has been great interest in developing a more general theory of irreversible polarographic waves[8-22], embracing also the familiar relations of reversible waves as a particular case. Conclusions based on the theory of irreversible waves can provide information concerning the mechanism of electrode processes and concerning certain properties of materials.

The approach of different authors to the study of irreversible electrode processes varies, but they all appear to start from the premiss that irreversible waves are determined by the rate of electrode reactions as well as by concentration polarisation. For the interpretation of irreversible polarographic waves, the equations of the delayed discharge theory are usually employed[23-26]. The substances at the surface of the electrode which determine the concentration potential can limit the electrode process not only by hindering diffusion[8-21], but also as a consequence of kinetic limitations, *i.e.* retardation of chemical reactions which precede the electrochemical stage of the process (kinetic currents)[27-37], and also because of the presence of an adsorbed film[38-41].

The present article examines only those irreversible polarographic waves for which the concentrations of the reactants at the electrode surface are determined solely by the diffusion rate. Certain earlier theories of irreversible polarographic waves are considered briefly. The analyses of the waves made by Eyring *et al.*[9] and by Tanaka and Tamamushi[42,43] were based on the Nernst hypothesis concerning the diffusion layer. According to Nernst[44] a layer of liquid of thickness δ close to the surface of the electrode is stationary. From this assumption and also from the condition for constant transfer of material through this layer it follows that the concentration of the reacting substance inside the diffusion layer changes linearly with distance.

Let the following reaction take place at the electrode:

$$\mathrm{O} + ne \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{R}, \tag{1}$$

where O and R are the oxidised and reduced forms of the depolariser, and k_1 and k_2 are the rate constants for the direct and reverse electrochemical reactions. The following general assumptions, which are known to apply approximately under the conditions of ordinary polarography, were made for the derivation: the migration of the reacting ions can be neglected in considering the presence of an excess of inert electrolyte in the solution, provided this is not agitated; adsorption effects at the electrode surface are also absent; the diffusion coefficient is independent of the distance from the electrode surface; the reactants and reaction products are soluble in the solution or in the electrode material; the difference between activities and concentrations can be neglected; apart from the delayed reactions considered there are no other stages which could limit the course of the whole process. Under the specified conditions Fick's first law enables us to write for the current, for the reduction of substance O:

$$i = \frac{D_{\mathrm{O}}}{\delta_{\mathrm{O}} l}\left(c_{\mathrm{O}}^{0} - c_{\mathrm{O}}\right)\frac{nF}{N}, \tag{2}$$

where D_{O} is the diffusion coefficient of substance O, δ_{O} the thickness of its diffusion layer, l the thickness of a monomolecular layer, c_{O}^{0} and c_{O} the concentrations of substance O in the bulk of the solution and at the surface of the mercury drop, n the number of electrons taking part in the reaction, F the Faraday number, and N the Avogadro number.

On the other hand, the general expression for current can be presented in the following form[45-47]:

$$i = \frac{nFs}{N}\left[c_{\mathrm{O}}(0)\,k_1 e^{\alpha n\varphi F/RT} - c_{\mathrm{R}}(0)\,k_2 e^{-(1-\alpha)nF\varphi/RT}\right], \tag{3}$$

where s is the sum of the transport numbers of all the ions except those discharging, $k_i = (KT/h)\exp\left(-\Delta G_i/RT\right)$, $c_{\mathrm{R}}(0)$ is the concentration of substance R at the surface of the electrode, α the transport coefficient, φ the electrode potential, R the gas constant, and T the absolute temperature. The value of the concentration is designated by $c(0)$ and not $c(0t)$ since it is assumed that the transfer of substance remains constant.

From Eqns. (2) and (3) and the assumption that $D_{\mathrm{R}} = D_{\mathrm{O}} = D$ and $\delta_0 = \delta_{\mathrm{O}} = \delta$, we obtain the general equation[9]:

$$i = \frac{c_{\mathrm{O}}^{0} - c_{\mathrm{R}}(0)\,e^{-nF(\varphi-\varphi^0)/RT}}{\dfrac{s\delta l}{D} + \dfrac{1}{k_1}e^{-\alpha nF\varphi/RT}}\,\frac{nF}{N}, \tag{4}$$

where φ^0 is the standard electrode potential, δ_{R} the thickness of the diffusion layer for substance R, and D_{R} the diffusion coefficient for substance R.

If the rate-determining stage in the electrode process is diffusion, then

$$\frac{s\delta l}{D} \gg \frac{1}{k_1}e^{-\alpha nF\varphi/RT}$$

and the second term in the denominator of Eqn. (4) can be disregarded. Eqn. (4) then takes the form:

$$i = \frac{D}{s\delta l}\left[c_{\mathrm{O}}^{0} - c_{\mathrm{R}}(0)\,e^{-nF(\varphi-\varphi^0)/RT}\right]\frac{nF}{N}. \tag{5}$$

In the more general case when $(1/k_1)\exp(-\alpha nF\varphi/RT) < < s\delta l/D$ but cannot be disregarded, Eqn. (4) can be written in the form:

$$i = \left\{\frac{D}{s\delta l}\left[c_{\mathrm{O}}^{0} - c_{\mathrm{R}}(0)\,e^{-nF(\varphi-\varphi_0)/RT}\right]\frac{nF}{N}\right\}\left[1 + \frac{D}{s\delta l k_1}e^{-\alpha nF\varphi/RT}\right]^{-1}.$$

Since the first term (within braces) is identical with Eqn. (5) for the reverse current wave (i_{rev}), then:

$$i = i_{\mathrm{rev}}\left[1 + \frac{D}{s\delta l}\frac{1}{k_1}e^{-\alpha nF\varphi/RT}\right]^{-1}. \tag{6}$$

According to Eqn. (6), at the potential corresponding to the limiting current, $i \simeq I_{\mathrm{lim}} \simeq i_{\mathrm{rev}}$, that is, the limiting current I_{lim} is independent of the rate of electrochemical reaction. Along the polarographic wave, $i < i_{\mathrm{rev}}$. From Eqn. (6) it also follows that the half-wave potential is independent of the concentration of the reacting substances. For larger values of overvoltage ($\eta > 0.1$ V) the second part of Eqn. (3) can be neglected – this is the case of completely irreversible waves. Starting from Eqns. (2) and (3), k can be determined, and therefore also the free energy of activation.

Results obtained on the basis of the assumptions concerning the diffusion layer are only approximate. It has been shown that the assumptions concerning the properties of the diffusion layer are not sufficiently strict and do not always agree with the experimental data[48-49]. The dependence of the layer thickness δ on the diffusion coefficient is more complex than that assumed when employing δ in Eqn. (2).[50-51] Also, in the theory stated above, the influence of the growth of the mercury drop on the diffusion process has not been considered. A study of electrode processes taking account of the diffusion layer is of great interest in the case of agitated liquids, where it is difficult to carry out more accurate calculations[52].

II. EQUATION FOR CURRENT, TAKING ACCOUNT OF THE GROWTH OF THE MERCURY DROP

Meiman[8] put forward a more rigorous approach to the study of irreversible polarographic waves. During the electrolysis, the concentration of the reacting particles is a function of the duration of the electrolysis and the distance from the electrode, *i.e.* $c(x,t)$. The current flowing through the electrode depends on the concentration of the reacting substances at the surface of the electrode. This concentration differs from that in the body of the solution and cannot be determined experimentally: in this lies the difficulty of obtaining an expression for the current. If the concentration at the electrode surface is determined only by the diffusion, then $c(x,t)$ can be found by solution of the appropriate differential equation of diffusion and use of the initial and boundary conditions of electrolysis. The solution of a diffusion problem gives a value of $c(x,t)$ expressed in terms of the known concentration in the bulk of the solution, c^0. For the simplest case, linear diffusion, Fick's second law is the diffusion equation. The equation for symmetrical spherical diffusion comes closest to the conditions existing in polarography:

$$\frac{\partial c(\rho,t)}{\partial t}=D\left[\frac{\partial^2 c(\rho,t)}{\partial\rho^2}+\frac{2}{\rho}\left(\frac{\partial c(\rho,t)}{\partial\rho}\right)\right], \tag{7}$$

where ρ is the radius of the sphere. Angular co-ordinates are not introduced here since it is assumed that the diffusion field is symmetrical. However, in the case of the mercury dropping electrode, owing to the radial growth of the drop, the area of the diffusion field is continually changing throughout the drop life and the solution moves in a direction opposite to the diffusion direction. Ilkovič[2-3] solved the problem of diffusion towards the mercury dropping electrode; the same expression was derived in another way by MacGillavry and Rideal[4]. In order to apply Eqn. (7) to diffusion at the dropping mercury electrode the fixed co-ordinate ρ must be replaced by a moving co-ordinate r to take into account the increase in area of the diffusion field during the growth of the mercury drop. The differential equation for diffusion towards the dropping electrode then takes the form[4]:

$$\frac{\partial c(r,t)}{\partial t}=\frac{D\rho^4}{r^5}\left[r\,\frac{\partial^2 c(r,t)}{\partial r^2}+2\,\frac{(r^3-\gamma t)}{r^3+\gamma t}\cdot\frac{\partial c(r,t)}{\partial r}\right],$$

where $\gamma = 3m/4\pi d$, m being the mass of mercury flowing from the capillary per second, and d the density of mercury. The solution of this equation is:

$$c(r,t)=\frac{2c^0}{\sqrt{\pi}}\int_0^b e^{-z^2}dz, \tag{8}$$

where

$$b=\frac{1}{6}\sqrt{\frac{7\gamma}{3D}}\cdot\frac{r^3}{(\gamma t)^{7/6}}.$$

Eqn. (8) enables us to obtain an expression for the mean limiting diffusion current (the Ilkovič equation):

$$I_d=\frac{6}{7}\cdot 4\left(\frac{7\pi}{3}\right)^{1/2}\left(\frac{3}{4\pi d}\right)^{2/3} nFD^{1/2}\,m^{2/3}\cdot\tau^{1/6}c^0. \tag{9}$$

In the derivation of this expression the following initial and boundary conditions have been assumed: at the initial moment of time ($t = 0$) the concentration of the solution is constant and equal to the concentration in the bulk of the solution, that is, $c(x,t) = c^0$; the drop potential during the period of polarography is held constant, that is $\varphi = \text{const.}$; at $t > 0$, $c(0,t) \ll c^0$ or $c(0,t) = 0$, that is, the concentration at the electrode surface during the lifetime of an individual drop is constant; at $x \to \infty$, $c(x,t) \to c^0$; the current density is inversely proportional to the square root of the time measured from the start of the formation of the drop, $i = \text{const.} \times t^{\frac{1}{2}}$. The combination of these conditions is practicable only in the case of a reversible electrochemical reaction, in which the electrode potential depends only on the concentration of the reacting substances, with $c = \text{const.} \times \exp(nF\Delta\varphi/RT)$, and the constancy of the potential denotes a constancy of the electrode surface potential.

In the case of irreversible electrode reactions both the potential and the concentration depend on the current density, and obviously on the rate of electrochemical reaction, $i = f(c, \varphi)$. Because of this, the boundary conditions for irreversible electrode reactions will not be those for reversible ones. For irreversible electrode reactions of the first order the boundary and initial conditions were formulated by Meiman, who was the first to solve the differential equation for diffusion towards the dropping electrode for an irreversible reaction[8]. This solution will be outlined.

We will consider a reaction of the first order, Eqn. (1), and assume that the rate of the reverse reaction can be neglected ($k_2 = 0$). The concentrations of the reacting substances at the surface of the electrode during the irreversible reaction will depend on both the potential and the current density:

$$c(0,t)=\vartheta_i, \tag{10}$$

where ϑ is a coefficient dependent upon the electrode potential. Since i is proportional to the concentration gradient:

$$i=nFD\left(\frac{\partial c}{\partial r}\right),$$

the concentration at the electrode surface is

$$c(r,t)=nFD\vartheta\left(\frac{\partial c}{\partial r}\right). \tag{11}$$

Eqn. (10) is the boundary condition which must be used for an irreversible electrode reaction instead of the corresponding condition for a reversible reaction. The conditions:

$$c(x,t)=c^0 \quad \text{at} \quad t=0 \tag{12}$$

and

$$c(x,t)=c^0 \quad \text{at} \quad x\to\infty \tag{13}$$

are independent of the nature of the electrochemical reaction and can therefore be used for both reversible and irreversible electrode reactions.

After substitution of variables, the equation for diffusion towards the surface of a dropping electrode becomes[49]:

$$\frac{\partial c}{\partial\tau}=\frac{\partial^2 c}{\partial z^2}. \tag{14}$$

In this the boundary conditions (11), (12), and (13) become:

$$\vartheta p\tau^{2/7}\frac{\partial c}{\partial z}=c \quad \text{at} \quad z=0, \tag{15}$$

where

$$p=nFD\left(\frac{7}{3D}\right)^{2/7},$$

$$c\to c^0 \quad \text{at} \quad z\to\infty \tag{16}$$

$$c\to c^0 \quad \text{at} \quad \tau=0. \tag{17}$$

Calculating the current in the case of an irreversible reaction consists in solving Eqn. (14) at boundary conditions (15)–(17).

In solving Eqn. (14) it is first necessary to convert it into an equation in complete differentials. A solution must be sought in the form:

$$c(\tau, z) = c^0 + \tau^\nu f_\nu(\eta),$$

where f_ν is some function of argument η,

$$\eta = \frac{z}{\sqrt{\tau}}, \tag{18}$$

and the index can take a series of positive values. Let the solution $c(\tau, z)$ be presented in the form of a convergent series:

$$c(\tau, z) = c^0 + \sum_\nu \tau^\nu f_\nu(\eta). \tag{19}$$

Taking condition (14) into account, we can write the equation:

$$c^0 + \sum \tau^\nu f_\nu(0) = \vartheta p \sum_\nu \tau^{\nu - \frac{3}{14}} f_\nu'(0).$$

Comparing coefficients for identical powers of τ, we obtain a set of equations which are true only if ν is a multiple of 3/14, *i.e.* $\nu = 3/14n$ ($n = 1, 2, 3 \ldots$). The resulting Eqn. (19) allows Eqn. (14) to be transformed into an expression in complete differentials:

$$\frac{d^2 f_\nu}{d\eta^2} + \frac{\eta}{2}\frac{df_\nu}{d\eta} - \nu f_\nu = 0 \quad . \tag{20}$$

This equation must be satisfied by a function f_ν. The solution of Eqn. (20) is obtained by using a Laplace transform in the form of the contour integral:

$$f_\nu(\eta) = \int_{ku} l^{-\frac{1}{4}\eta^2 u} P_\nu(u)\, du,$$

and then

$$\frac{d^2 f_\nu}{d\eta} + \frac{\eta}{2}\frac{df_\nu}{d\eta} - \nu f_\nu = \int_{ku} \left[\left(\frac{1}{2}u + \nu\right) - \frac{1}{4}\eta^2 (u-1) u\right] P_\nu(u)\, du.$$

Transforming to the variable ξ, where $u = 1/(1 - \xi)$, and carrying out a series of transformations, we obtain:

$$c(\tau, z) =$$
$$= c^0 \left\{1 - \frac{1}{\Gamma\left(\frac{1}{2}\right)} \int_0^t (1-\xi)^{-1/2} e^{-\frac{\eta}{4(1-\xi)}} \sum_{n=1}^{\infty} (-1)^{n-1} \frac{\Gamma\left(\frac{3}{14} + \frac{1}{2}\right)\Gamma\left(\frac{3}{14}\cdot 2 + \frac{1}{2}\right)}{\Gamma\left(\frac{3}{14} + 1\right)\Gamma\left(\frac{3}{14}\cdot 2 + 1\right)} \cdots\right.$$
$$\left.\cdots \frac{\Gamma\left[\frac{3}{14}(n-1) + \frac{1}{2}\right]}{\Gamma\left[\frac{3}{14}(n-1) + 1\right]} \xi^{\frac{3}{14}\cdot n - \frac{1}{2}} \mu^n d\xi\right\}, \tag{21}$$

where μ is a dimensionless quantity:

$$\mu = \frac{\tau^{3/14}}{\vartheta p} = \left(\frac{3}{7}\right)^{1/2} \frac{t^{1/2}}{D^{1/2}\vartheta}, \tag{22}$$

and Γ denotes a gamma function of the corresponding argument. At large values of η,

$$\frac{\Gamma\left(\frac{3}{14}n + \frac{1}{2}\right)}{\Gamma\left(\frac{3}{14}n + 1\right)} \propto \frac{1}{\sqrt{\frac{3}{14}n + 1}}.$$

Therefore series (21) is convergent for all values of μ and positive values of η. Expression (21) is the required solution of Eqn. (13). It permits determination of the concentration of the reacting substances at the electrode surface:

$$c(\tau, 0) = c^0 \theta(\mu), \tag{23}$$

where

$$\theta(\mu) = 1 - \frac{\Gamma\left(\frac{3}{14} + \frac{1}{2}\right)}{\Gamma\left(\frac{3}{14} + 1\right)}\mu + \frac{\Gamma\left(\frac{3}{14} + \frac{1}{2}\right)}{\Gamma\left(\frac{3}{14} + 1\right)} \cdot \frac{\Gamma\left(\frac{3}{14}\cdot 2 + \frac{1}{2}\right)}{\Gamma\left(\frac{3}{14}\cdot 2 + 1\right)}\mu^2 \ldots \tag{24}$$

The concentration at the electrode surface is a function of the dimensionless parameter μ, in which, in addition to time, there appear the diffusion coefficient of the reactants and the coefficient, $1/\vartheta$, *cf.* Eqn. (22). If the diffusion coefficient falls or if the rate of electrochemical reaction increases, then the depolariser concentration at the electrode surface falls, since under these conditions, μ increases at a constant value of τ. Knowing $c(\tau, 0)$, on the basis of Eqn. (9), it is possible to write an expression for current density:

$$i = \frac{c(\tau, 0)}{\vartheta} = \frac{c^0}{\vartheta}\theta(\mu)\,. \tag{25}$$

If the reaction rate is quite small, then $\vartheta \to \infty$, and $\mu \to 0$, so that in the limit we obtain:

$$c(\tau, 0) = c^0,\ i = 0\,.$$

Since the series determining $\theta(\mu)$ at $\mu \gg 1$ converges extremely slowly it is necessary to give an asymmetric expression for $\mu \to \infty$. Introducing a new function $v(\mu, \eta)$ and changing the boundary conditions (15–17), after transformation the asymmetric representation can be written in the form:

$$\theta(\mu) = \left\{\frac{\mu^{-1}}{\Gamma\left(\frac{1}{2}\right)} - \frac{\mu^2}{\Gamma\left(\frac{1}{2}\right)\frac{\Gamma\left(\frac{1}{2} - \frac{3}{14}\right)}{\Gamma\left(1 - \frac{3}{14}\right)}} + \ldots\right\}. \tag{26}$$

The current density is expressed thus:

$$i = \frac{c(\tau, 0)}{\vartheta} = \frac{c^0}{\vartheta}\left\{\frac{\mu^{-1}}{\sqrt{\pi}} - \frac{\mu^2}{\sqrt{\pi}\frac{\Gamma\left(\frac{1}{2} - \frac{3}{14}\right)}{\Gamma\left(1 - \frac{3}{14}\right)}} + \ldots\right\}. \tag{27}$$

It follows from Eqns. (26) and (27) that at high reaction velocities $\vartheta \to 0$, and μ^{-1} at all terminal values tends to zero, so that $c(\tau, 0) \simeq c^0/\mu\sqrt{\pi}$ and for the limiting current density i_d we obtain

$$i_d = \frac{c^0}{\Gamma\left(\frac{1}{2}\right)} \lim_{\vartheta \to 0} \frac{\sqrt{\frac{7}{3}}\, nFD^{1/2}\vartheta}{\vartheta t^{1/2}} = \frac{c^0}{\sqrt{\pi}}\sqrt{\frac{7}{3}}\, nFD^{1/2} t^{-1/2},$$

that is, the Ilkovič equation is applicable under these conditions.

Thus, to calculate the concentration at the electrode surface and the current density it is sufficient to determine function $\theta(\mu)$, for which it is necessary to use Eqn. (24) at $\mu \leqslant 1$, and Eqn. (26) at $\mu \gg 1$.

Table 1 gives values of the function $\theta(\mu)$ for different values of the argument μ.[8] The values of $\theta(\mu)$ for $\mu < 1.2$ were calculated from Eqn. (24) and those for $\mu > 2.5$ by use

TABLE 1. Dependence of $\theta(\mu)$ on the parameter μ.

μ	$\theta(\mu)$	μ	$\theta(\mu)$	μ	$\theta(\mu)$	μ	$\theta(\mu)$	μ	$\theta(\mu)$	μ	$\theta(\mu)$
0.00	1.0000	0.2	0.7753	1.0	0.3881	1.8	0.252	2.8	0.1758	5.0	0.1040
0.01	0.9862	0.4	0.6263	1.2	0.3431	2.0	0.232	3.2	0.1565	10.0	0.0543
0.04	0.9467	0.6	0.5221	1.4	0.306	2.2	0.214	3.6	0.1410	40.0	0.0140
0.1	0.8754	0.8	0.4456	1.6	0.276	2.5	0.1936	4.0	0.1282	100.0	0.0056
											0.0000

of the asymmetric expansion (26). In the interval $1.2 < \mu < 2.5$, values of the function $\theta(\mu)$ are obtained by graphical integration. The function $\theta(\mu)$ decreases monotonically as μ increases (Fig. 1).[8]

The total current I is connected with the current density by the following expression:

$$I = 4\pi\rho^2 i = \frac{4\pi\gamma}{\vartheta} t^{2/3} c^0 \theta(\mu). \tag{28}$$

For calculations it is usual to employ the reduced current $\tilde{I}$:

$$\tilde{I} = \frac{I}{I_d} = \frac{7\sqrt{\pi}}{6} \frac{\mu^{4/3}}{\mu_0^{1/3}} \theta(\mu), \tag{29}$$

where I_d is given by Eqn. (9).

The mean value of the reduced current for the lifetime of an individual drop, $\bar{\tilde{I}}$, is:

$$\bar{\tilde{I}} = \frac{1}{t}\int_0^t \tilde{I}\,dt = \frac{7\sqrt{\pi}}{6}\int_0^t \mu^{4/3}\theta(\mu)\,dt = \frac{7\sqrt{\pi}}{3}\frac{1}{\mu_0^{7/3}}\int_0^{\mu_0} \mu^{4/3}\theta(\mu)\,d(\mu), \tag{30}$$

i.e. the mean reduced current is a function only of the parameter μ_0. Substituting in Eqn. (30) the series expansion of the function $\theta(\mu)$, we obtain an expansion for $\bar{\tilde{I}}$ in powers of μ_0. For values $\mu_0 \ngtr 1$, from Eqns. (24) and (30) we obtain:

$$\bar{\tilde{I}} = 7\sqrt{\pi}\left\{\frac{1}{10}\mu_0 - \frac{1}{13}\frac{\Gamma\left(\frac{3}{14}+\frac{1}{2}\right)}{\Gamma\left(\frac{3}{14}+1\right)}\mu_0^2 + \ldots\right\} =$$

$$= 1.241\mu_0 - 1.332\mu_0^2 + 1.278\mu_0^3 \ldots . \tag{31}$$

At $\mu \geqslant 10$, using Eqns. (26) and (30), the mean reduced current is:

$$\bar{\tilde{I}} = 1 - \frac{7}{4}\frac{\Gamma\left(1-\frac{3}{14}\right)}{\Gamma\left(\frac{1}{2}-\frac{3}{14}\right)}\mu_0^{-1} + 7\frac{\Gamma\left(1-\frac{3}{14}\right)\cdot\Gamma\left(1-2\cdot\frac{3}{14}\right)}{\Gamma\left(\frac{1}{2}-\frac{3}{14}\right)\cdot\Gamma\left(\frac{1}{2}-2\cdot\frac{3}{14}\right)}\mu_0^{-2} - \ldots =$$

$$= 1 - 0.656\mu_0^{-1} + 0.303\mu_0^{-2}. \tag{32}$$

Hence, as the parameter μ_0 increases, the mean reduced current tends to unity, *i.e.* at $\mu \gg 1$, the current of the irreversible polarographic wave agrees with the current calculated by the Ilkovič equation. Fig. 2 shows the dependence of the mean reduced current on $\log \mu_0$; it is the universal reduced curve of the concentration polarisation at the dropping mercury electrode during an irreversible electrochemical reaction of the first order.

It is possible to obtain information on the kinetics of an electrochemical reaction from experimental data on the irreversible polarographic curve using the dependence of $\bar{\tilde{I}}$ on μ_0 (Eqns. 30–32), since μ_0 is connected by a definite relation – Eqn. (22) – with the coefficient $1/\vartheta$, which characterises the reaction rate and is in general dependent on the electrode potential. Alternatively, if the kinetics of the electrochemical reaction is known then the current *vs.* potential curve can be calculated.

The dependence of the reduced current on the parameter μ was verified experimentally by Bagotskii[53], who studied the evolution of hydrogen at the mercury dropping electrode in hydrochloric acid solutions.

The dependence of current on potential can be calculated by use of Eqns. (30)–(32) and (22), taking into account the overvoltage[24] and the coefficient ϑ[54]. A comparison of these calculations with experimental results for a solution 3.9×10^{-4} *N* HCl + 0.33 *N* KCl is shown in Fig. 3.[53] The continuous line denotes a curve calculated from the equation for reduced current, Eqn. (30), the circles represent the experimental results; they are in good agreement. For comparison, Fig. 3 also includes a broken *I vs.* φ curve calculated assuming a constant concentration of reacting substances at the surface of the mercury drop throughout its life. This curve is displaced towards the side of more negative potentials. The greatest separation between the curves corresponds to a certain negative half-wave potential. The curve calculated for reversible processes (broken line in Fig. 3) coincides with a curve calculated for the case of irreversible reactions only for limiting values of μ, namely $\mu \to 0$ and $\mu \to \infty$. The theory advanced for irreversible electrode reactions[8] is thus more general and includes reversible reactions as a particular case.

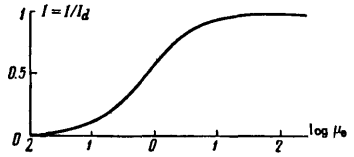

Fig. 2. Dependence of I on $\log \mu_0$.

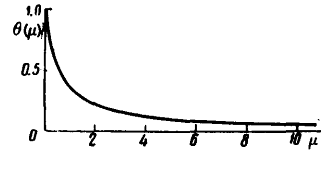

Fig. 1. Dependence of $\theta(\mu)$ on μ.

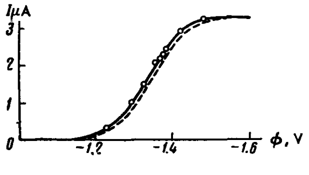

Fig. 3. Concentration polarisation in the solution 3.9×10^{-4} *N* HCl + 0.33*N* KCl. Full curve: calculated by Eqn. (30); broken curve: calculated for $c(\tau, 0) = \text{const.}$; circles: experimental data.

If in the reaction represented by Eqn. (1) $k_2 \neq 0$, then in order to obtain equations for the current at a growing droplet it is necessary to solve a system of differential equations:

$$\left.\begin{aligned}\frac{\partial c_O}{\partial t} &= D_1\frac{\partial^2 c_O}{\partial x^2}+\frac{2x}{3t}\frac{\partial c_O}{\partial x}\\ \frac{\partial c_R}{\partial t} &= D_2\frac{\partial^2 c_R}{\partial x^2}+\frac{2x}{3t}\frac{\partial c_R}{\partial x}\end{aligned}\right\} \tag{33}$$

with the following initial and boundary conditions:

$$t=0,\ x>0:\ c_O=c_O^0:\ x\gtreqless 0,\ c_R=c_R^0 \tag{34}$$

$$x=0,\ t>0:\ D_1\frac{\partial c_O}{\partial x}\pm D_2\frac{\partial c_R}{\partial x}=0;\ -D_1\frac{\partial c_O}{\partial x}=k_2c_R-k_1c_O \tag{35}$$

$$x\to+\infty,\ t>0:\ c\to c^0;\ x\to\pm\infty;\ c_R\to c_R^0. \tag{36}$$

In conditions (35) and (36) the plus sign refers to the case when the product of the electrochemical reaction (R) is soluble in the solution; if R is soluble in the electrode, the sign will be negative. In both cases the symmetry of the diffusion processes leads to identical expressions for the current.

Koutecký[17,55] solved Eqns. (33)–(36) by a method similar to that used by Meiman[8]. The expression obtained for instantaneous current is:

$$i=-nFq\sqrt{\frac{7D_O}{12t}}\left(\frac{\partial c}{\partial s_1}\right)_{s_1=0},$$

where

$$\left(\frac{\partial c}{\partial s_1}\right)_{s_1=0}=\frac{1}{\sqrt{D_O}}\frac{k_1c_O^0-k_2c_R^0}{\frac{k_1}{\sqrt{D_O}}+\frac{k_2}{\sqrt{D_R}}}\sum_{i=1}\nu_i\kappa^i,$$

$$\nu_1=1,\quad \frac{\nu_{i+1}}{\nu_i}=-\frac{1}{p_{\frac{3}{7}i}},\quad \kappa=\left(\frac{k_1}{\sqrt{D_O}}+\frac{k_2}{\sqrt{D_R}}\right)\sqrt{\frac{12t}{7}}. \tag{37}$$

The results can be simplified if we put:

$$i_\infty=-nFq\frac{2}{\sqrt{\pi}}\sqrt{\frac{7D_O}{12t}}\frac{1}{\sqrt{D_O}}\frac{k_1c_O^0-k_2c_R^0}{\frac{k_1}{\sqrt{D_O}}+\frac{k_2}{\sqrt{D_R}}},$$

where i_∞ is the current for an electrode reaction for which these conditions are maintained on the electrode surface:

$$\kappa=0,\quad t>0:\quad c_O=\frac{k_2}{k_1}c_R.$$

The solution can be written in the form:

$$\frac{i}{i_\infty}=F(\kappa), \tag{38}$$

where

$$F(\kappa)=\frac{\sqrt{\pi}}{2}\sum_{i=1}^{\infty}\nu_i\kappa.$$

This solution is applicable for values of κ not greatly exceeding unity. For $\kappa \gg 1$, an asymmetric solution is used, in which we obtain

$$F(\kappa)=\sum_{i=0}^{\infty}v_i\left(\frac{1}{\kappa}\right)^i,$$

where

$$v_0=1,\quad \frac{v_{+1}}{v_i}=-p_{-\frac{3}{7}(i+1)}.$$

The dependence of the function $F(\kappa)$ on the argument is shown in Table 2.[17]

In the derived equations, as in Eqns. (25) and (28), the current is proportional to some function which can be presented in the form of two different series corresponding to values of the argument near to unity and much greater than unity.

TABLE 2. Dependence of $F(\kappa)$ on the parameter κ.

κ	$F(\kappa)$	κ	$F(\kappa)$	κ	$F(\kappa)$	κ	$F(\kappa)$	κ	$F(\kappa)$	κ	$F(\kappa)$
0.1	0.0828	0.6	0.369	1.2	0.555	2.5	0.740	5	0.858	10	0.927
0.2	0.155	0.7	0.409	1.4	0.597	3.0	0.777	6	0.880	12	0.939
0.3	0.219	0.8	0.444	1.6	0.623	3.5	0.803	7	0.895	14	0.946
0.4	0.275	0.9	0.476	1.8	0.662	4.0	0.827	8	0.909	16	0.953
0.5	0.325	1.0	0.505	2.0	0.690	4.5	0.844	9	0.919	18	0.958
										20	0.963

For the mean polarographic currents, Eqn. (38) takes on the form:

$$\frac{\bar{i}}{i_\infty}=\frac{7}{3}\kappa_1^{-\frac{7}{3}}\int_0^{\kappa_1}F(\kappa)\cdot\kappa^{\frac{4}{3}}d\kappa=\bar{F}(\kappa_1). \tag{39}$$

For small values of κ_1:

$$F(\kappa_1)=\sum_{i=1}^{\infty}m_i\kappa_1^i,\text{where } m_i=\frac{\nu_i}{1+\frac{3}{7}i}. \tag{40}$$

Function $F(\kappa_1)$ has an approximate form for $\kappa_1 > 3$:

$$F(\kappa_1)=\sum_{i=0}^{5}n_i\kappa^{-i}-0.01\left(\frac{3}{\kappa_1}\right)^{\frac{7}{3}},\quad n_i=\frac{v_i}{1-\frac{3}{7}i}.$$

The mean polarographic current is given sufficiently accurately by the equation:

$$\frac{\bar{i}}{i_\infty}=\frac{0.87\left(\frac{k_1}{\sqrt{D_O}}+\frac{k_2}{\sqrt{D_R}}\right)\sqrt{t_1}}{1+0.87\left(\frac{k_1}{\sqrt{D_O}}+\frac{k_2}{\sqrt{D_R}}\right)\sqrt{t_1}} \tag{41}$$

III. EQUATION FOR LINEAR DIFFUSION AND THE DROPPING ELECTRODE

Expressions for the current at the mercury dropping electrode can also be obtained by transformation of equations derived for an irreversible electrode reaction in the case of linear diffusion. However, it must be noted that such a procedure[13,14,56] leads to less accurate results than the direct solution of diffusion problems taking into account the growing surface of the mercury drop[8,17,55].

The expression for the current dependent on reaction (1) taking place was obtained for linear diffusion by various authors[11,14,57]:

$$i=nFqc_Ok_1\exp(Q^2t)\,\mathrm{erfc}(Qt^{1/2}), \tag{42}$$

$$Q=\frac{k_1}{D_O^{1/2}}+\frac{k_2}{D_R^{1/2}},\quad \mathrm{erf}(a)=\frac{2}{\sqrt{\pi}}\int_0^a\exp(-z^2)\,dz,$$

$$\mathrm{erfc}(a)=1-\mathrm{erf}(a).$$

The dependence of function $\exp(Q^2t).\mathrm{erfc}(Qt^{\frac{1}{2}})$ on the argument $Qt^{\frac{1}{2}}$, is analogous to the dependence of function $\theta(\mu)$ on the argument μ.[8] It follows from this equation that the current is proportional to the product $\exp(Q^2t).\mathrm{erfc}(Qt^{\frac{1}{2}})$. Hence, just like this product, the current falls with increasing time (the argument).

In order that Eqn. (42), developed for linear diffusion, can be applied to the mercury dropping electrode it is necessary to express the electrode surface q in terms of the capillary characteristics m and t and to multiply the right-hand side of the equation by the Ilkovič coefficient[14], $(7/3)^{\frac{1}{2}}$. After transformation, we obtain an equation for the instantaneous current during the life of a drop for any point along the wave:

$$i = 1255\, n m^{2/3} t^{2/3} c_O^0 k_1 \exp(Q^2 t) \operatorname{erfc}(Q^2 t)^{1/2}, \tag{43}$$

in which i is expressed in mA, m in mg sec^{-1}, t in sec, c_O^0 in mM, and k_1 and k_2 in cm sec^{-1}. Eqn. (43) is a general expression for polarographic currents (reversible and irreversible waves), determined by diffusion and electrode reactions. The Ilkovič equation is a particular case of Eqn. (43), in which the rate constant is very large ($k_1 \rightarrow \infty$).

If the reverse reaction is negligible, *i.e.* if $k \ll k_1$, then in Eqn. (43) Q takes the value $k_1/D_O^{\frac{1}{2}}$ and the wave will be irreversible. The effect of the reverse process cannot be taken into account for those portions of the wave in which the overvoltage exceeds 0.1 V. This condition is easily verified by taking oscillograms[58,59] or by comparing the cathodic and anodic polarographic waves. If the electrode process is accompanied by subsidiary chemical reactions, the comparison may indicate an irreversible electrode process although it is actually reversible. From Eqn. (43) the following condition of reducibility[14] is deduced:

$$k_s > \sim 2 \times 10^{-2} \text{ cm sec}^{-1} \tag{44}$$

where $k_s = k_1 = k_2$.

If k_s for a certain electrode process is less than $\sim 2 \times$ $\times\ 10^{-2}$ cm sec^{-1}, then the wave obtained acquires an irreversible character, shifts to more negative potentials and becomes more sloping. The smaller the value of constant k_s, the greater the displacement. If $k_s \leqslant 3 \times 10^{-5}$ cm sec^{-1}, then the overvoltage exceeds $2 \times 2.3\ (RT/nF)$ by ~ 0.12 mV, since the influence of the reverse reaction can be neglected, *i.e.* the waves at such an overvoltage are almost completely irreversible. Condition (44) can be expressed in terms of the free energy of activation. The rate constant k_s (puting $n = n_a$, where n_a is the number of electrons in the activation phase) is equal to[60]:

$$k_s = \frac{kT}{h} \rho \exp\left[\alpha \Delta G^0 - \Delta G_1^{\ddagger}/RT\right]$$

and condition (44) is expressed (with $\rho \simeq 10^{-6}$ cm, $T =$ $= 298°$):

$$\Delta G_1^{\ddagger} \leqslant 11.5 + \alpha \Delta G^0.$$

Analysis of Eqn. (43) shows that in the lower part of the irreversible wave the current is independent of the height of the mercury column (h_{Hg}), since in this equation m and t are raised to the same power (2/3) and it is known that m is directly proportional to h_{Hg} and t is inversely proportional to h_{Hg}. In the expressions for the currents in the upper part of the wave, where $i \rightarrow i_d$, we have $m^{2/3}$ and $t^{1/6}$, so that the current is proportional to the square root of the height of the mercury column[13,61]. The dependence of the current on the height of the mercury column can be used as a criterion of reversibility, since in the case of a reversible polarographic wave, the current at any point along the wave is proportional to the square root of the height of the mercury column[61,62].

Kuta and Smoler[22] recently showed that for reversible oxidation–reduction systems the dependence of the exponent of the $i = kt^{\kappa}$ curve on the potential varies according as to whether the reaction product is soluble or insoluble in the mercury: in the first case the exponent is independent of the potential, in the second it increases with increasing potential up to a constant value at the potential of the limiting current. For irreversible processes, this dependence is determined by the magnitude of the overvoltage. At low overvoltages the dependence of the exponent of the *i vs. t* curves on the potential exhibits a maximum, and at greater values of η the value of the exponent changes monotonically along the wave from 1/6 to 2/3.

The expressions for the current of irreversible electrode processes enable us to determine the rate constant of the electrochemical reaction. From the dependence of the reaction rate constant on the potential it is possible to obtain the value of the free energy of activation ΔG^0 and the product αn_a. In order to find the reaction rate constant it is necessary to measure experimentally the ratio of the current along the irreversible polarographic wave to that determined only by the diffusion rate[62].

For irreversible processes where the rate of the rereverse reaction can be neglected, in the case of linear diffusion this ratio is found by comparison of Eqn. (42) with the equation for the diffusion current; it is equal to:

$$\frac{i}{i_d} = \pi^{1/2} \lambda \exp(\lambda^2) \operatorname{erfc}(\lambda),$$

where

$$\lambda = k_1 t^{1/2} / D_O^{1/2}. \tag{45}$$

The value of k_1 is found from the dependence of i/i_d upon λ. When determining the reaction constant for the case of the mercury dropping electrode Eqns. (38) and (41) are used for the instantaneous and mean polarographic currents respectively[17]. The parameter κ is given by Eqns. (37) and (39). Table 2[17] gives the dependence of $F(\kappa)$ on the parameter κ. In practice the current is limited by diffusion when λ or κ exceed 15, which occurs when the reaction rate constant is sufficiently large.

The reaction rate constant can also be determined graphically[13,56,63]. The mean value of the current obtained from Eqn. (43) can be expressed:

$$i_{\text{mean}} = 1255\, n m^{2/3} \tau^{2/3} c^0 k_1 z, \tag{46}$$

where

$$z = \gamma \operatorname{erfc}(k_1 t^{1/2} D^{-1/2}) \exp(k_1^2 t D^{-1}). \tag{47}$$

The value of γ (the ratios of the mean current to the maximum current) is found from Fig. 4, which gives the variation of γ with mercury drop time for different values of

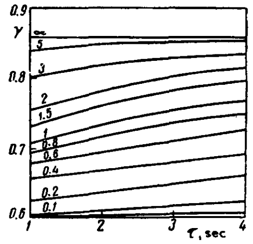

Fig. 4. Dependence of γ on τ for different values of $kD^{-\frac{1}{2}}$.

$kD^{-\frac{1}{2}}$. Values of z for different values of $kD^{-\frac{1}{2}}$ are calculated by use of Eqn.(47) and Fig.4. Fig.5 gives the variation of $zkD^{-\frac{1}{2}}$ with mercury drop time.

In order to determine the reaction rate constant, zk is calculated by Eqn.(46) and then the product $zkD^{-\frac{1}{2}}$ is obtained. A point is found on Fig.5 with abcissa of τ (drop time) and ordinate $zkD^{-\frac{1}{2}}$ and the value of $kD^{-\frac{1}{2}}$ for the curve passing through the point is obtained by interpolation. k is calculated from this value of $kD^{-\frac{1}{2}}$.

Fig.4 shows that $\gamma \simeq 0.60$ when $kD^{-\frac{1}{2}} < 0.05$. The magnitude of the current is then determined by the rate of reaction. When $kD^{-\frac{1}{2}} > 5$, then $\gamma = 0.857$, or 6/7, *i.e.* the value found from the Ilkovič equation. When $kD^{-\frac{1}{2}} < 0.05$, the rate constant can be calculated directly from the value of the limiting current by Eqn.(46), in which z is put equal to 0.60.

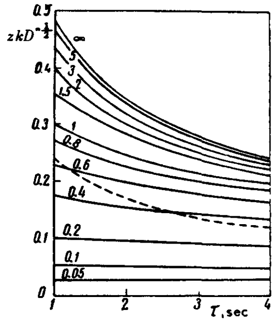

Fig.5. Dependence of $zkD^{-\frac{1}{2}}$ on τ. Figures on the curves give values of $kD^{-\frac{1}{2}}$ in sec$^{-\frac{1}{2}}$.

The dependence of the reaction rate constant on the overvoltage (η) can be expressed by the equation:

$$k = \frac{kT}{h}\,\delta \exp\frac{-\Delta G^0 + \alpha n_a F\eta}{RT}, \tag{48}$$

where k is the Boltzmann constant, and h the Planck constant. From this formula it follows that finding the dependence of the logarithm of the reaction rate constant on the overvoltage makes it possible to determine αn_a and the free energy ΔG^0.[13] The slope of the log k *vs.* η curve is proportional to αn_a. The value of log k at $\eta = 0$ characterises the speed of the electrode process. This quantity is a linear function of the free energy of activation ΔG^0. By determining the values of k and ΔG^0 at various temperatures, the entropy of activation can be calculated from the equation $\Delta G = \Delta H - T\Delta S$. These data are very important in studying the mechanism of electrochemical reactions.

IV. SUCCESSIVE ELECTROCHEMICAL REACTIONS

In considering irreversible polarographic waves above it was assumed that the rate of reduction of the substance was determined by the kinetics of only one electrochemical step. If this step did not include all the number of electrons necessary for the reduction of substance O to R, then it was proposed that an intermediate substance Z is formed, having a high rate of reduction and no effect on the form of the wave. In the more general case it is necessary to calculate the influence of the successive individual electrochemical steps[16,64].

We will consider two particular cases of successive electrochemical reactions, examined by Delahay[64]. In the first case, the effect of the reverse reaction is neglected for both electrochemical stages, *i.e.*

$$\mathrm{O} \xrightarrow[n_1e]{k_\mathrm{I}} \mathrm{Z} \xrightarrow[n_2e]{k_\mathrm{II}} \mathrm{R}. \qquad 49)$$

The boundary conditions are obtained from the balance for substance Z at the electrode surface:

$$c^0k_\mathrm{I}\exp(k_\mathrm{I}^2tD_\mathrm{O}^{-1})\,\mathrm{erfc}\,(k_\mathrm{I}t^{1/2}D_\mathrm{O}^{-1/2}) - k_\mathrm{II}c_\mathrm{Z}(0,t) + D_\mathrm{Z}\,[\partial c_\mathrm{Z}(x,t)/\partial x]_{x=0} = 0. \tag{50}$$

The first term of Eqn.(50) gives the rate of reduction O → Z, the second Z → R, and the third term expresses the rate of diffusion of substance Z from the surface of the electrode into the solution. The initial conditions have the normal form: $c_\mathrm{Z}(x,0) = 0$; $c_\mathrm{Z}(x,t) \to 0$ at $x \to \infty$. The current for reaction (49) is the sum of those for the reductions O → Z and Z → R. For stage O → Z, the current is given by Eqn.(42) for a single-stage irreversible reaction.

To find the current for stage Z → R, our knowledge of the concentration $c_\mathrm{Z}(0,t)$ is used. This concentration is found by solving, for the cited conditions, the differential equation expressing Fick's second law. Using the conditions for linear diffusion the total current of reaction (49) is:

$$i = n_1Fqc_\mathrm{O}k_\mathrm{I}\exp(k_\mathrm{I}^2tD_\mathrm{O}^{-1})\,\mathrm{erfc}\,(k_\mathrm{I}t^{1/2}D_\mathrm{O}^{-1/2}) + \\ + n_2Fqc^0\,\frac{k_\mathrm{II}}{(D_\mathrm{Z}/D_\mathrm{I})^{1/2} - \dfrac{k_\mathrm{II}}{k_\mathrm{I}}}\left\{\begin{array}{l}\exp(k_\mathrm{II}tD_\mathrm{Z}^{-1}) \quad \mathrm{erfc}\,(k_\mathrm{II}\;t^{1/2}D_\mathrm{Z}^{-1/2}) \\ -\exp(k_\mathrm{I}^2tD_\mathrm{O}^{-1})\,\mathrm{erfc}\,(k_\mathrm{I}t^{1/2}D_\mathrm{O}^{-1/2})\end{array}\right\}. \tag{51}$$

If the surface of the electrode is expressed in terms of the capillary characteristics m and τ, and a correction coefficient[2,3] of $(7/3)^{\frac{1}{2}}$ is introduced, then Eqn.(51) can be applied approximately to the mercury dropping electrode. Fig.6 depicts the dependence of the average current on the potential calculated by Eqn.(51) for the following conditions: $\tau = 3$ sec, $m = 10^{-3}$ g sec^{-1}, $c^0 = 10^{-6}$ mole cm^{-3}, $n_1 = n_2 = 1$, $D_\mathrm{O} = D_\mathrm{Z} = 10^{-5}$ cm^2 sec^{-1}, $k^0 = 10^{-6}$ cm sec^{-1}, with k_0 determined by the expression $k = k_0\exp(-\alpha n_a F\varphi/RT)$. In the calculations it was found that the products αn_a for the successive stages of reaction (49) were identical. In this case the ratio of rate constants $k_\mathrm{I}/k_\mathrm{II}$ is independent of the potential and this makes it possible to construct polarographic waves for different $k_\mathrm{I}/k_\mathrm{II}$ ratios. From Eqn.(51) and Fig.6 it is seen that separation into two waves is noticeable at ratios $k_\mathrm{I}/k_\mathrm{II} > 100$. If the rate constant of the second stage is significantly greater than that of the first, the wave has practically the same form as in the case of a single-stage process. If k_II is appreciably less than k_I then the lower part of the wave is determined mainly by the kinetics of the first stage (curves *4* and *5*). If $k_\mathrm{II} \to \infty$, Eqn.(51) takes the form of Eqn.(42), with n_1 replaced by the total $n_1 + n_2$. If $k_\mathrm{I} \to \infty$ and $k_\mathrm{II} \to \infty$, then Eqn.(51) will become identical with the equation for current determined only by diffusion.

In order to find out whether the electrode process takes place in a single stage or several successive stages, it is

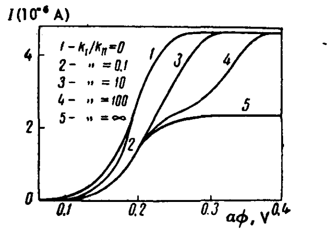

Fig. 6. Dependence of the average current on the product $\alpha\varphi$, calculated from Eqn. (51).

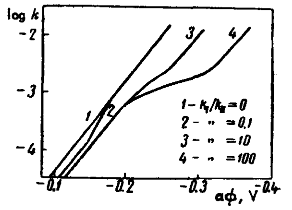

Fig. 7. Dependence of log k on $\alpha\varphi$ for the curves of Fig. 6.

necessary to look at the polarographic wave plotted on co-ordinates log k *vs.* φ. The polarographic waves presented in Fig. 6 have been plotted on these co-ordinates in Fig. 7, from which it is evident that the existence of successive stages of the reaction can be detected even within the limits of one wave from the presence of separate parts of different slope in the log k *vs.* φ curve. If the values of n_1 and n_2 are known, then the kinetics of each stage can be determined separately. In the analysis of the lower part of the wave it is necessary to calculate only the diffusion current (i'_d) which depends on the n_1 part of the electrons, that is, $i'_d = i_d n_1/(n_1 + n_2)$; for the upper part, the diffusion current (i''_d) corresponding to the transfer of n_2 electrons, $i''_d = i_d n_2/(n_1 + n_2)$.

Waves for the reduction of chromium and certain polyphosphate complexes[64-66] are examples of electrode processes proceeding in successive electrochemical stages. The process depends on the temperature and pH of the electrolyte. The slope of the lower part of the log k *vs.* φ curve for the $Cr^{VI}-Cr^{III}$ wave is approximately twice the slope of the upper portion, and since the total number of electrons is equal to three then the first stage we can take $n_1 = 2$, and for the second $n_2 = 1$. This provides a basis for the hypothesis that Cr^{IV} is the intermediate product in the reduction of Cr^{VI}. This assumption is confirmed by studying the potential *vs.* time curves at constant current[67]. For studying unstable intermediate products of electrochemical reactions rotating electrodes have recently been used[68,69].

In the second case two successive electrochemical reactions are assumed; that between the substances O and Z is determined by electrochemical equilibrium but the second stage is completely irreversible and its reverse reaction can be neglected:

$$\mathrm{O} \underset{n_1 e}{\overset{\text{equilibrium}}{\rightleftharpoons}} \mathrm{Z} \xrightarrow[n_2 e]{k} \mathrm{R}\,. \tag{52}$$

For this process:

$$i = n_1 F q D_{\mathrm{O}} [\partial c_{\mathrm{O}}(x, t)/\partial x]_{x=0} + n_2 F q c_{\mathrm{Z}}(0, t).$$

The terms $[\partial c_{\mathrm{O}}(x,t)/\partial x]_x = 0$ and $c_{\mathrm{Z}}(0,t)$ are the solution of a system of two differential equations with corresponding boundary and initial conditions. Use of a Laplace transform leads finally to the expression:

$$\frac{i}{nFq} = \frac{c^0}{\theta + (D_{\mathrm{Z}}/D_{\mathrm{O}})^{1/2}} \left[\left(\frac{D_{\mathrm{Z}}}{\pi t} \right)^{1/2} + \frac{k\,[2\theta + (D_{\mathrm{Z}}/D_{\mathrm{O}})^{1/2}]}{\theta + (D_{\mathrm{Z}}/D_{\mathrm{O}})^{1/2}} \exp(a^2 t)\,\mathrm{erfc}\,(a t^{1/2}) \right], \tag{53}$$

where

$$a = k/(\theta D_{\mathrm{O}}^{1/2} + D_{\mathrm{Z}}^{1/2}),\ n_1 = n_2 = n.$$

The condition that the slope of the straight line log $[(i_a - i)/i]$ *vs.* φ is 2.3 RT/nF does not hold for processes with successive electrochemical stages.

For electrochemical processes conforming to schemes (49) or (52), the half-wave potential does not have a simple physical significance. In general, the half-wave potential for irreversible polarographic waves has no special significance, unlike that for reversible waves. In the case of irreversible waves the half-wave potential depends on the concentration of the reacting substances, the diffusion coefficient, the product αn_a, and the drop time of the mercury[14,56,61,70]. Actually, by defining as $\lambda_{\frac{1}{2}}$ the value of $kt^{\frac{1}{2}}D^{\frac{1}{2}}$ at half-wave potential we obtain for an irreversible wave with one retarded stage[62]:

$$\varphi_{1/2} = \frac{RT}{\alpha n_a F} \ln \frac{k_0}{\lambda_{1/2} D_{\mathrm{O}}^{1/2}} + \frac{RT}{2\alpha n_a F} \ln t. \tag{54}$$

The variations in half-wave potential with the drop time are insignificant. Thus the half-wave potential for the reduction of Ni^{2+} changes from -0.959 V to -1.016 V when the drop time changes from 7.66 sec to 2.09 sec[61]; in the case of the reduction of weak acids the shift in half-wave potential when t is changed from 2 to 4 sec amounts to 0.0083 V. The changes are more noticeable for $t < 3$ sec[56].

V. IRREVERSIBLE WAVES AND EXCHANGE CURRENT DENSITY

With the presence of both the oxidised and reduced forms of the depolariser at the beginning of electrolysis, polarography enables the cathodic and anodic processes to be studied simultaneously. Both forms of the depolariser may be in the solution being examined, or one of them may be in the solution and the other in the amalgam. In the case of reversible systems a general anodic-cathodic reversible wave is obtained. Irreversible oxidation-reduction systems give branched anodic and cathodic waves[11,12,18,71-73].

In studying irreversible electrode processes of oxidation-reduction systems, Smutek[11,15] and Tockstein[12] used methods previously examined by us[8,17]. We will deal with the approach of Stromberg[18,19], which is based on the theory of retarded discharge and employs ideas concerning current exchange. The rate of discharge ($\overrightarrow{i}$) of ions from solution and the rate of ionisation ($\overleftarrow{i}$) of atoms from the amalgam at potential φ can be expressed[74]:

$$\overrightarrow{i} = k_1 c_O \exp(-\alpha nF/RT)\varphi,$$

$$\overleftarrow{i} = k_2 c_R \exp(\beta nF/RT)\varphi,$$

where k_1 and k_2 are rate constants for the discharge and ionisation processes, and α and β are the coefficients for the theory of retarded discharge ($\alpha + \beta = 1$). At the equilibrium potential (φ_{eq}), $\overrightarrow{i} = \overleftarrow{i}$ and these equal the exchange current (i_0):

$$i_0 = \overrightarrow{i} = \overleftarrow{i} = k_1 c_O^0 \exp(-\alpha nF/RT)\varphi_{eq} = k_2 c_R^0 \exp(\beta nF/RT)\varphi_{eq}.$$

Expressing the constants k_1 and k_2 in terms of the exchange current and the concentrations of O and R in terms of the current, we obtain the fundamental equation of the irreversible electrode process of oxidation-reduction systems[18]:

$$\frac{i}{i_0} = \frac{I_k - i}{I_k}\exp(\alpha nF/RT)\eta - \frac{I_a + i}{I_a}\exp(-\beta nF/RT)\eta, \tag{55}$$

where I_k and I_a are the cathodic and anodic limiting currents.

When $i_0 \to \infty$, Eqn. (55) is transformed into the equation for the reversible overall anodic-cathodic wave:

$$\varphi = \varphi_{1/2\,rev} - \frac{2.3RT}{nF}\log\frac{I_a + i}{I_k - i},$$

and

$$\text{and } \varphi_{1/2\,rev} = \varphi_{eq} - \frac{2.3RT}{nF}\log\frac{I_k}{I_a}, \tag{56}$$

where $\varphi_{\frac{1}{2}rev}$ is the reversible half-wave potential of the anodic-cathodic wave (Fig. 8, curve *1*). It follows from this equation that the reversible cathodic wave ($I_a = 0$) and the reversible anodic wave ($I_k = 0$) have half-wave potentials and slopes identical with those of the reversible anodic-cathodic wave.

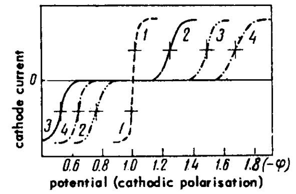

Fig. 8. Dependence of the current on the potential calculated by Eqn. (55) for different values of i_0 α and β : $I_k = I_a = I$; t = 25°; n = 2. Curve *1*) reversible anodic-cathodic wave ($i_0 \to \infty$); *2*) $i_0 = 10^{-4}I$, $\alpha = \beta = 0.5$; *3*) $i_0 = 10^{-8}I$, $\alpha = \beta = 0.5$; *4*) $i_0 = 10^{-8}I$, $\alpha = 0.35$, $\beta = 0.65$; φ_0 conditionally taken as 1.0 V. In the case taken $\varphi_0 = \varphi_{\frac{1}{2}\,rev}$.

When the exchange current is sufficiently small and the polarisation sufficiently high, then one of the terms in the right-hand side of Eqn. (55) can be neglected, and we can write the following expressions for the cathodic and anodic waves:

$$\left.\begin{aligned} \varphi_{1/2k} &= \varphi_{eq} - \frac{2.3RT}{\alpha nF}\log\frac{I_k}{i_0} \\ \varphi_{1/2a} &= \varphi_{eq} + \frac{2.3RT}{\beta nF}\log\frac{I_a}{i_0} \end{aligned}\right\}, \tag{57}$$

where $\varphi_{\frac{1}{2}a}$ and $\varphi_{\frac{1}{2}k}$ are the cathodic and anodic half-wave potentials.

It follows from Eqns. (56) and (57) that:

$$\left.\begin{aligned} \Delta\varphi_{1/2k} &= \varphi_{1/2\,rev} - \varphi_{1/2\,k} = \frac{2.3\,RT}{\alpha nF}\log\frac{I_k}{i_0} + \frac{2.3RT}{nF}\log\frac{I_a}{I_k} \\ \Delta\varphi_{1/2a} &= \varphi_{1/2a} - \varphi_{1/2\,rev} = \frac{2.3RT}{\beta nF}\log\frac{I_a}{i_0} + \frac{2.3RT}{nF}\log\frac{I_k}{I_a} \end{aligned}\right\}. \tag{58}$$

Eqn. (58) shows that in the case of irreversible electrode processes in oxidation-reduction systems, not one but two waves appear on the polarogram: the cathodic, shifted to negative voltages, and the anodic shifted to positive voltages by comparison with the half-wave potential of the reversible anodic-cathodic wave. On the basis of Eqn. (58) we can write:

$$\left.\begin{aligned} \Delta\varphi_{1/2\,ak} &= \varphi_{1/2\,a} - \varphi_{1/2\,k} = \Delta\varphi_{1/2\,k}\,\Delta\varphi_{1/2\,a} = \frac{-2.3\,RT}{\alpha\beta nF}\lg\frac{i_0}{I_k^{\beta} I_a^{\alpha}} \\ \alpha\varphi_{1/2\,k} + \beta\varphi_{1/2\,a} &= \varphi_{1/2\,rev} \quad \text{and} \quad \frac{\Delta\varphi_{1/2\,k}}{\Delta\varphi_{1/2\,a}} = \frac{\beta}{\alpha} \end{aligned}\right\}. \tag{59}$$

It follows from these expressions that the difference between the half-wave potentials of the anodic and cathodic waves increases as the exchange current (expressed in terms of the limiting current) decreases (Fig. 8, curves *2* and *3*). In addition, the displacement of the wave from the reversible curve is directly proportional to the slope of the wave.

If $\alpha = \beta$, then the maximum deformation of the wave occurs at the half-wave potential of the equilibrium curve, the anodic and cathodic branches being symmetric relative to this point. If $\alpha > \beta$, the maximum deformation is transferred to a more positive (if $\alpha < \beta$ to a more negative) potential, the anodic and cathodic branches then being unsymmetrical (Fig. 8, curves *2*–*4*).[18] Smutek[11] reached this conclusion in another way.

The magnitude of the exchange current is characteristic of the degree of reversibility of the electrode process. Introducing the conception of reduced exchange current (i_0^0):

$$i_0^0 = \frac{i_0}{I_k^{\beta} I_a^{\alpha}},$$

we obtain a simple relation between the departure from reversibility $\Delta\eta$ ($\Delta\eta = \eta - \eta_{rev}$) and the exchange current. A plot of log i_0^0 against log $\Delta\eta$ shows that with an increase in the departure from reversibility by more than 0.1 V there is an appreciable reduction in the reduced exchange current (Fig. 9).[19]

As is evident from Eqn. (55), a plot of $\log[(I_a + i)/(I_k - i)]$ *vs.* η can serve as an indication and measure of polarographic reversibility; it is generally non-linear; only for a reversible wave is the dependence expressed by a straight line with slope $2.3RT/nF$. When $\eta \gg 0$, the slope of the curve tends to the value $2.3RT/\alpha nF$, and at $\eta \ll 0$ to $2.3\,RT/\beta nF$. These conclusions are analogous to those of Tockstein[12]. The departure from the equilibrium curve increases with reduction in drop time of the mercury or

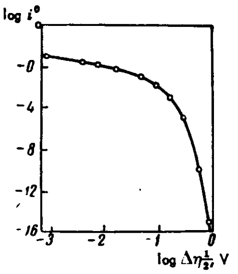

Fig. 9. Theoretical form of the relation between the reduced exchange current and the departure from reversibility in logarithmic co-ordinates. I_k-I_a-I ; $i=\frac{1}{2}I$; $\alpha=\beta=0.5$; $n=2$.[19]

amalgam, the rate constant of the electrode process, and the coefficients α and β.

The effect of the drop time on the half-wave potential for oxidation-reduction systems can be represented by the expression:

$$-\varphi_{1/2} = A + B\log\tau, \tag{60}$$

where

$$B = \frac{2.3\,RT}{2\alpha nF}, \quad A = -(\varphi_{1/2})_{\tau=1} = -\varphi^0 - \frac{2.3\,RT}{\alpha nF}\log 0.0051\, j_0 k_{\text{dif}}.$$

$$(\text{where } j_0 = k_1^{\alpha} k_2^{\beta}).$$

This equation differs from Eqn. (54) in its first term. Eqn. (60) shows that with an increase in the drop time the half-wave potential must be displaced in the direction of more positive potentials; the plot of $\varphi_{\frac{1}{2}}$ *vs.* log τ must be linear with a slope equal to half that of the wave. An analysis of the irreversible wave for manganese confirms the correctness of Eqn. (60).[75]

Surface-active substances affect the degree of reversibility of electrode processes significantly. Their influences on polarographic curves are diverse: displacement of the wave towards the side of more negative values of the potential, reduction of the limiting current, the appearance of a second wave, branching of the anodic-cathodic wave, and variation in the slope of the wave[38-41,58,76-86].

The theories advanced to explain the influence of surface-active substances on the electrode process are varied; they consider the influence of the adsorbed film on the migration of the depolariser, or on its discharge, or on the conjugate chemical reaction[38-40,58,76-88].

A study of the dependence of current on time at various potentials along the wave[85,86,89,90] helps to explain the mechanism of the action of surface-active substances on polarographic curves. Schmid and Reilley[89] considered three limiting types of *i vs. t* curves in relation to what determines the growth of the adsorption film. Quantitative evaluation of the first type, determined by the rate of diffusion of the surface-active substance (electrically inactive), is expressed by the following equation[86,90]:

$$\frac{i_{\text{ads}}}{i} = 1 - \frac{k^0 - k_1}{k^0}\left(\frac{t}{t'}\right)^{1/2}, \tag{61}$$

where k^0, k_1 are rate constants for the electrode reaction on the free surface and surface occupied by the adsorbed substance respectively, and t' is the time necessary for complete coverage of the electrode surface. The experimental *i vs. t* curve shows good agreement with Eqn. (61) only for surface-active substances of the molecular type. The marked discrepancies which are observed in the presence of surface-active cations can be explained by supposing that their specific adsorption on the mercury cathode is followed by potential changes in the electrical double layer. In the presence of surface-active substances the change in the ψ_1-potential can become significant[74]. Eqn. (55) for calculating the ψ_1-potential takes the form[18]:

$$\frac{i}{i_0}\exp\left\{\frac{\beta nF}{RT}(\psi_{1\text{eq}} - \psi_1)\right\} = \frac{I_k - i}{I_k}\exp\frac{\alpha nF\eta}{RT} - \frac{I_a + i}{I_a}\exp - \frac{\beta nF}{RT}\,\eta,$$

where $\psi_{1\,\text{eq}}$ is the value of the potential ψ_1 at equilibrium potential. This dependence has been confirmed experimentally.

Measurements of the capacity of the electrode can be used to evaluate the coverage on it[85].

The *i vs. t* curves and the effect of potential on the rate constant of the electrode reaction on the coated part of the electrode surface (k_1) provide an explanation for the anomalous course of the polarographic wave in the presence of an adsorbed substance[86]. If the reaction rate constant is zero on the occupied surface, then in the presence of surface-active substances the limiting current of reversible waves is reduced, and in the case of irreversible waves the wave is shifted towards the side of negative potentials as well as being diminished in height. When k_1 on the rising part of the wave is greater than zero and changes with potential, then there is a displacement of the wave and a change in its steepness. A second wave is formed if, at the potential of limiting current, the value of k_1 grows with rising potential.

The value of the coefficient α is reduced in the presence of a surface-active substance; this can be explained by assuming that polarisation of the depolariser is the determining factor for an irreversible electrode process[91].

VI. CONCLUSION

Electrode processes in agitated solutions have been studied less[49,92]. Expressions for non-stationary irreversible electrode processes have been obtained only for linear diffusion[52], and then – because of the difficulties in solving the differential equations for convection-diffusion with laminar flow – starting from the equations:

$$\left.\begin{aligned} \frac{\partial c_{\text{O}}}{\partial t} &= D_{\text{O}}\frac{\partial^2 c_{\text{O}}}{\partial x^2}, \quad 0 \leqslant x \leqslant \delta_{\text{O}} \\ \frac{\partial c_{\text{R}}}{\partial t} &= D_{\text{R}}\frac{\partial^2 c_{\text{R}}}{\partial x^2}, \quad \text{R} \leqslant x \leqslant \delta_{\text{R}} \end{aligned}\right\}, \tag{62}$$

the convective transfer of the reacting substances is calculated with the quantities δ_{O} and δ_{R} in the boundary conditions $c_{\text{O}}(\delta_{\text{O}}, t) = c_{\text{O}}^0$ and $c_{\text{R}}(\delta_{\text{R}}, t) = 0$. δ is the thickness of the pre-electrode layer in which the change in concentration of substances O and R takes place. In the case of non-stationary processes δ will be equal to the distance between the electrode surface and the moving boundary of the solution of changing concentration. This distance, the so-called distance to the diffusion front, is a variable dependent on the duration of electrolysis, the rate of electrode reaction, and hence also on the electrode potential.

The expression for the current, obtained for small values of t (or large values of δ) agrees with Eqn. (42), obtained for stationary solutions[11,14,57] under conditions when the effect of agitation can be neglected. For large values of t (or small values of δ), the current density is expressed as follows:

$$i = nFkc_{\text{O}}^{0}\left[\frac{1}{1+\frac{Q\delta_{\text{O}}}{D_{\text{O}}^{1/2}}} + H\exp\left(-\frac{\gamma^{2}D_{\text{O}}}{\delta_{\text{O}}^{2}}t\right)\right],$$

where $H = \sin 2\gamma/[\frac{1}{2}(\sin 2\gamma) - \gamma]$; γ is a quantity appearing in the solution of Eqn. (62) and taking values between $\pi/2$ and π ($\pi/2 \leqslant \gamma \leqslant \pi$) for different values of the ratio $Q\delta_{\text{O}}/D_{\text{O}}^{\frac{1}{2}}$. Unlike the stationary solutions, the value of i does not tend to zero as t tends to infinity, but takes the value:

$$i_{t\to\infty} = nFk_{0}c_{\text{O}}^{0}\frac{1}{1+\frac{Q\delta_{\text{O}}}{D^{1/2}}}\quad. \tag{63}$$

The solution of the differential equations for convective diffusion for the particular case of the stationary state gives an expression identical with Eqn. (63) when $i \to \infty$.[49,52]

In the cases analysed above, when considering irreversible electrode processes it was supposed that the concentration of the potential-determining substances at the electrode surface is determined only by their diffusion rate. However, this concentration can be limited also by so-called kinetic hindrances.

Kinetic polarographic waves began to be studied much later than diffusion waves. Initially, the concept of the pre-electrode reaction layer[93-95] was used to calculate the kinetic component of the limiting current, and this idea has been criticised[17,96]. A firmer basis for the study of kinetic currents was provided by the method used in the analysis on irreversible polarographic waves. By suitable substitution of variables, problems of kinetic currents can be changed into problems of irreversible electrode processes for which the concentration of reacting substances at the electrode surface is determined by diffusion. In both cases the solution is similar in form. Thus the expression for instantaneous kinetic currents can be presented as a relationship analogous to Eqn. (38), except that the values of κ and i are different. The expression for mean polarographic kinetic currents is analogous to Eqn. (39) but with different values of κ_1.

Surveys of the work on kinetic currents with various depolarisers have been made by Delahay[62], Brdička and Koutecký[97-99], Koryta[100], and Hans[101]. In particular, a solution has been found for the case where the reacting electrochemical substance is partially regenerated as a result of a chemical process with part of the product of the electrochemical reaction (catalytic wave). Several papers[102-115] contain interesting material on kinetic and catalytic currents. Kinetic hindrance affects the height of the limiting current but not the slope of the wave, which remains at the theoretical value for diffusion waves, nor does it cause branching of the wave in oxidation-reduction systems. The study of kinetic and catalytic currents began with irreversible electrochemical reactions[116-119]. Solutions were obtained for the problems of slow electrode reactions with a previous unimolecular chemical reaction of any speed[117] and also with previous and subsequent chemical reactions[118].

More recently it has been shown that the rotating disc electrode[120] can be used successfully in the study of kinetic and catalytic currents. The conditions for the supply of a substance to any point on the surface of such an electrode are identical if boundary effects are neglected. On the rotating disc electrode, reversible electrode reactions with quasi-unimolecular and bimolecular rapid chemical reactions have been examined[120-121]. This method of solving problems is also used for other types of process with other systems of differential equations for diffusion and boundary conditions. On the rotating disc electrode, as opposed to the dropping electrode, processes take place under steady state conditions, which simplifies calculations. This extends the range of processes which can be studied, and in particular, the range of irreversible electrochemical reactions.

The theory of irreversible polarographic waves is still being developed. It does not provide a general approach to the solution of various depolarisation schemes and it cannot always be used in cases where different irreversible processes are taking place simultaneously in a system. However, even in this the theory has already enabled wider use to be made of the polarographic method and a nearer approach to the study of electrode processes.

The theory of irreversible polarographic waves has made it more possible to study the kinetics of electrode processes where slow electrode reactions are concerned. In this respect, the polarographic method and the method of superimposed alternating current[122] are complementary.

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POLYARYLATES

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CONTENTS

I. INTRODUCTION

Polyarylates are hetero-chain polyesters of dihydric phenols. Polymers of this type were first described in 1898 by Einhorn[1], who studied the reaction between phosgene and catechol, resorcinol, and quinol. A cyclic monomeric carbonate was obtained with catechol and polymeric products with resorcinol and quinol. Bischoff and Hedenström[2], in 1902, described the formation of polyarylates of oxalic acid by the reaction of diphenyl oxalate with quinol and resorcinol.

Until recent times little or no work on polyarylates was reported in the literature, but in the last decade a number of articles have appeared concerning this class of polymers. Particular attention was paid to the study of polyarylates after Schnell[3] had reported the results of his studies on polyesters of dihydric phenols of various structures with carbonic acid, which possessed a number of technically valuable properties. Since then articles devoted to a study of these types of polyarylates have been published regularly[4-28].

Data concerning other polyarylates have become available[29-72], the most interesting concern the polyesters of dihydric phenols and aromatic dicarboxylic acids[31-40,46,47,48,51-54,70,71] and some mixed polyesters of dihydric phenols[33-35,54,72]. These polyesters also have the following useful properties: high softening point, good dielectric properties, resistance to attack by chemical reagents, the ability to produce stable films, etc. There is, therefore, every reason to expect that these polymers will be extensively used in the future.

II. METHODS OF PREPARATION OF POLYARYLATES

1. Transesterification Reactions

(a) **The preparation of polyarylates from dihydric phenol diacetates and dicarboxylic acids.** Wallsgrove and Reeder[30], and Levine and Temin[48] describe the preparation of polyarylates by the reaction of dihydric phenol diacetates with dicarboxylic acids:

$$CH_3COOArOCOCH_3 + HOOCRCOOH \rightarrow CH_3COOH + (-OArOCORO-)_n.$$

For example, Levine and Temin obtained by this method the polyesters of 2,2-bis(4-hydroxyphenyl)propane with adipic, 3-methyladipic, and sebacic acids, and of *p,p'*-dihydroxydiphenyl with adipic acid, as well as other polyarylates.

To prepare polyarylates by this method, the polycondensation is carried out in the fused state in the presence of a catalyst, for example metallic magnesium, at high temperatures in a current of an inert gas, the mixture being heated *in vacuo* at a certain stage of the reaction.

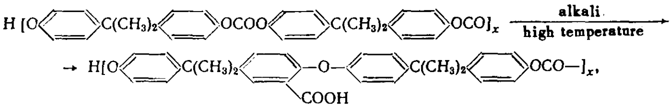
This method is not entirely satisfactory because it cannot be used successfully for the preparation of high-softening-point polyarylates. Moreover, the polyarylates produced frequently become highly coloured during the reaction.

(b) Synthesis of polyarylates by the reaction of dicarboxylic esters with dihydric phenols:

$$R'OCORCOOR' + HOArOH \rightarrow ROH + (-OArOCORCO-)_n.$$

This method has been used for the preparation of polycarbonates[3,20,21,25]. Diphenyl carbonate is usually used as the starting material. The polycondensation is conducted in the molten state at 150°–300° in an oxygen-free atmosphere. Polyesterification is accelerated by the use of a vacuum and by stirring[3]. Thompson and Goldbaum[21] showed that an excess of diphenyl carbonate was desirable during the initial stages of its reaction with 2,2-bis-(4-hydroxyphenyl)propane (dian or bisphenol A). This allowed a more rapid and complete conversion of the bisphenol A, desirable because this phenol may decompose at temperatures above 180°.

The polyesterification reaction is markedly accelerated in the presence of a catalyst. Schnell[3] showed that acidic catalysts (boric acid, toluene-*p*-sulphonic acid, zinc chloride) were only slightly effective. Basic catalysts such as the alkali and alkaline-earth metals, their oxides and hydroxides, amines, zinc oxide, lead oxide, etc., significantly increased the rate of polycondensation. Large quantities of strongly basic catalysts could, however, cause side reactions, leading to the formation of branched and cross-linked structures, under the conditions used for the polycondensation. Schnell[3] postulated that this was due to the following rearrangement:



leading to the appearance of carboxyl groups in the polymer chain, as possible centres for branching and cross-linking.

Transesterification can be used to produce polyarylates on an industrial scale. The high viscosity of the melt during the production of polycarbonates precludes the preparation of polymers with very high molecular weights by this method. It is difficult to obtain polycarbonates of molecular weight greater than 50 000.[3]

2. Reaction of Dicarboxylic Acid Chlorides with Dihydric Phenols

(a) Preparation of polyarylates by the polycondensation of dicarboxylic acid chlorides with dihydric phenols at high temperatures has been described in a number of papers[31-35,39,41-45,49,56-69]:

$$ClCORCOCl + HOArOH \rightarrow HCl + (-OArOCORCO-)_n.$$

Korshak and Vinogradova synthesised several polyarylates by heating dicarboxylic acid chlorides with dihydric phenols, initially in a stream of nitrogen and then at a reduced pressure (~1–2 mm Hg). They obtained polyesters of terephthalic and isophthalic acids with 2,2′-dihydroxydiphenyl[31], and of sebacic acid with resorcinol and bisphenol A[35], and other polyarylates.

Several workers have used the method of polycondensation in the melt to prepare phosphorus-containing polyarylates using phosphorus oxychloride and the dichlorides of phosphorus-containing acids (phosphinic, phosphinous, thiophosphinic, and phosphoroamidic) with dihydric phenols[41-45,56-66].

In general the production of these polyarylates is accomplished with equimolar quantities of the starting materials, at high temperatures, with good mixing of the reaction mixture, and usually in the presence of a catalyst (*e.g.* heavy-metal halides). A current of inert gas is maintained during the reaction to ensure the rapid removal of the hydrogen chloride produced and to exclude air from the system. In the last stage of the reaction the temperature is increased (sometimes up to 250°–300°) and the pressure reduced[57].

Piiroya[44] studied the kinetics and mechanism of the polycondensation in the melt of resorcinol and phenoxyphosphoryl dichloride at 110°, 150°, and 200°, with reaction times from 8 h to 25 h and with equimolar and other ratios of the starting materials. Piiroya's studies showed that the yield of polyester and its molecular weight varied linearly with the reaction temperature. Any alteration from the equimolar ratio of the starting materials caused significant reduction in the molecular weight of the polymer. The production of polyester during the first hour of the experiment was very rapid but later slowed down considerably. The molecular weight and yield of polyester at 150° reached a maximum after 20 h and could not be increased, although some of the starting materials remained unconverted. The author concluded that the retardation of the reaction rate was caused by the high viscosity of the reaction mixture.

With the aim of increasing the rate of reaction between resorcinol and phenoxyphosphoryl dichloride, Raudsepp and Piiroya[45] studied the catalytic effect of calcium chloride and aluminium chloride on the polycondensation. The use of calcium chloride permitted the reaction to be carried out at much lower temperatures. Thus, at 110°, the molecular weight of the polyester reached 1350 after only 8 h, and the polyester of maximum molecular weight (~2300) was obtained at 150°. In the presence of aluminium chloride, polyester of molecular weight up to 2500 was obtained with complete conversion of the initial materials. The authors concluded that the molecular weight of the polyesters in these systems ceased to increase because of the high viscosity of the reaction medium.

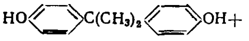
These authors[45] subjected the polyesters of molecular weight ~2500, obtained by polycondensation in the melt at 150° in the presence of aluminium chloride, to further polycondensation in chlorobenzene. They were thus able to obtain polymers of molecular weight ~5000. Even higher increases in the molecular weight of the polyester (up to 7500) were achieved by the addition of pyridine to the chlorobenzene to combine with the hydrogen chloride evolved during the reaction.

Synthesis from dicarboxylic acid chlorides and dihydric phenols in the molten state has only limited application and cannot be used for the production of high softening-point polyarylates such as those from terephthalic acid and quinol, resorcinol, bisphenol A and some other phenols. Because of the high softening point of these polyesters the reaction mass solidifies soon after the start of the reaction and cannot be remelted without decomposition. Consequently, the reaction stops during its very early stages. The above disadvantages can be avoided by carrying out the polycondensation in solution.

Korshak and Vinogradova[31],[32-35] have described the preparation of a number of homogeneous and mixed polyarylates by heating dicarboxylic acid chlorides with dihydric phenols in a high-boiling solvent at high temperatures. They also studied[32] the kinetics and mechanism of this reaction in solution in Dowtherm A using as examples isophthaloyl chloride and terephthaloyl chloride with bisphenol A between 150° and 210°, terephthaloyl chloride with 2,2′-dihydroxydiphenyl, resorcinol, and quinol at 170°, and sebacic acid chloride with bisphenol A at 150°.

It was shown that the reaction proceeds by a bimolecular mechanism. Rate constants and extent of reaction are shown in Table 1. These authors also found that the rate constants for the reaction of bisphenol A with isophthaloyl and terephthaloyl chloride varied according to the Arrhenius equation (*cf.* Fig. 1). By applying the method of least squares to the experimental data from these two reactions, Arrhenius equations of the following form are obtained: $K = 7.13 - 4963/T$ and $K = 5.81 - 4308/T$ respectively. From the above equations, the activation energy for the isophthaloyl chloride–bisphenol A reaction is 19 700 cal with a frequency factor of 0.646×10^6. The corresponding values for the terephthaloyl chloride–bisphenol A reaction are 22 700 cal and 0.135×10^8. The higher value of the frequency factor for the latter reaction was explained by the authors as due to a steric effect. The reactive groups in isophthaloyl chloride present greater obstacles to the approach of a second molecule than in the case of the *para*-substituted compound.

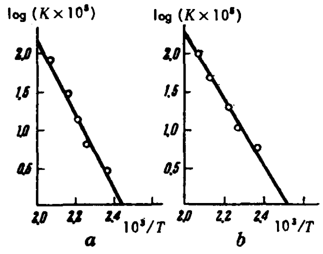
TABLE 1. **Rate constants and extent of reaction between dicarboxylic acid chlorides and dihydric phenol.**

Reactants	Reaction temp., °C	Rate constant, 10^{-5} litre × × mole^{-1} × × sec^{-1}	Extent of reaction after 7 h
 (I) + isophthaloyl chloride	150 170 180 200 210	5.72 10.70 17.99 50.30 92.00	0.17 0.26 0.38 0.63 0.72
(I) + terephthaloyl chloride (II)	150 170 180 190 210	2.99 6.56 14.30 30.40 79.60	0.09 0.17 0.33 0.46 0.64
(I) + sebacoyl chloride	150	34.40	—
2,2′-Dihydroxydiphenyl + (II)	170	6.90	0.16
Resorcinol + (II)	170	7.06	0.19
Quinol + (II)	170	11.70	0.27

Comparison of the rate constants of the various reactions, shown in Table 1, permits certain conclusions concerning the influence of the structure of the starting materials on the reaction rates[32]. It was shown that isophthaloyl chloride reacts with bisphenol A at a higher rate than terephthaloyl chloride. Replacement of an aromatic by an aliphatic acid chloride markedly increases the reaction rate. Thus, at 150° the reaction of sebacic acid chloride with bisphenol A proceeds at a rate about 60 times greater than that with isophthaloyl chloride and 115 times greater than that with terephthaloyl chloride.

The reaction rate also depends on the structure of the dihydric phenol. The reaction rates of the various phenols studied, with terephthaloyl chloride at 170°, varies in the following manner: quinol > resorcinol > 2,2′-dihydroxydiphenyl > bisphenol A.

The authors[32] also found that the extent of reaction, in a given time, increased with the temperature and concentration of reactants. The variation of the composition of the reaction mixture and the change in reduced viscosity of the polyester in cresol during the reaction of isophthaloyl chloride with bisphenol A at 220° are shown in Fig. 2. It can be seen that the reduced viscosity of the polyester in cresol continuously increases as the reaction proceeds, *i.e.* the molecular weight increases. Since the quantity of polymer changes only slightly after the third hour and the quantity of the low-molecular fraction is very small at this time, it follows that increase in polymer chain length must involve mainly polymer molecules.



a *b*

Fig. 1. Temperature variation of the rate constant for the reaction of bisphenol A with *a*) terephthaloyl chloride and *b*) isophthaloyl chloride.

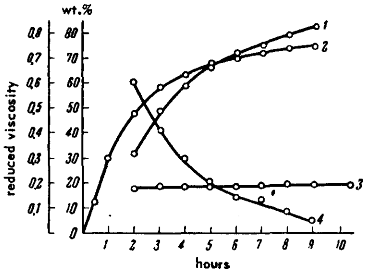


Fig. 2. Kinetics of the polycondensation of isophthaloyl chloride with bisphenol A at 220°: 1) quantity of hydrogen chloride liberated during the reaction; 2) quantity of polyester present in the reaction mixture; 3) quantity of reactants and low-molecular polyesters in the reaction mixture; 4) inherent viscosity of the polyester.

A detailed study of the influence of the various factors on the polycondensation of terephthaloyl chloride and bisphenol A was described by Korshak and coworkers[39]. They studied the effect of a number of solvents, the ratios of starting materials, the temperature, and reaction time on the reduced viscosity of the polyester and its yield.

The results obtained (Table 2) show that polyarylates with the greatest reduced viscosity were obtained in solution in ditolylmethane with an initial reactant concentration 0.6 M. The polymers prepared in Dowtherm A and tetralin were discoloured and difficult to extract, whereas those produced in ditolylmethane were pale yellow and easily extracted.

A study of the effect of temperature (220° and 240°) and reaction time on the reduced viscosity of the polyarylate in ditolylmethane solution showed that the best results were obtained at 220°. The authors[39] established that polyarylates with the highest molecular weight were obtained when an equimolar mixture of reactants was used. The variation of the reduced viscosity of the polyester with the initial reactant ratio is shown in Fig. 3. Yamaguchi, Takayanagi, and Kuriyama[49] describe the production of poly(quinol adipate) by heating adipoyl chloride with quinol in nitrobenzene in an inert atmosphere.

It was found[43,69], during a study of the influence of various factors on the reaction of methylphosphinic acid dichloride with quinol in Dowtherm A between 140° and 170°, that the extent of reaction increased with increase in the temperature and concentration of reactants (*cf.* Fig. 4). An especially marked increase was observed during the first hour, when the reaction is mainly between the monomers. Determination of the composition of the reaction mixture and of the reduced viscosity during the course of the reaction showed that the molecular weight of the polyester increases with time. In view of the relative quantities of free monomers and polymer in the reaction mixture, the authors concluded that after 4 – 5 h the growth of the polymer chains was largely due to reaction between polymer molecules. The reaction of methylphosphinic acid dichloride with quinol was found to be of second order. At 150° the reaction rate constant was 0.00033; at 160°, 0.000444; at 170°, 0.000557 litre $mole^{-1}$ sec^{-1}. The authors[43] established that the variation of the rate constant with temperature was in accordance with the Arrhenius equation. The activation energy is 10 470 ± 700 cal $mole^{-1}$.

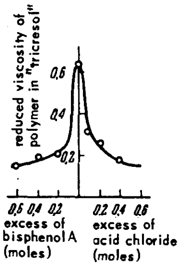


Fig. 3. Variation of the reduced viscosity of the polyarylate in cresol in relation to the initial ratio of reactants.

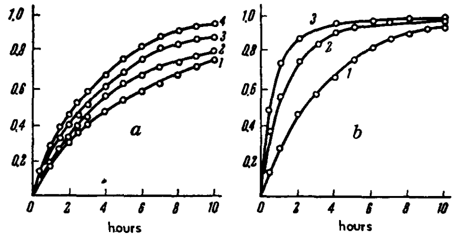


Fig. 4. The degree of completion (ordinate) of the reaction between methylphosphinic dichloride and quinol in nitrobenzene solution:
a) at different reaction temperatures: 1) 140°; 2) 150°; 3) 160°; 4) 170°;
b) with different initial concentrations of reactants (170°), M: 1) 0.1; 2) 0.3; 3) 0.5.

TABLE 2. Dependence of the reduced viscosity in "tricresol" and the yield of terephthalic acid-bisphenol A polyarylates on the solvent and the concentration of the reactants.

Concentration of reactants, M	Reduced viscosity in tricresol			Yield, %		
	polycondensation in					
	ditolylmethane*	Dowtherm A	tetralin**	ditolylmethane	Dowtherm A	tetralin
0.05	0.30	0.25	0.15	44.0	70.0	—
0.10	0.40	0.33	0.20	57.0	70.0	15.2
0.20	0.42	0.35	0.22	67.0	76.5	48.0
0.30	0.40	0.29	0.26	67.0	81.5	70.0
0.40	0.49	0.43	0.30	71.0	76.0	73.0
0.60	0.62 (0.69)	0.42	0.28	76.0	81.0	43.5
0.80	0.60	0.47	0.36	73.5	75.0	46.0
1.00	0.54 (0.60)	0.50	0.30	81.0	77.0	58.0

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* The polycondensations were carried out in a stream of nitrogen with a gradual increase in temperature from 100° to 220° over a period of 3 h, and then at 220° for 10 h.

** The temperature was gradually increased during the polycondensation (under nitrogen) from 100° to 195° over 2.5 h and maintained at 195° for 10 h.

The synthesis of phosphorus-containing polyarylates from phosphorus oxychloride and the dichlorides of phosphonic acids with dihydric phenols by polycondensation in solution has also been described in a number of other papers[57,61,67,68].

(b) Preparation of polyarylates by polycondensation at phase boundaries. This type of polycondensation was first used for the preparation of

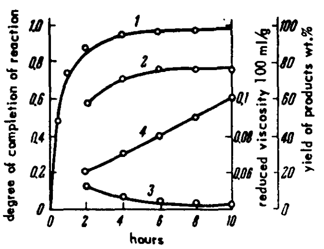


Fig. 5. Kinetics of the reaction between methylphosphinic dichloride and quinol in nitrobenzene of 170° (concentration 0.5 M): 1) degree of completion of the reaction; 2) overall yield of polyesters; 3) quantity of low-molecular compounds; 4) reduced viscosity of the polyester.

polyarylates as long ago as 1898 by Einhorn[1]. The application and detailed study of this method of preparing polymers began only during recent years[3,20,21,35-37,46,47,51-54].

In principle "interfacial" polyesterification involves the reaction of dicarboxylic acid chlorides and dihydric phenols at the boundaries of two phases. The acid chloride dissolved in an organic solvent is caused to react with a solution of the phenol in aqueous alkali. The reactions are carried out at atmospheric pressure at low, sometimes even at room, temperature at a very rapid rate (minutes).

The advantages of this method are readily apparent in comparison with the high-temperature reaction which is carried out in solution or in the melt in a current of inert gas, sometimes over a period of many hours, and which requires the application of a vacuum during the last stages of the reaction in the melt. The advantages of polycondensation at phase boundaries permit the use of this method for the production of polymers from thermally unstable reactants and also from substances which contain reactive groups (for example, double bonds) which could react under the usual conditions of homogeneous polycondensations. Recent literature data show that the interfacial method gives polyarylates with very much higher molecular weights (up to 275 000 [47]) than those produced by high-temperature polycondensation.

Data concerning interfacial polyesterification and its mechanism are very scarce[36-38,52-54]). Morgan[53] suggested that polyesterifications of this type apparently involve nucleophilic attack of the phenoxide ion on the dicarboxylic acid chloride. The reaction of a dihydric phenol with an acid chloride proceeds very slowly at room temperature unless the phenol is ionised.

Because the interaction takes place at phase boundaries, the area of boundary surface should have a significant effect on the polycondensation process, the amount of contact between the reactants depending on the surface area. The boundary surface in two immiscible liquids can be varied by the use of emulsifying agents and by agitating of the reaction mixture.

Korshak, Vinogradova, and Lebedeva[36] studied the interfacial reaction of isophthaloyl chloride with bisphenol A and found that the yield of polyarylate was strongly dependent on the rate of agitation. An increase in the agitation rate from 500 r.p.m. to 1500–1700 r.p.m. led to an increase in the yield from 46% to 93%.

The presence in the reaction mixture of an emulsifying agent, its nature, and concentration, also had a marked influence on the reduced (inherent) viscosity and yield of the polyarylate. The influence of emulsifying agents, such as sodium stearate, "Mersolate" (sodium salts of aliphatic sulphonic acids), "Novost' " (sulphonated higher alcohols), "OP-20" (mono- and di-alkylphenyl ethers of polyethylene glycol), "Trilon B" (the disodium salt of ethylene diamine tetra-acetic acid), "Nekal" (mixed sodium salts of mono-, di-, and tri-s-butylnaphthalenesulphonic acids), on the interfacial polyesterification of isophthaloyl chloride and bisphenol A has been investigated. The best results were obtained when Mersolate and Nekal were used as emulsifying agents. Thus, the reduced viscosity of the polyarylate in cresol obtained in the presence of Nekal approached 1.44, and with Mersolate 1.54, while in the absence of an emulsifying agent it was only 1.02 after the same time and under similar conditions. The use of Mersolate and Nekal clearly leads to a product of high molecular weight.

The relation between the concentration of emulsifying agent and the reduced viscosity and yield of polyarylate was studied. The results showed that the optimum concentrations of Mersolate and Nekal were 1 wt.% and 1–2 wt.% respectively.

Eareckson[54] also investigated the influence of a series of emulsifying agents on the reduced viscosity of solutions of the mixed polyarylate prepared from bisphenol A and a 1 : 1 (mole ratio) mixture of isophthaloyl and terephthaloyl chlorides. The emulsifiers studied were: "Triton X-100", a non-ionic polyoxyethylene detergent, "MP 189" (the sodium salt of a sulphonated kerosene fraction), and "Duponol ME" (mainly sodium lauryl sulphate). The results in Table 3 show that Duponol ME was the best emulsifying agent.

TABLE 3. The influence of various emulsifying agents on the viscosity of the mixed polyarylate of bisphenol A with isophthalic and terephthalic acids (composition 1:0.5:0.5).

Solvent	Emulsifying agent	η_{inh}	Yield, %
Trichloroethylene	MP 189	0.74	92
»	Triton X-100	0.74	92
»	Duponol ME	1.45	92
Toluene	MP 189	0.92	92
»	Triton X-100	0.88	92
»	Duponol ME	1.46	95
o-Dichlorobenzene	MP 189	0.45	92
»	Triton X-100	0.64	—
»	Duponol ME	1.00	89

Note: $\eta_{inh} = \ln \eta_{rel}/c$ determined at 0.5% concentration in *sym*-tetrachloroethane–phenol (40/60 w/w) at 30°.

The influence of the rate and sequence of adding the reactants on the reduced viscosity of the polyarylate was also examined[36]. It was found that under similar experimental conditions the highest reduced viscosity was obtained by the addition of a solution of isophthaloyl chloride (in *p*-xylene) to an alkaline solution of bisphenol A. Moreover, the time taken to add the reactants was found to have an effect: the best results were obtained by mixing over a period of 9–18 min. The yield of polyester (85–94%) was not significantly affected by the rate of addition of the reactants nor by the sequence of addition.

The initial concentration of reactants has a marked influence on the molecular weight of the polyester produced. Korshak, Vinogradova, and Lebedeva[36] presented data concerning the relation between the yield and the reduced viscosity of the polyarylate from bisphenol A – isophthaloyl chloride and the concentration of the equimolar mixture of reactants. It can be seen from Fig. 6. that the reduced viscosity of the polyester passes through a maximum obtained when the concentration of the starting materials is 0.10 M. Lower and higher initial concentrations were found to yield polyesters of lower reduced viscosities. The reduced viscosity was not further affected by concentrations greater than 0.3 M. Variation in the initial reactant concentrations had little influence on the yield of polyester (78–91%).

The dependence of the reduced viscosity and yield of polyester on the nature of the solvent was studied (Table 4). A large variety of compounds were used as solvents: aliphatic hydrocarbons (n-heptane), aromatic hydrocarbons (benzene, toluene, and xylenes), chlorinated aliphatic hydrocarbons (chloroform, carbon tetrachloride, dichloroethane, and *sym*-tetrachloroethane), chlorinated aromatic hydrocarbons (chlorobenzene) and also tetralin, diethyl ether, and petroleum ether.

The reduced viscosity of the polyester produced was found to depend strongly on the nature of the solvent. In the absence of an emulsifier the highest reduced viscosities of the polyester were obtained when aromatic hydrocarbons were used as solvents for isophthaloyl chloride, the best results being obtained with xylenes. The reduced viscosity of the polyester prepared in the isomeric xylenes increased in the following manner: *p*-xylene > *m*-xylene > *o*-xylene.

Emulsifying agents widen the range of solvents which can be used for interfacial polyesterification reactions[38]. Data are also given in Table 4 concerning the yield and reduced viscosity of polyesters prepared by the interfacial polyesterification of isophthaloyl chloride in various solvents in the presence of Nekal.

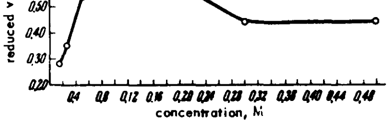


Fig. 6. Variation of the reduced viscosity of polyester in cresol with the concentration of reactants.

TABLE 4. The influence of the solvent on the reduced viscosity and yield of the polyarylate.

Solvent for the isophthaloyl chloride	Experiments with emulsifying agent (Nekal*)		Experiments without emulsifying agent	
	reduced viscosity of polyester in cresol	yield, %	reduced viscosity of polyester in cresol	yield, %
p-Xylene	1.46	80	1.02	88
Tetralin	0.64	80	0.28	86
n-Pentane	0.94	84	0.30	quantitative
Carbon tetrachloride	1.12	83	0.40	»
Chloroform	0.44	77	0.12	»
Dichloroethane	0.72	80	0.16	80
Tetrachloroethylene	1.02	82	—	—
Trichloroethylene	0.96	80	—	—
Chlorobenzene	0.72	80	0.20	83
Diethyl ether	0.58	87	0.33	77
Petroleum ether (b.p. 70°–72°)	—	—	0.22	91
Tetrachloroethane	—	—	0.10	17
Benzene	—	—	0.25	91
Toluene	—	—	0.26	84
m-Xylene	—	—	0.60	88
o-Xylene	—	—	0.45	80

* A 1.5% solution of Nekal in the aqueous phase was used.

In every case the use of an emulsifier increased the reduced viscosity of the polyarylate in cresol 2–3 times, compared with the reduced viscosity of polyarylates prepared in the absence of emulsifiers. Thus, polyesters of high reduced viscosity were prepared in n-heptane, carbon tetrachloride, tetrachloroethane, and trichloroethane solutions, as well as in *p*-xylene.

Eareckson[54] studied the influence of the nature of the solvent on the reduced viscosity of the mixed polyarylate of bisphenol A with isophthalic and terephthalic acids, of composition 1 : 0.5 : 0.5. His results are set out in Table 5. The author concluded that the proper choice of solvent was very important since it determined the molecular weight of the polymer. Thus, solvents which dissolved the polymer favoured the formation of polymers of higher molecular weight.

The polyester of highest molecular weight was obtained in chlorinated hydrocarbons in which the mixed polyarylate was readily soluble. According to Eareckson[54] these solvents have the capacity to swell the polymer films at the phase-boundaries through which the acid chloride migrates and reacts with the phenoxide ions in the aqueous phase. If the polymer becomes completely insoluble in the organic phase, hard polymer films prevent the migration of the acid chloride molecules and seriously limit the yield and molecular weight of the polymer.

The effect of temperature on the interfacial polycondensation of isophthaloyl chloride with bisphenol A was studied[36] at 20°, 30°, 50°, 60°, and 70°. It was shown (Fig. 7) that the reduced viscosity was lowered from 0.74 to 0.16 as the temperature was increased from 20° to 70°. The yield of polyarylate was also reduced to 70–75% from 88% at 20°.

TABLE 5. Effect of solvent on the reduced (inherent) viscosity of the mixed polyarylate.

Solvent for the acid chloride	Yield of polyester, %	η_{inh}
Chloroform	89	2.31
1,1,2;Trichloroethane	95	1.73
Dichloroethylene	92	1.59
Trichloroethylene	94	2.02
o-Dichlorobenzene	89	1.00
o-Nitrotoluene	87	0.86
Toluene	95	1.62
Xylene	92	1.15
Cyclohexane	94	1.38

Note. η_{inh} was determined at 0.5% concentration in *sym*-tetrachloroethane–phenol (40/60 w/w) at 30°, $\eta_{inh} = ln\,\eta_{rel}/c$.

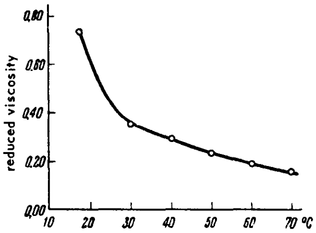


Fig. 7. Relationship between the reduced viscosity of polyester in cresol and the reaction temperature.

The following competing reactions are possible during polyesterifications at phase-boundaries when one of the phases is aqueous:

$$ClCOC_6H_4COCl + NaOC_6H_4C(CH_3)_2C_6H_4ONa \rightarrow \\ \rightarrow NaCl + Cl[-COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O-]_xNa; \quad (1)$$

$$ClCOC_6H_4COCl + H_2O \rightarrow HOCOC_6H_4COOH + HCl\,; \\ \searrow ClCOC_6H_4COOH + HCl\,; \quad (2)$$

$$NaOC_6H_4C(CH_3)_2C_6H_4ONa + HCl(HOCOR-\ldots) \rightarrow \\ \rightarrow HOC_6H_4C(CH_3)_2C_6H_4OH + NaCl(NaOCOR-\ldots); \quad (3) \\ \searrow NaOC_6H_4C(CH_3)_2C_6H_4OH + NaCl$$

$$Cl[COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O]_xNa + H_2O \rightarrow \\ \rightarrow HO[COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O]_xNa + HCl; \quad (4)$$

$$Cl[COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O]_xNa + \\ + HCl(HOCOR-\ldots) \rightarrow Cl[COC_6H_4COOC_6H_4C. \\ .(CH_3)_2C_6H_4O]_xH + NaCl(NaOCOR-\ldots). \quad (5)$$

The first leads to the synthesis of polymer. The remainder [(2)–(5)] prevent polymer formation either by converting the reactants or the growing chains to unreactive compounds, *i.e.* chain termination takes place. Since polymers were obtained in good yields in most of the cases studied, the authors conclude that the first type of reaction predominates and proceeds at a much higher rate than the others.

The reduction in yield and molecular weight of the polyester with increased temperature may be explained by the increased role of these latter reactions, the rate of which increases at higher temperatures. The removal of the reactive groups from the reactants leads, on the one hand, to a reduction in the yield of polymer and, on the other hand, to a change in the reactant ratio which eventually leads to chain termination (*i.e.* causes a reduction in the molecular weight of the polyester). These reactions may also affect the functional groups of the growing chains and likewise cause chain termination.

In many classical homogeneous polycondensations it was found[73,74] that the initial ratio of the reactants had a considerable bearing on the molecular weight of the polymer. Attempts have also been made[37] to determine the influence of the reactant ratio on the molecular weight and yield of the polyester prepared by the interfacial method.

The relationship between the reduced viscosity of the polyarylate, prepared from isophthaloyl chloride and bisphenol A, and the reactant ratio is shown in Fig. 8. In all experiments the concentration of sodium hydroxide used was equivalent to the diol (*i.e.* the molar ratio of diol to sodium hydroxide was 1 : 2).

It can be seen from Fig. 8 that the polyarylate prepared from equimolar quantities of reactants possessed the highest reduced viscosity (*i.e.* the highest molecular weight). An increased concentration of isophthaloyl chloride (to the left of the maximum) or of the dihydric phenol (to the right of the maximum) caused a reduction of the reduced viscosity of the polyarylate. An excess of bisphenol A has the greater effect. When an 80% excess of isophthaloyl chloride was used, a polyester with a reduced viscosity more than half that of the product made with an equimolar ratio was obtained (0.46 and 0.74 respectively).

The authors compared the variation of the molecular weight of the polyesters prepared with an excess of the acid component in the above example and in the polycondensation of ethylene glycol with adipic acid[73,74] in the melt. They noted that in both cases the molecular weight fell as the excess of the acid compound was increased, but in the latter case an 80% excess of adipic acid led to an approximately sixfold reduction in the molecular weight of the polyester.

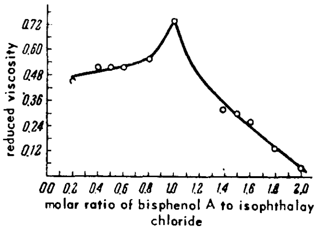


Fig. 8. Variation of the reduced viscosity of polyester in cresol with the reactant ratio.

It may be concluded from the above data that the ratio of the reactants has a significant effect on the molecular weight of the polyester produced by both interfacial polycondensation and those in the melt, although the mechanism of the action of the component in excess is different.

The possible competing reactions during polyesterification at phase boundaries, when one of the phases is aqueous, have already been indicated. One reaction leads to the synthesis of polyester while the others are chain breakers. In the presence of excess isophthaloyl chloride the following reactions, which would prevent the growth of polyester chains, are possible:

$$\begin{aligned} &ClCOC_6H_4COCl + H_2O(NaOH) \rightarrow \\ &\quad \rightarrow HOCOC_6H_4COOH + HCl(NaCl); \qquad (1) \end{aligned}$$

$$\begin{aligned} &Cl[COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O]_xNa + \\ &\quad + H_2O(NaOH) \rightarrow HO[COC_6H_4COOC_6H_4C. \\ &\quad .(CH_3)_2C_6H_4O]_xNa + HCl(NaCl); \qquad (2) \end{aligned}$$

$$\begin{aligned} &NaOC_6H_4C(CH_3)_2C_6H_4ONa + HCl(HOCOR-\ldots) \rightarrow \\ &\quad \rightarrow HOC_6H_4C(CH_3)_2C_6H_4OH + NaCl(NaOCOR-\ldots); \qquad (3) \end{aligned}$$

$$\begin{aligned} &Cl[COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O]_xNa + \\ &\quad + HCl(HOCOR-\ldots) \rightarrow Cl[COC_6H_4COOC_6H_4C). \\ &\quad .(CH_3)_2C_6H_4O]_xH + NaCl(NaOCOR-\ldots); \qquad (4) \end{aligned}$$

$$\begin{aligned} &Cl[COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O]_xNa + \\ &\quad + ClCOC_6H_4COCl \rightarrow Cl[COC_6H_4COOC_6H_4C. \\ &\quad .(CH_3)_2C_6H_4O]_xCOC_6H_4COCl + NaCl. \qquad (5) \end{aligned}$$

Since the authors obtained polymers in good yields in each experiment of this series, it clearly follows that the extent of reactions (1) and (3) was small, although some of the isophthaloyl chloride must be hydrolysed. The fact that the polyester made with an excess of isophthaloyl chloride has a much greater reduced viscosity than that produced from an excess of bisphenol A was explained on the grounds that partial hydrolysis of the acid chloride does in fact compensate for and reduce the excess of this component.

The role of the excess component during polycondensation in the melt is twofold. Under certain conditions and at a definite stage of the reaction, it may act as a chain breaker. This would explain why the polymers obtained had similar terminal groups. On the other hand, the excess component could cause the destruction of polymer chains (notably those of the greatest length) which would also contribute to a reduction in the molecular weight.

During polyesterification at the boundary between two phases the destructive reaction is clearly not possible. The reduced molecular weight of the polymer must, therefore, arise from the prevention of chain growth. This clearly also explains why an excess of the acid component has less effect (in reducing the molecular weight of the polyester) in interfacial polyesterification than it has during polycondensation in the melt or in homogeneous solutions at high temperature.

As has been indicated above, the growth of the molecular weight of the polyester may be stopped not only by hydrolysis reactions which act as chain breakers but also by the conversion of the phenoxide group to a hydroxy group by hydrogen chloride [reactions (3) and (4) above] produced by the hydrolysis of the acid chloride. Korshak and coworkers carried out a series of reactions in which the amount of sodium hydroxide used was sufficient to neutralise completely the isophthaloyl chloride (*i.e.* in the molar ratio 4 : 1) in order to eliminate the influence of hydrogen chloride during a study of the effect of the reactant ratio on the polycondensation process. The results of these experiments (Fig. 9) indicated that the polymer of maximum reduced viscosity was obtained when the molar ratio bisphenol A : : isophthaloyl chloride was 1.7 rather than equimolar (*cf.* Figs. 8 and 9). This shift of the maximum to the region where a relatively high excess of the phenol was used must be associated with an increase in the role played by the acid chloride hydrolysis reactions because large quantities of free alkali are present in the reaction mixture.

The authors conclude that the results obtained in interfacial polyesterification depend on the quantity of sodium hydroxide in the aqueous phase. The alkali is necessary both to produce the phenoxide and to combine with the hydrogen chloride liberated during the polyesterification process. In view of this, Korshak *et al.*[37] carried out a series of experiments in which the bisphenol A : isophthaloyl chloride ratio and the other experimental conditions were kept constant and the quantity of alkali in the aqueous phase was varied. The results (Fig. 10) show that the polymer of greatest reduced viscosity was obtained when the alkali used was only slightly in excess (0.2 – 0.3 mole) of that required for the conversion of the dihydric phenol to the phenoxide. Higher concentrations of sodium hydroxide clearly led to an increase in the hydrolysis of both isophthaloyl chloride and the terminal acyl chloride groups of the growing chains. This prevented chain growth and caused a fall in the polymer yield and a marked lowering of its reduced viscosity.

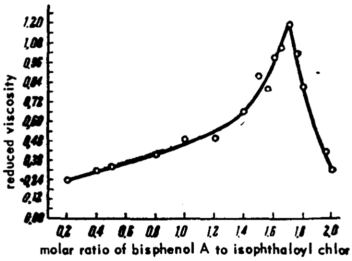


Fig. 9. Variation of the reduced viscosity of polyester in cresol with the reactant ratio.

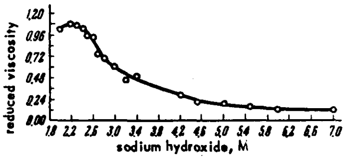


Fig. 10. Variation of the reduced viscosity of polyester in cresol, in relation to sodium hydroxide concentration.

Eareckson[54] found that the base used to combine with the hydrogen chloride also has an effect on interfacial polyesterification. The best results were obtained with sodium hydroxide. Potassium hydroxide gave poorer results and the yield was greatly reduced when pyridine was employed. It is obvious from the above results that the reaction cannot be accomplished successfully merely by ensuring the presence of a substance in the reaction mixture which can combine with acid. The presence of phenoxide ions in the system appears to be a necessary condition for the production of high-molecular polyarylates[54].

The structure of the reactants also has a marked effect on the reaction. Thus, dihydric phenols which contain electronegative substituents (*e.g.* sulphonic acid and carbonyl groups) do not enter into polycondensation reactions as readily as unsubstituted dihydric phenols or those with electropositive substituents[54].

Electronegative groups, which increase the acidity of the phenol, lower the reactivity of phenoxide ion which, according to Morgan[52,53] and Eareckson[54], is the active species in interfacial polyesterification. Eareckson[54] explained the much lower molecular weights of the polyarylates obtained from 4,4′-dihydroxybenzophenone, 2,4-dihydroxybenzophenone, 4,4′-dihydroxydiphenylsulphone and 2,4-dihydroxybenzaldehyde (Table 6) as due to the electronegative substituents in the dihydric phenol.

The addition of monofunctional substances to the reactants in interfacial polyesterification was also studied[37]. Substances of a chemical nature similar to that of the reactants (benzoyl chloride and phenol) were used as additives. The addition of either benzoyl chloride or phenol caused a significant lowering of the reduced viscosity (*i.e.* the molecular weight) of the polyarylate (Figs. 11 and 12). Small quantities of either benzoyl chloride or phenol are the most effective.

The additive reacts with either the reactant or the growing polymer chain and blocks their reactive end groups and consequently their ability to enter into further reactions.

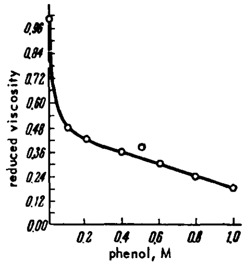


Fig. 11. Variation of the reduced viscosity of polyester in cresol, in relation to phenol concentration.

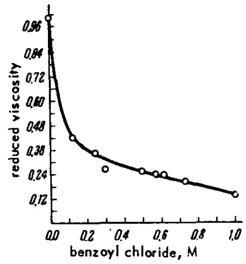


Fig. 12. Variation of the reduced viscosity of polyester in cresol, in relation to benzoyl chloride concentration.

TABLE 6. Effect of dihydric phenol structure on the reduced (inherent) viscosity of the polyarylate

Dihydric phenol	Acid chloride	η_{inh}
4.4′-Dihydroxybenzophenone	sebacoyl	0.01
2.4-Dihydroxybenzophenone	isophthaloyl : : terephthaloyl (50 : 50)	0.38
4.4′-Dihydroxydiphenylpropane	ditto	1.38
4.4′-Dihydroxydiphenyl sulphone	isophthaloyl	0.41
4.4′-Dihydroxydiphenylpropane	»	1.86
4.4′-Dihydroxydiphenyl sulphone	isophthaloyl : : terephthaloyl (50 : 50)	0.54
2.4-Dihydroxydiphenylbenzaldehyde	ditto	0.20
Resorcinol	»	1.01

Note. η_{inh} was determined at 0.5% concentration in *sym*-tetrachloroethane–phenol (40/60 w/w) at 30°, $\eta_{inh} = ln\,\eta_{rel}/c$.

These reactions may be described by the following equations:

$$NaOC_6H_4C(CH_3)_2C_6H_4ONa + C_6H_5COCl \rightarrow \rightarrow C_6H_5COOC_6H_4C(CH_3)_2C_6H_4OCOC_6H_5 + NaCl; \quad (1)$$

$$\ldots - COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4ONa + C_6H_5COCl \rightarrow \rightarrow \ldots - COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4OCOC_6H_5 + NaCl; \quad (2)$$

$$ClCOC_6H_4COCl + C_6H_5ONa \rightarrow \rightarrow C_6H_5OCOC_6H_5COOC_6H_5 + NaCl; \quad (3)$$

$$\ldots - COC_6H_4C(CH_3)_2C_6H_4OCOC_6H_4COCl + C_6H_5ONa \rightarrow \rightarrow \ldots - OC_6H_4C(CH_3)_2C_6H_4OCOC_6H_4COOC_6H_5 + NaCl. \quad (4)$$

A number of compounds have been suggested as catalysts for polyesterification at phase boundaries, *e.g.* quaternary ammonium bases[3,20,21,46,47,53], sulphonium compounds[47], tertiary amines and their salts[20,53].

(b) Preparation of polycarbonates by the polycondensation of phosgene and dihydric phenols in pyridine or in the presence of pyridine. The polycondensation of phosgene with dihydric phenols, *e.g.* bisphenol A, proceeds according to the equation

$$x\mathrm{HOC_6H_4C(CH_3)_2C_6H_4OH} + x\mathrm{COCl_2} \rightarrow$$
$$\rightarrow [-\mathrm{OC_6H_4C(CH_3)_2C_6H_4OCO}-]_x + 2x\mathrm{HCl}.$$

The reaction is usually carried out by passing phosgene into a solution of the dihydric phenol in pyridine. Pyridine is used (a) to combine with the liberated hydrochloric acid, (b) as a solvent, and (c) because it apparently catalyses the reaction[21]. When the volume of phosgene admitted reaches the stoichiometric quantity, the reaction mixture suddenly becomes very viscous. The polymer is precipitated from the reaction mixture with methanol, isopropanol, or other similar substances.

Phosgene may also be polycondensed with a dihydric phenol in benzene, toluene, chlorobenzene, dioxan, methylene chloride, trichloroethylene, and other solvents by the addition of a stoichiometric or larger quantity of pyridine (based on the available hydrogen chloride) to these solvents.

The molecular weight of polycarbonates prepared by this method may be varied by changing the reaction temperature, the concentration of dihydric phenol, the rate of addition of phosgene, etc.[21] This method for the production of polycarbonates is economically less attractive than other syntheses because of the consumption of pyridine.

3. Preparation of Polyarylates from Diketenes and Dihydric Phenols

In 1959 Korshak, Rogozhin, and Volkov[55] suggested a new method for the synthesis of polyesters based on the known reaction of glycols and dihydric phenols with carbon suboxide. The authors obtained polyarylates of malonic acid by the reaction of carbon suboxide with quinol and bisphenol A:

$$x\mathrm{HOArOH} + x\mathrm{O{=}C{=}C{=}C{=}O} \rightarrow$$
$$\rightarrow x\mathrm{O{=}C{=}CH{-}COOArOH} \rightarrow [-\mathrm{OCCH_2COOArO}-]_x.$$

The polymerisations were carried out in chloroform in sealed tubes. The reaction temperature was increased from -50° to +10° over a period of 24 h, and continued for a period of 5–10 days at room temperature.

Analogous reactions might be anticipated with other bis-ketenes.

III. PROPERTIES OF POLYARYLATES

1. Chemical Properties

The chemical properties of polyarylates have been described in a number of papers [3,17,19-21,26,40,47,54,69]. Schnell[3,20], Rémond[19], Hechelhammer and Peilstöcker[26], and others have reported data concerning the chemical properties of polycarbonates. Stability to water, aqueous solutions of neutral salts, concentrated mineral acids (including nitric and hydrofluoric acids), aqueous organic acids, oxidising agents (even in acid media), solutions of weak alkalis (such as sodium carbonate and bicarbonate), higher alcohols, aliphatic and alicyclic hydrocarbons, oils, fats, grape, orange, and tomato juices, and tincture of iodine is a characteristic property of polycarbonates[3,17,19,20,21,26].

Polycarbonates possess limited stability to the action of strong alkalis, such as sodium and potassium hydroxides, which slowly corrode the sample surface, while its molecular weight and other physical properties remain substantially unaltered[3]. The thickness of a bisphenol A polycarbonate film was reduced from 110μ by 24, 29, and 46μ after treatment with 5, 10, and 20% solutions of sodium hydroxide respectively for a period of 13 weeks[3]. The polycarbonate of 2,2-di(4-hydroxy-3,5-dichlorophenyl)propane was significantly more resistant to hydrolysis. The properties of this polymer were unaltered after contact with a 20% solution of sodium hydroxide for 13 weeks at room temperature. Polycarbonates are not stable to ammonia and amines[17,19,26].

Schnell[3] established that the colour and mechanical properties of bisphenol A polycarbonate films were unaltered after 72 h irradiation with ultra-violet light. The properties of a similar polycarbonate film were also found to be essentially unchanged after storage in air at 150° for 26 weeks, or 8 weeks at 170°. Data concerning the stability of polycarbonate films to atmospheric oxygen at various temperatures are presented in Table 7.[20]

The physical properties of the polyarylates from bisphenol A and terephthalic acid were described in a paper by Korshak *et al.*[40] They showed that these polyarylates were stable to ethanol, chloroform, dioxan, carbon tetrachloride, methylene chloride, dimethylformamide, ethyl methyl ketone, benzene, chlorobenzene, *p*-xylene, tetrachloroethane, tetrachloroethylene, tetrahydrofuran, and n-heptane. Partial solubility was achieved in some of the above solvents after heating for 3 h at the boiling point (if this was less than 100°) or at 100°; this treatment did not significantly lower the reduced viscosity of the polymers in cresol.

The stability of polyarylates to the action of *m*-cresol at different temperatures was also studied (Figs. 13–15). From Figs. 13 and 14 it can be seen that the viscosity of the solutions of polyarylates, produced from bisphenol A and isophthaloyl chloride by either interfacial polyesterification (Fig. 14) or by the high-temperature polyesterification in homogeneous solution, decreased with increasing temperatures and heating periods. The polyarylate prepared by the interfacial technique was, however, more prone to

TABLE 7. Stability of polycarbonate films to the action of atmospheric oxygen[20].

Bisphenol	Thickness of film, μ	Temp., °C	Duration of treatment, weeks	Tensile strength, kg cm^{-2}	Elongation at rupture, %
Bisphenol A	45	140	0	663	54
			4	664	8
			8	749	7
			12	684	8
	50	150	0	868	105
			14	695	15
			26	705	12
	80	160	0	774	148
			8	647	58
			12	635	14
1,1-di-(4-Hydroxyphenyl)-cyclohexane	65	170	0	814	56
			4	769	8
2,2-di(4-Hydroxy-3,5-dichlorophenyl)propane	60	190	0	1023	7
			4	1006	10
			8	1007	9

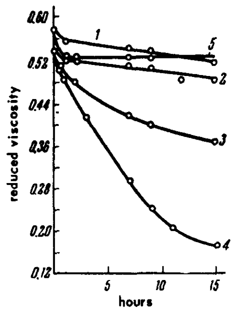


Fig. 13. Decomposition of the bisphenol A-isophthaloyl chloride polyarylate, prepared by homogeneous polycondensation in cresol:
1) 105°; 2) 140°; 3) 164°; 4) 183°, in an atmosphere of nitrogen;
5) 105° in air.

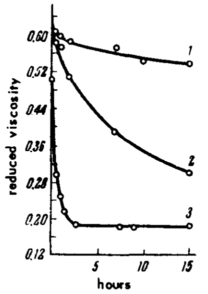


Fig. 14. Decomposition of the bisphenol A-isophthaloyl chloride polyarylate, prepared by interfacial polycondensation of *m*-cresol in an atmosphere of nitrogen:
1) 85°; 2) 105°; 3) 183°.

depolymerisation than that made by homogeneous (equilibrium) polycondensation. Thus, the reduced viscosity of the polyarylate made by the latter method was reduced from 0.56 to 0.48 after heating for 15 h at 105° in *m*-cresol, whereas the reduced viscosity of the polyarylate made by the heterogeneous procedure was approximately halved (0.64 to 0.30) by a similar treatment. Evidently this is a reflection of the different molecular-weight distribution in the polyarylates made by the equilibrium and non-equilibrium polycondensations. There is every reason to believe that there is a wider distribution of molecular weights in polyarylates made by the heterogeneous method. If this is so, the polymer must contain some molecules of very high molecular weight which are most prone to decomposition.

The stability of the polyarylate to cresol also depends on its chemical structure. A comparison of Figs. 15 and 13 shows that the bisphenol A – terephthalic acid polyarylate is more stable to *m*-cresol than the corresponding isophthalic polyester. Thus, the terephthalic acid polyarylate is virtually unaffected by heating with *m*-cresol at 105°; after 15 h at 183° the reduced viscosity in *m*-cresol decreased by a factor of approximately 2.5 (from 0.36 to 0.14), whereas that of the isophthalic acid polyarylate was reduced threefold (0.56 to 0.18) under similar conditions.

The authors concluded from the above data that, under the influence of a large excess of *m*-cresol (0.5% solutions) at high temperatures, polyarylates undergo decomposition, by an alcoholysis mechanism:

$$\ldots-COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O-\ldots + CH_3C_6H_4OH \rightarrow$$
$$\rightarrow \ldots-COC_6H_4COOC_6H_4CH_3 + HOC_6H_4C(CH_3)_2C_6H_4O-\ldots$$

The chemical decomposition of polyarylates by the action of dicarboxylic acid chlorides, dicarboxylic acids, and dihydric phenols has also been investigated (Fig. 16)[40].

Conix[47] investigated the stability of the polyarylates of structures A and B,

$$[-COC_6H_4OC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O-]_x \text{ polyarylate A},$$
$$[-COCH=CHCOOC_6H_4C(CH_3)_2C_6H_4O-]_x \text{ polyarylate B},$$

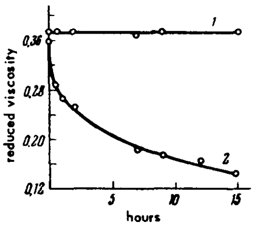


Fig. 15. Decomposition of the bisphenol A-terephthaloyl chloride polyarylate, prepared by homogeneous polycondensation in *m*-cresol in an atmosphere of nitrogen:
1) 105°; 2) 183°.

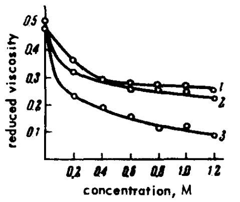


Fig. 16. Decomposition of polyarylates by bisphenol A:
1) polyarylate, prepared by homogeneous polycondensation of bisphenol A-terephthaloyl chloride; 2) polyarylate, prepared by homogeneous polycondensation of bisphenol A-isophthaloyl chloride; 3) polyarylate, prepared by interfacial polycondensation of bisphenol A-isophthaloyl chloride.

TABLE 8. Decomposition of polyarylates in boiling ethanol[47].

Duration of treatment, h	Reduced viscosity of the polyarylate		
	polyarylate A	polyarylate B	
0	0.82	1.3	1.0
3	0.72	0.80	0.75
66	0.66	insoluble	0.45

TABLE 9. Effect of various substances on polyarylate films[47].

Reagent	Temp., °C	Duration of treatment, h	Loss in weight (%) and property	
			polyarylate A	polyarylate B
0.1 *N* NaOH	Boiling	1	0.8 (stable, transparent)	decomposed
	»	19	3.5 (ditto)	
	»	90	13.5 (stable, opaque)	
	25	75	unchanged	19 (brittle, opaque)
	25	360	»	
$NaHCO_3$ (10%)	Boiling	24	»	8.4 (stable, opaque)
	»	164	2.3 (stable, transparent)	
NH_4OH (3.5%)	25	70	unchanged	decomposed
	25	164	»	
NH_4OH (25%)	25	60	decomposed	
0.1 *N* H_2SO_4	Boiling	24	unchanged	unchanged

to the action of boiling alcohol and solutions of acids and alkalis. His results (Tables 8 and 9) show that prolonged boiling of the polyarylates in ethanol caused some decrease in the reduced viscosity, the lowest value being obtained for the polyarylate of the aromatic dicarboxylic acid. The data in Table 9 show that films of both polyarylates are stable to the action of aqueous acids and alkalis at room temperature and even at the boiling point. They were, however, decomposed by concentrated ammonia solutions.

Eareckson[54] found that polyarylates are virtually non-inflammable. The mixed polyarylate of 4-chlororesorcinol with isophthalic and terephthalic acids was non-combustible even when the chlorine content was 12.5%. The mixed polyarylate of bisphenol A with isophthalic and terephthalic acids is particularly resistant to the hydrolytic attack of acids and alkalis. Polyarylates are stable to ultra-violet light, apart from acquiring a yellow colour. Korshak, Gribova, and Andreeva[69] described the effect of X-rays on phosphorus-containing polyarylates. They showed that the polyarylates of phosphinic acid were amenable to radiation vulcanisation. Thus, the phenoxyphosphinic acid – quinol polyester after only 30 h irradiation had a cross-linked structure, whereas 50 h irradiation was necessary to vulcanise the phenylphosphinic – quinol polyarylate.

2. Physical Properties

The physical properties of polyarylates, like those of other polymers, are intimately connected with their chemical structure, molecular weight, and polydispersity.

(a) Thermal properties. The softening temperatures of polyarylates are determined, to a considerable extent, by their chemical structure. Most polyarylates do not possess a clearly defined softening temperature; they melt over a range of temperatures. For the polycarbonates this temperature range is usually 10°–20°[3,19]. A very high melt viscosity is a characteristic of many polyarylates[3,19,20,31,46].

The softening temperatures of a number of polyarylates which are described in the literature are shown in Table 10. These data are not strictly comparable since they were obtained by different workers who used different methods for the synthesis and studies of the polymers. Nevertheless, they give an indication of the relationship between the softening temperature and the structure of the polyarylates.

Comparison of the softening temperatures of the polycarbonates of a number of dihydric phenols (Table 10, Nos. 1 – 26)[3] shows that the polycarbonates of di(4-hydroxyphenyl)methane and di(4-hydroxyphenyl)ethane, *i.e.* polycarbonates of dihydric phenols in which the aromatic rings are connected by unbranched methylene chains, have the highest softening temperatures.

The softening temperature is reduced by substitution at one of the central hydrogen atoms of an alkyl group. If the aliphatic substituent in the bisphenol is replaced by an aromatic or alicyclic group, then the softening temperature is increased.

Korshak and Vinogradova[31,35] studied the influence of reactant structure on the softening temperatures of the polyarylates of terephthalic, isophthalic, sebacic, and adipic acids with dihydric phenols of various structures (Table 10, Nos. 31 – 34, 40 – 42, 45 – 48, 52 – 59, 63 – 65). They found that the softening temperatures of the polyesters were strongly dependent on the structure of the polymer chain. The polyarylate of quinol and terephthalic acid had the highest softening point. It did not melt in a capillary below 500° but merely became cream-coloured at high temperatures. At temperatures below 360° this polyarylate does not undergo deformation and, therefore, its glass temperature and softening temperature must be above 360°. Poly(quinol isophthalate) has a much lower softening temperature, although it is still relatively high; deformation begins at about 350°.

The softening temperature of a polyarylate is also dependent on the orientation of the functional groups in the dihydric phenol. The polyesters from resorcinol and terephthalic and isophthalic acids, for example, have considerably lower softening temperatures than the corresponding quinol polyesters. Thus, similar regularities are observed for the polyarylates, whose chains comprise aromatic rings and ester groups only, as those found for the polyesters derived from aromatic dicarboxylic acids and aliphatic glycols[75,76]. The polyesters of acids and dihydric phenols, in which the functional groups are in the *para*-positions, have much higher softening temperatures than those from *meta*-substituted reactants. The authors' studies[31] of the polyarylates of terephthalic and isophthalic acids with bisphenol A, di(*p*-hydroxyphenyldiphenyl)-α,α'-*p*-xylene, and dihydroxynaphthylamines confirmed this rule.

It may be concluded[35] from a comparison of the softening temperatures of the adipic and sebacic acid polyarylates with the corresponding polyesters of terephthalic acid that the substitution of an aliphatic residue for the terephthalic acid residue in the polymer chain significantly

TABLE 10. Softening temperatures of polyarylates of various structures.

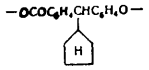
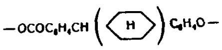
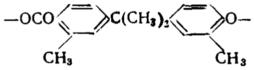
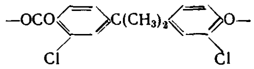
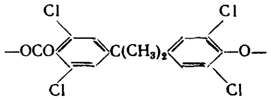
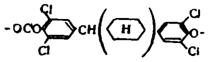
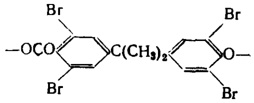
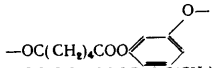
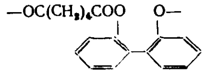
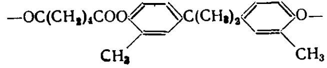
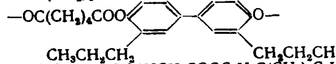
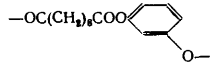
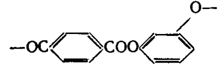
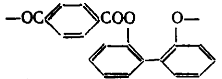
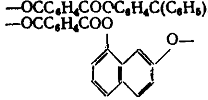
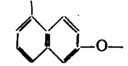
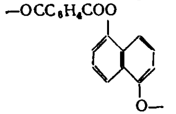
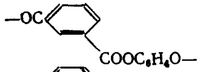
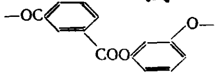
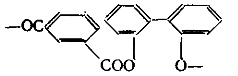
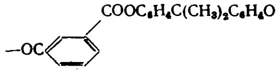
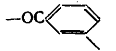
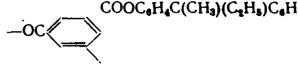
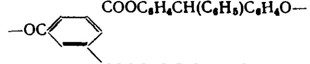
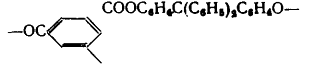
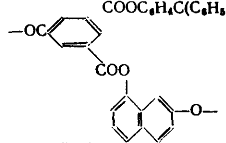
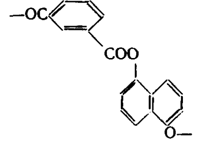
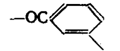
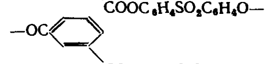
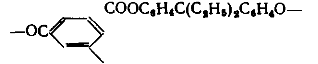
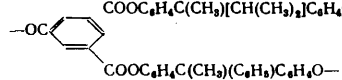
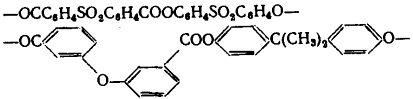
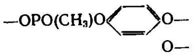
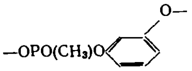
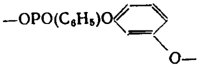
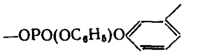
No.	Repeating unit	Softening temp., °C	Reference
1	—$OCOC_6H_4CH_2C_6H_4O$—	>300	3,19,20
2	—$OCOC_6H_4CH(CH_3)C_6H_4O$—	185	3,19,20
3	—$OCOC_6H_4CH(C_3H_7)C_6H_4O$—	150	3,19,20
4	—$OCOC_6H_4CH[CH(CH_3)_2]C_6H_4O$—	170	3,19,20
5		240	3,19,20
6		250	3,19,20
7	—$OCOC_6H_4CH(C_6H_5)C_6H_4O$—	200	3,19
8	—$OCOC_6H_4C(CH_3)_2C_6H_4O$—	220	3,19,20
9		150	3,20
10	—$OCOC_6H_4C(CH_3)(C_2H_5)C_6H_4O$—	205	3,19,20
11	—$OCOC_6H_4C(CH_3)(C_3H_7)C_6H_4O$—	200	3,19,20
12	—$OCOC_6H_4C(CH_3)[CH(CH_3)_2]C_6H_4O$—	200	3,19
13	—$OCOC_6H_4(CH_3)(C_4H_9)C_6H_4O$—	180	3,19,20
14	—$OCOC_6H_4C(CH_3)(C_7H_{15})C_6H_4O$—	170	3,19,20
15	—$OCOC_6H_4C(CH_3)(C_6H_5)C_6H_4O$—	210	3,19
16	—$OCOC_6H_4(C_3H_7)_2C_6H_4O$—	190	3,19,20
17	—$OCOC_6H_4CH_2CH_2C_6H_4O$—	290	3,19,20
18	—$OCOC_6H_4C(C_6H_5)_2C_6H_4O$—	210	20
19	—$OCOC_6H_4OC_6H_4O$—	230	20
20	—$OCOC_6H_4SC_6H_4O$—	220	20
21	—$OCOC_6H_4SOC_6H_4O$—	230	20
22	—$OCOC_6H_4SO_2C_6H_4O$—	200	20
23		190	20
24		250	20
25		260	20
26		240	20
27	—$OCCOOC_6H_4C(CH_3)_2C_6H_4O$—	155	54
28	—$OCCH_2COOC_6H_4O$—	230	55
29	—$OCCH_2COOC_6H_4C(CH_3)_2C_6H_4O$—	85	55
30	—$OC(CH_2)_2COOC_6H_4O$—	230, 270	54,48
31	—$OC(CH_2)_4COOC_6H_4O$—	225, 235, 190	35,48,49,54
32		50	35
33	—$OC(CH_2)_4COOC_6H_4C(CH_3)_2C_6H_4O$—	80	35,48,54
34		55	35
35		—	48
36	—$OC(CH_2)_4COOC_6H_4CH_2C_6H_4O$—	140	48
37	—$OC(CH_2)_4COOC_6H_4C_6H_4O$—	300	48
38		—	48
39	—$OC(CH_2)_2C(CH_3)HCH_2COOC_6H_4C(CH_3)_2C_6H_4O$—	—	48
40	—$OC(CH_2)_8COOC_6H_4O$—	172.150	35,54
41		38	35
42	—$OC(CH_2)_8COOC_6H_4C(CH_3)_2C_6H_4O$—	60	35,48,54
43	—$OC(CH_2)_8COOC_6H_4C(CH_3)(C_2H_5)C_6H_4O$—	—	48
44	—$OC(CH_2)_8COOC_6H_4COC_6H_4O$—	50	54
45	—$OCC_6H_4COOC_6H_4O$—	—	31,54
46		270	31,54
47	—$OCC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O$—	250, 350	31,47,48,54
48		172	31
49	—$OCC_6H_4COOC_6H_4C(C_2H_5)_2C_6H_4O$—	150	47
50	—$OCC_6H_4COOC_6H_4CH(C_6H_5)C_6H_4O$—	200	47
51	—$OCC_6H_4COOC_6H_4CH(CCl_3)C_6H_4O$—	250	47
52	—$OCC_6H_4COCC_6H_4C(C_6H_5)_2C_6H_4C(C_6H_5)_2C_6H_4O$—	220	31
53		230	31
54		—	31
55		—	31
56		~320	
57		230, 245	31,64
58		158	31
59		275, 243, 280	31,46,54
60		130, 120	46,47
61		164, 160	46,47
62		190	46,47
63		157	31
64		188	31
65		—	31
66		250	54
67		120	47
68		135	47
69		175	47
70		130	47
71	—$OCC_6H_4OC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O$—	220, 200	46,47
72	—$OCC_6H_4OC_6H_4COOC_6H_4CH(CH_3)C_6H_4O$—	112	47
73	—$OCC_6H_4OC_6H_4COOC_6H_4(C_2H_5)_2C_6H_4O$—	130	47
74	—$OCC_6H_4OC_6H_4COOC_6H_4C(CH_3)(C_2H_5)C_6H_4O$—	160	47

TABLE 10 (contd.)

No.	Repeating unit	Softening temp., °C	Reference
75	$-OCC_6H_4OC_6H_4COOC_6H_4CH(C_6H_5)C_6H_4O-$	175	47
76	$-OCC_6H_4OC_6H_4COOC_6H_4C(CH_3)(C_6H_5)C_6H_4O-$	160	47
77	$-OCC_6H_4COC_6H_4COOC_6H_4C(CH_3)_2C_6H_4O-$	160	47
78	$-OCC_6H_4C(CH_3)_2C_6H_4COOC_6H_4COC_6H_4O-$	122	47
79	$-OCC_6H_4CH_2C_6H_4COOC_6H_4C(CH_3)_2C_6H_4O-$	170	47
80	$-OCC_6H_4C(CH_3)_2C_6H_4COOC_6H_4CH_2C_6H_4O-$	130	47
81	$-OCC_6H_4CH_2C_6H_4COOC_6H_4C(C_2H_5)_2C_6H_4O-$	170	47
82	$-OCC_6H_4C(CH_3)_2C_6H_4COOC_6H_4C(CH_3)_2C_6H_4O-$	225	46,47
83	$-OCC_6H_4SO_2C_6H_4COOC_6H_4C(CH_3)_2C_6H_4O-$	190,230	47,54
84	$-OCC_6H_4CCl_2C_6H_4COOC_6H_4C(CH_3)_2C_6H_4O-$]	220	47
85	$-OCC_6H_4SO_2C_6H_4COOC_6H_4SO_2C_6H_4O-$	—	54
86		85	46
87	$-OCC_6H_4C(CH_3)_2C_6H_4COOC_6H_4CH(CH_3)C_6H_4O-$	190	46
88	$-OCC_6H_4C(CH_3)_2C_6H_4COOC_6H_4CH(C_6H_{11})C_6H_4O-$	170	46
89	$-OCC_6H_4C(CH_3)_2C_6H_4COOC_6H_4CH(C_6H_5)C_6H_4O-$	218	46
90	$-OCC_6H_4CH(CH_3)C_6H_4COOC_6H_4C(CH_3)_2C_6H_4O-$	225	46
91	$-OCCH=CHCOOC_6H_4C(CH_3)_2C_6H_4O-$	150,240	46,54
92	$-OCCH=CHCOOC_6H_4C(CH_3)(C_2H_5)C_6H_4O-$	130	46
93	$-OCCH=CHCOOC_6H_4CH(C_6H_{11})C_6H_4O-$	180	46
94		63	41,42
95		36	42
96	$-OPO(CH_3)OC_6H_4C_6H_4O-$	110	42
97	$-OPO(CH_3)OC_6H_4C(CH_3)_2C_6H_4O-$	88	42
98	$-OPO(C_6H_5)OC_6H_4O-$	83	41,42
99		55	42
100	$-OPO(C_6H_5)OC_6H_4C_6H_4O-$	120	42
101	$-OPO(C_6H_5)OC_6H_4C(CH_3)_2C_6H_4O-$	55	42
102	$-OPO(OC_6H_5)OC_6H_4O-$	23	41,42
103		17	42
104	$-OPO(OC_6H_5)OC_6H_4C_6H_4O-$	55	42
105	$-OPO(OC_6H_5)OC_6H_4C(CH_3)_2C_6H_4O-$	12	42
106	$-OPO(OC_6H_4NO_2)OC_6H_4O-$	36	41
107	$-OPO(OC_6H_4OCH_3)OC_6H_4O-$	35	41

reduces the softening point. Thus, the softening temperatures of the polyarylates obtained from quinol and adipic and sebacic acids were 225° and 172° respectively, while poly(quinol terephthalate) does not melt below 500°. The softening temperature of poly(resorcinol terephthalate) is 270°, whereas that of the corresponding polyadipate is only 50°. The polyarylates of adipic acid have higher softening points than the corresponding derivatives of sebacic acid. This is apparently connected with the greater flexibility of the polymer chains in the latter case owing to the reduced proportion of aromatic nuclei[35].

The synthesis and properties of the polyarylates of various phosphinic acids (Table 10, Nos. 94–107) have been described[41,42]. The softening temperature of a polyester is markedly reduced by the replacement of the carboxyl CO group by a PO(R) group. The polycarbonate of bisphenol A, for example, has a softening temperature of 220°, whereas the corresponding polyarylates with methylphosphinic, phenylphosphinic, and phenoxyphosphinic acids begin to soften at only 88°, 55°, and 12° respectively.

It has been shown[33-35] that the softening temperatures in several series of mixed polyarylates depend on the structure and proportions of the starting materials from which they were prepared. The properties of the mixed polyarylates synthesised are presented in Tables 11–14. The results show that the variation of softening temperature with composition in the aromatic dicarboxylic acid polyarylates passes through a minimum. Thus, the minimum softening temperature in the resorcinol–bisphenol A–terephthalic acid polyarylate series was observed when the resorcinol : bisphenol A ratio in the mixed polyester was 0.7 : 0.3. Clearly, with this ratio of reactants the polymer chain must be least closely packed. An increase in the concentration of either phenol, *i.e.* more than 70% resorcinol or more than 30% bisphenol A, leads to the production of a mixed polyarylate with a higher softening temperature.

The softening temperatures of polyarylates, which contain an aliphatic carboxylic acid, invariably increase with the proportion of aromatic acid in the original mixture (Tables 13 and 14). Thus, as the proportion of terephthalic acid increases, the softening temperatures of the polyarylates in the bisphenol A–adipic acid–terephthalic acid system rise from 63° to > 350°, etc. The replacement of adipic by sebacic acid in the mixed polyarylate is accompanied by a reduction in the softening temperature[34].

Schnell's results[3,20] concerning the vitrification temperature of some polycarbonates, determined by refractometry or dilatometry, are presented in Table 15, together with density and refractive index data. The vitrification temperatures of most polycarbonates lie in the 130°–170° range.

Other thermal properties of bisphenol A polycarbonate have also been studied[21]; the results are set out in Table 16.

(b) **Crystallinity.** The crystallinity of polyarylates is very dependent on the structure. Schnell[3] noted that the polycarbonates of di(4-hydroxyphenyl)methane and 1,2-di(4-hydroxyphenyl)ethane were very easily crystallised. The polycarbonates of bisphenol A had a somewhat lower tendency to crystallise than the above two polyesters.

TABLE 11. Mixed polyesters from terephthaloyl chloride, resorcinol, and bisphenol A.

Molar ratio of components	Reduced viscosity in cresol	Softening temperature, °C		σ, kg cm^{-2}	ϵ, %	Dielectric constant	Dielectric loss factor at 20°, f=400 c/s	Crystallinity, %
		in a capillary	from thermomechanical curve					
1 : 0 : 1	**insoluble**	~350	>350	610	8	3.5	0.002	~10
1 : 0.2 : 0.8	0.54	310–317	310	780	20	3.6	0.0045	**amorphous**
1 : 0.4 : 0.6	0.69	255–280	294	720	30	3.7	0.0045	»
1 : 0.6 : 0.4	0.70	240–270	254	720	60	3.8	0.004	**slight indications of crystallinity**
1 : 0.7 : 0.3	0.46	180–205	188	690	14	—	—	**amorphous**
1 : 0.8 : 0.2	0.36	205–230	—	770	11	8.7	0.005	»
1 : 0.9 : 0.1	**insoluble**	245–255	233	—	—	—	—	~50
1 : 1 : 0	**insoluble**	270–285	275	—	—	3.6	0.006	~70

Note. The polymers were white powders. Solubilities of the samples: in ethanol 0–0.2 g litre^{-1}; in benzene 0–0.9 g litre^{-1}; in dichlorethane 0–1.4 g litre^{-1}; σ – tensile strength; ϵ – relative elongation at break.

TABLE 12. Mixed polyesters produced from quinol, bisphenol A, and terephthaloyl and isophthaloyl chlorides.

Molar ratio of components	Softening temperature, °C		Tensile strength, kg cm^{-2}	Relative elongation at break, %	Physical state
	in a capillary	from thermo-mechanical curve			
0.2 : 0.8 : 0.5 : 0.5	310—320	274	640	36	the sample has a completely random structure with no indication of polymer ordering
0.4 : 0.6 : 0.5 : 0.5	300—310	226	690	12	amorphous
0.5 : 0.5 : 0.5 : 0.5	300—310	265	630	10	ditto
0.6 : 0.4 : 0.5 : 0.5	310—320	—	670	11	amorphous; strong indications of an ordered structure. Ordered chains have a gas-crystal structure
0.7 : 0.3 : 0.5 : 0.5	320—340	325	610	6	ordered structure. The chains have a highly ordered arrangement
0.8 : 0.2 : 0.5 : 0.5	>350	—	—	—	ditto

TABLE 13. Mixed polyesters prepared from bisphenol A and the chlorides of adipic and terephthalic acids.

Molar ratio of components	Reduced viscosity in cresol	Softening temp., °C (from thermo-mechanical curve)	σ, kg cm^{-2}	ϵ, % **	Physical state	Remarks
1 : 1 : 0	0.44	63	—	—	amorphous with little order within chains	solid. Solubility (g litre^{-1}): in alcohol 0.7, in benzene 9.9
1 : 0.8 : 0.2	0.42	88	—	—	ditto	solid
1 : 0.6 : 0.4	0.56	185	600	25	amorphous with marked order within chains	white powder
1 : 0.5 : 0.5	0.70	242	580	72	ditto	white powder solubility (g litre^{-1}) in alcohol 0.3, in benzene 9.8, in dichloroethane 0.6
1 : 0.4 : 0.6	0.58	248	700	15	»	white powder
1 : 0.2 : 0.8	0.63	350	720	22	mainly amorphous with little order within chains	white powder; solubility (g litre^{-1}) in alcohol 0, in benzene 0.6, in dichloroethane – 0.3
1 : 0 : 1	insoluble	350	610	8	~10%	white powder

* σ — tensile strength.

** ϵ — relative eleongation at break.

TABLE 14. Mixed polyesters obtained from bisphenol A and the chlorides of sebacic and terephthalic acids.

Molar ratio of components	Reduced viscosity in cresol	Softening temp., °C (from thermo-mechanical curve)	Physical state	Remarks
1 : 1 : 0	0.58	26		an almost solid translucent substance. Tensile strength and relative elongation at break of films –450 kg cm^{-2} and 530%.
1 : 0.8 : 0.2	0.38	59	amorphous with little order within chains	transparent solid. Solubility (g litre^{-1}): in alcohol 0.4, in benzene 5.8, in dichloroethane 7.8
1 : 0.6 : 0.4	0.36	156	amorphous with considerable order within chains	white powder
1 : 0.5 : 0.5	0.38	171	ditto	white powder. Solubility (g litre^{-1}): in alcohol 0.2. in benzene 10.3, in dichloroethane 0.8
1 : 0.4 : 0.6	0.46	235	»	white powder
1 : 0.3 : 0.7	0.50	275	evidence of crystallinity	white powder, Solubility (g litre^{-1}): in alcohol 0, in benzene 3.7, in dichloroethane 0.3
1 : 0.2 : 0.8	0,42	305	ditto	white powder
1 : 0 : 1	insoluble	>350	~10%	white powder

TABLE 15. Vitrification temperature, density, and refractive index of some polycarbonates.

Bisphenol	Vitrification temp., °C	Density, g cm^{-2}	Refractive index
R_1R_2*-1,1-Ethane	130	1.22	1.5937
R_1R_2-1,1-Butane	123	1,17	1.5792
R_1R_2-1,1-Isobutane	149	1.18	1.5702
R_1R_2-2,2-Propane	149	1.20	1.5850
R_1R_2-2,2-Butane	134	1.18	1,5827
R_1R_2-2,2-Pentane	137	1.13	1.5745
R_1R_2-4,4-Heptane	148	1,16	1.5602
R_1-Phenylmethylmethane	176	1.21	1.6130
R_1R_2-Diphenylmethane	121	1.27	1.6539
R_1R_2-1,1-Cyclopentane	167	1.21	1.5993
R_1R_2-1,1-Cyclohexane	175	1.20	1.5900
2,2-di(4-hydroxy-3-chlorophenyl) propane	147	1.32	1.5900
2,2-di(4-hydroxy-3,5-dichlorophenyl) propane	180	1.42	1.6056
1,1-di(4-hydroxy-3,5-dichlorophenyl) cyclohexane	163	1.38	1.5858
2,2-di(4-hydroxy-3,5-dibromophenyl) propane	157	1.91	1.6147
2,2-di(4-hydroxy-3-methylphenyl) propane	95	1.22	1.5783

* R_1R_2 = di(4-hydroxyphenyl)-.

As a general rule, it appears that polycarbonates which have the more asymmetric or branched substituent at the central carbon atom of the dihydric phenol are less likely to be crystalline[19].

Many polycarbonates yield colourless transparent products after melting and cooling, irrespective of the rate of cooling or the size of sample. This indicates that if crystallites are produced their dimensions are less than the wavelength of visible light. Treatment of the polymer with a swelling agent can induce the crystallisation of certain polycarbonates.

Prietzschk[23] studied in detail the crystal structure of the polycarbonate of bisphenol A by X-ray methods. He concluded that, despite the unwieldy molecular structure, this polycarbonate may be oriented and crystallised, and its crystal lattice is very stable.

Korshak and Vinogradova[31,33-35,70] concluded, from a study of the X-ray patterns of homogeneous and mixed polyarylates of widely different structures, that a reduction of packing density of the polymer chain leads to the production of amorphous compounds. Such a reduction in packing density would result from the presence, in the aromatic reactants, of functional groups in the *meta*- or *ortho*- rather than *para*-positions (*e.g.* the polyarylates of isophthalic acid with 2,2′-dihydroxydiphenyl, resorcinol, etc.) or by the presence of side-chains in the dihydric phenol.

TABLE 16. Thermal properties of bisphenol A polycarbonate[21].

Property	Test result		
Heat resistance	138°–143° with a load of 18.5 kg cm^{-2} 140°–145° with a load of 4.6 kg cm^{-2}		
Calculated shrinkage	0.005–0.007 cm cm^{-1}		
Thermal conductivity	4.6×10^4 cal sec^{-1} cm^{-2} deg^{-1} cm		
Coefficient of linear expansion	7×10^{-5} cm cm^{-1} deg^{-1}		
M.p. of crystalline material	268°		
Inflammability	self-extinguishing		
Shrinkage on aging (after 2000 h at 125°)	0.001 cm cm^{-1}		
Viscosity of melt at 300°	4000–6000 poises		
	Temp., °C	Load, kg	Deformation, %
Deformation under load (of a 12.7 cm cube)	70	454	0.282
	70	227	0.080
	25	454	0.220
	25	227	0.101

Thus polyarylates of isophthalic and terephthalic acids with 2,2'-dihydroxydiphenyl and of isophthalic acid with di(*p*-hydroxyphenyldiphenyl)-*α*,*α'*-*p*-xylene are amorphous, but poly(quinol terephthalate) is crystalline.

It was also found[33,35] that the physical structure of mixed polyarylates were intimately connected with their composition (Tables 11–14). The mixed polyarylates of the resorcinol–bisphenol A–terephthalic acid series, for example, are amorphous if the resorcinol content is less than 90%. A very high resorcinol content in the polymer leads to a high degree of order in the polymer chain and hence to an increase in the extent of crystallinity.

The crystallinity of polyarylates is also dependent on the method of manufacture of articles from the polymer. Mikhailov and Eidel'nant[71], for example, found that films of bisphenol A–isophthalic acid polyarylate cast from solution were more crystalline than films obtained from the melt; generally films produced by the latter method were amorphous. A bisphenol A–terephthalic acid polyarylate with a high degree of crystallinity may be obtained by annealing a pressed sample for several hours at 320°–350°.[71]

Conix[46,47] noted, during a study of the properties of the polyarylates of aromatic dicarboxylic acids of different structures, that the presence of an asymmetric substituent at the central atom of a dihydroxydiphenyl derivative reduced the tendency of the polyester to crystallise. Thus, the polyarylate of 2,2-di(4-hydroxyphenyl)butane and isophthalic acid will not crystallise under conditions similar to those in which the corresponding bisphenol A polyester does.

(c) Mechanical properties. The mechanical properties of polyarylates have been described in a number of papers[3,19-21,31,33-35,46,47]. Schnell[3,20], Thompson and Goldbaum[21], Hechelhammer and Peilstöcker[26] and others have reported data concerning mechanical properties of polycarbonates.

It has been found that the mechanical properties of polycarbonates depend on the method of preparation, the crystallinity, and molecular weight[3,19]. Thus polycarbonates made by interfacial polycondensation have good mechanical properties only when they have relatively high molecular weights, compared with those made by homogeneous polycondensation in solution or in the melt. Schnell[3] considers that this was due to the anomalous molecular-weight distribution of the polyarylates produced at phase boundaries (Fig. 21).

Polycarbonates may be stretched[3]. The macromolecules of polycarbonates can be reoriented in the direction of a stretching force and thus acquire increased tensile strength and double refraction. The length of a polycarbonate can be increased up to double by stretching below the vitrification temperature, whereas stretching above the vitrification temperature can lead to larger increase in the length through thermoplastic deformation[3,19].

The stability characteristics of polycarbonate films of various structures are set out in Table 17.[19] The load–elongation curve for the bisphenol A polycarbonate is shown in Fig. 17. The mechanical stability of the film also depends on its method of production. Data concerning the mechanical properties of polycarbonate films prepared by different methods from bisphenol A are given in Table 18. The stability characteristics of polycarbonate films vary with temperature. The relevant data for the polycarbonate of bisphenol A are presented in Table 19.

Articles moulded from bisphenol A polycarbonate are colourless, transparent, and possess good mechanical properties (Table 20).

The mechanical properties of homogeneous and mixed polyarylates of different structures were studied by Korshak and Vinogradova[31,33-35]. It was found that the stability characteristics of unoriented polyarylate films, produced from a melt, were related to the structure of the polymer. Thus, the tensile strength and relative elongation at the breaking point for the polyarylate of sebacic acid and bisphenol A were 450 kg cm^{-2} and 530% respectively. The corresponding values for the polyterephthalate derivative of bisphenol A were 610 kg cm^{-2} and 8% only. These data demonstrate that the substitution in the polyarylate of an aliphatic dicarboxylic acid residue for the aromatic one slightly reduces the tensile strength of the film and markedly increases its elasticity.

The dependence of the mechanical properties of mixed polyarylates on their composition is evident from Tables 11–14. The tensile strengths of the mixed polyarylates of the resorcinol–bisphenol A–terephthalic acid series (Table 11) lie in the range 610–780 kg cm^{-2}. The relative

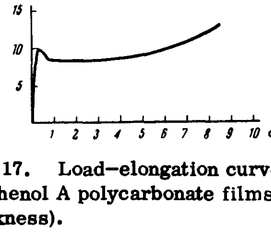


Fig. 17. Load–elongation curve for bisphenol A polycarbonate films (100μ thickness).

TABLE 17. Mechanical properties of polycarbonate films (thickness 50—60μ) prepared from solution[19].

Bisphenol	Orientation	Tensile strength, kg cm^{-2}	Elongation at break, %	Impact strength, cm kg cm^{-2}	No. of bonds to failure
R_1R_2*-1,1-Ethane	unstretched	759	167	1013	>10 000
R_1R_2-1,1-Isobutane	»	775	147	300	>10 000
R_1R_2-2,2-Propane	»	820	180	900	>10 000
R_1R_2-2,2-Propane	stretched 1 : 2	1400—1700	32—40	—	>10 000
R_1R_2-2,2-Propane	stretched 1 :4.7, crystalline	2150	15	425	>10 000
R_1R_2-2,2-Propane	stretched 1 : 11	3500	20	320	>10 000
R_1R_2-2,2-Butane	unstretched	725	70	363	5800
R_1R_2-2,2-Pentane	»	665	66	703	900
R_1R_2-Methylphenylmethane	»	824	55	172	1000
R_1R_2-1,1-Cyclohexane	»	814	56	169	5000
R_1R_2-1,1-Cyclopentane	»	708	119	552	>10 000
2,2-di(4-Hydroxy-3-dichlorophenyl) propane	»	995	19	65	>10 000
2,2-di(4-Hydroxy-3,5-dichlorophenyl) propane	»	1154	10	33	3000
2,2-di(4-Hydroxy-3,5-dibromophenyl) propane	»	1112		36	1000

* R_1R_2 = di(4-hydroxyphenyl)-.

TABLE 18. Mechanical properties of bisphenol A polycarbonate films (the polymers had Z_η = 0.087 and were flexed more than 10 000 times)[3].

Method of preparing films	Degree of orientation	Tensile strength, kg cm^{-2}	Elongation at break, %	Impact strength, cm kg cm^{-2}
Cast from solution	unstretched	820	180	900
ditto	stretched 200%	1400—1700	32—40	—
Blown	not further stretched	890	155	700

TABLE 19. Temperature variation of the strength of polycarbonate films (cast from solution), with differing degrees of orientation[3].

Temp., °C	Original film		Film stretched 1.5 times		Film stretched 1.9 times	
	tensile strength, kg cm^{-2}	elongation at break, %	tensile strength, kg cm^{-2}	elongation at break, %	tensile strength, kg cm^{-2}	elongation at break, %
30	680	95	891	9	1110	17
50	640	99	871	18	970	19
100	475	133	555	22	826	44
150	100	460	186	54	411	66

TABLE 20. Physical properties of polycarbonate articles cast under pressure.

Property	Numerical value
Flexural strength, kg cm^{-2}	800—1000
Impact strength	100%, not broken
Resistance to thermal shock, kg cm^{-2}	9—10
Yield point, kg cm^{-2}	650—700
Brinell hardness after 10 sec	930
Brinell hardness after 60 sec	900
Modulus of elasticity, kg cm^{-2}	22 000
Heat resistance (Martens), °C	125
Heat resistance (Vica), °C	165
Heat distortion point, °C	140

elongations of these films at the breaking point were between 8–60%. The polyarylate film obtained from a 60% resorcinol–40% bisphenol A mixture was the most elastic, *i.e.* it had the greatest relative elongation.

Conix has measured[46] the mechanical properties of a number of polyarylate films, obtained from solution in chlorinated hydrocarbons (Table 21). Similar data for cellulose triacetate, polystyrene, and bisphenol A polycarbonate films are given for comparison. Conix noted that, although the mechanical properties of his unoriented polyarylate films depended on their chemical structure, they varied only within the following ranges: tensile strength 6–9 kg mm^{-2}, the yield point 5 to 8 kg mm^{-2}, elongation at rupture 20–100%, and the modulus of elasticity 170 to 250 kg mm^{-2}. The good mechanical properties of a polyarylate are maintained right up to the softening temperature. Orientation of polyarylate films, in two directions, can significantly improve their mechanical properties. The tensile strengths of oriented polyarylates vary from 15 to 20 kg mm^{-2} and the elongation at rupture from 15 to 30%.[47]

According to Conix[46], the reduced viscosity of polyarylates (in 1,2-dichloroethane or tetrachloroethane) must be at least 0.4–0.5 if they are to possess film-forming properties. For fibre formation a reduced viscosity of ~ 1.0 is necessary.

(d) Electrical properties. The electrical properties of polycarbonates were studied by Schnell[3,20] (Table 22) especially those of bisphenol A polycarbonate (Table 23).[3,19,20,21]

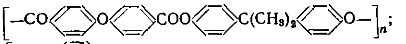
It has been shown that the dielectric loss factor (tan δ) and the dielectric constant of bisphenol A polycarbonate vary only slightly at temperatures below 150°. Above the vitrification temperature, these constants tend to a maximum at 175°.[3,19]

The dielectric properties of the polyarylates of several dicarboxylic acids are given by Korshak and Vinogradova[33] (Table 11), and Mikhailov and Eidel'nant[71,72]. The latter workers[71] studied the temperature dependence of the dielectric loss factor (tan δ) and the dielectric constant of bisphenol A polycarbonate and the polyarylates of bisphenol A with sebacic, terephthalic, and isophthalic acids. It can be seen from Fig.18 that the variation of the dielectric loss factor (tan δ) with temperature proceeds through two maxima. One maximum in tan δ occurs above 20°. The authors concluded, from the nature and mechanism of this

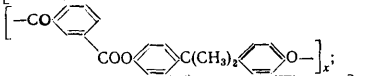
TABLE 21. Physical properties of various polymer films[46].

Property	Cellulose triacetate	Polystyrene	Polycarbonate	Polyarylate A	Polyarylate B	Polyarylate C
Tensile strength, kg mm^{-2}	11	6.3	8.4	8.4	7.0	6.3
Yield point, kg mm^{-2}	8	—	6.0	5.8	7.0	5.8
Elongation at the break, %	27—35	2.5—3.5	160	80	90	50
Modulus of elasticity, kg mm^{-2}	340	315	210	200	220	200
Softening temperature, °C	—	70—80	160	220	250	160
Absorption of water, % (after 24 h immersion)	4.3	0.5	0.2	0.3	0.2	0.3
Density, g cm^{-3}	1.28—1.30	1.05	1.20	1.21	—	—
Refractive index	1.48	1.59	1.58	1.62	1.61	1.60
Reduced viscosity	—	—	1.0	1.1	1.0	0.8

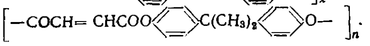
Note. Polyarylate A —



Polyarylate B —



Polyarylate C —



The polymers were plasticised with 15% triphenyl phosphate.

TABLE 22. Electrical properties of polycarbonates of various structures[22].

Bisphenol	Dielectric loss factor (tan δ)×10^4, at 1000 c/s and 25°	Dielectric constant, at 1000 c/s and 25°	Dielectric loss factor × 10^4, at 1000 c/s and 100°	Dielectric constant, at 1000 c/s and 100°
R_1R_2*-1,1-Ethane	4.9	2.9	4.9	2.9
R_1R_2-1,1-Butane	5.2	3.3	5.2	3.3
R_1R_2-1,1-Isobutane	5.2	2.4	5.2	2.4
R_1R_2-2,2-Propane	4.9	2.8	4.9	2.8
R_1R_2-2,2-Butane	4.5	3.1	4.5	3.1
R_1R_2-2,2-Pentane	4.2	2.3	4.2	2.3
R_1R_2-Methylphenylmethane	5.0	3.3	5.0	3.3
R_1R_2-1,1-Cyclopentane	5.0	2.9	5.0	2.9
R_1R_2-1,1-Cyclohexane	11.2	3.0	11.2	3.0
1,1-di(4-Hydroxy-3-methylphenyl)ethane	9.9	3.4	90.0	3.6
2,2-di(4-Hydroxy-3-methylphenyl)propane	20.4	2.5	40.0	2.6
2,2-di(4-Hydroxy-3-chlorophenyl)propane	11.5	3.3	16.0	3.6
2,2-di(4-Hydroxy-3,5-dichlorophenyl)propane	10.0	3.0	37.0	3.0
1,1-di(4-Hydroxy-3,5-dichlorophenyl)cyclohexane	5.0	2.6	40.0	2.6
2,2-di(4-Hydroxy-3,5-dibromophenyl)propane	20	2.7	38.0	2.7

---

* R_1R_2 = di(4-hydroxyphenyl)-.

TABLE 23. Electrical properties of bisphenol A polycarbonate (Lexan)[21].

Property	Temperature, °C				
	−30	−3	23	100	125
Dielectric constant at 60 c/s	3.12	3.12	3.17	3.15	3.13
Dielectric constant at 10^6 c/s	—	—	2.96	—	—
Dielectric loss factor (tan δ) at 60 c/s	0.005	0.004	0.0009	0.009	0.0011
Dielectric loss factor (tan δ) at 10^6 c/s	—	—	0.01	—	—
Bulk resistivity, ohm cm	$>10^{17}$	$>10^{17}$	2.1×10^{16}	2.1×10^{15}	2.0×10^{14}
Arc stability, stainless steel plate electrodes	—	—	10—11 sec	—	—
Dielectric strength, during short-time tests at 25°	98000 V mm^{-1} at sample thickness 0.038 mm 77250 V mm^{-1} at sample thickness 0.075 mm 64200 V mm^{-1} at sample thickness 0.120 mm 28300 V mm^{-1} at sample thickness 0.575 mm 10000 V mm^{-1} at sample thickness 3.125 mm				
Dielectric strength, during short-time tests at 100°	85000 V mm^{-1} at sample thickness 0.075 mm 31400 V mm^{-1} at sample thickness 0.575 mm 15000 V mm^{-1} at sample thickness 3.125 mm				
Resistance to electron radiation	No change up to 50 μr dose				

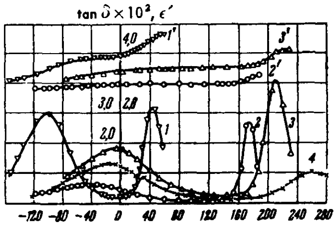


Fig. 18. Temperature dependence of the dielectric loss factor (1–4) and the dielectric constant (1′–4′) for bisphenol A polyarylates:
1) and 1′) with sebacic acid; 2) and 2′) with carbonic acid; 3) and 3′) with isophthalic acid; 4) and 4′) with terephthalic acid.

dielectric loss, that it may be related to "dipole-elasticity" losses. The other maximum in tan δ, which occurs below 20°, was considered by the authors to be connected with losses of the dipole-radical type. They assigned "dipole-radical" losses of the polyesters to vibrations of the ester parts of the chain. Dipole-elasticity losses were assigned to the relaxation of segments of the macromolecule.

It has been reported[71] that an increase in the concentration of aromatic nuclei in a polyarylate increases the temperature of the maximum dipole-elasticity losses (t_{max}); this indicates an increase in the relaxation time (Table 24).

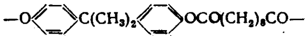
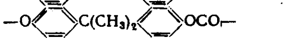
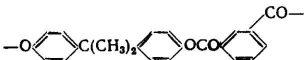
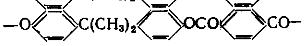
The relaxation time is also affected by the crystallinity of the polymer and the concentration and distribution of polar groups in the chain. Mikhailov and Eidel'nant considered that the differences in t_{max} for dipole-elasticity losses in polyarylates of bisphenol A possessing similar concentrations of polar groups were connected with their different crystallinities.

The temperature variation of tan δ for polyarylates, of differing degrees of crystallinity, obtained by pressing and by extrusion from solution, and of annealed samples, is shown in Fig. 19. It can be seen that the maximum in dipole-elasticity losses for the annealed sample is shifted to a much higher temperature (by ~ 40°); the maximum in dipole-radical losses is reduced. An increase in the crystallinity of the bisphenol A-terephthalic acid polyarylate after annealing is thus indicated.

The dielectric properties (Table 25) of a number of mixed polyarylates have also been studied[72]. It was established that the dipole-elasticity losses in mixed polyarylates are due to the relaxation of amorphous parts of the polymer. The temperature for the maximum dielectric loss factor (tan δ) is determined by the composition of the mixed polyester. In the vitreous state two maxima for dipole-radical losses were observed, corresponding to the two acids of the mixed polyarylate.

(e) Solubility. The solubility of polyarylates depends on their chemical structure and molecular weight. Polycarbonates obtained from quinol or from other symmetrical dihydric phenols, which contain small substituents between the aromatic rings, are reported to be insoluble,

TABLE 24. Values of tan δ_{max} and t_{max} for "dipole-elasticity" and "dipole-radical" losses at 20 kc/s [71].

Polyarylate	Concn. of aromatic rings in the chain	"Dipole-elasticity" losses		"Dipole-radical" losses	
		tan δ_{max}	t_{max}	tan δ_{max}	t_{max}
	0.154	3.1	47	3.0	—100
	0.500	2.65	174	0.6	— 40
	0.600	4.0	210	1.85	— 9
	0.600	1.0	260	1.30	— 13

Note. The concentration of aromatic rings in the chain was determined from the ratio of the number of aromatic rings to the total number of other groups in a unit.

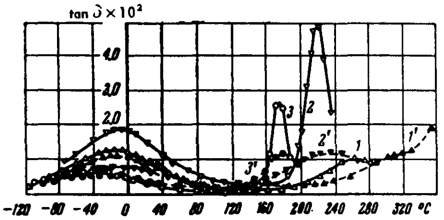


Fig. 19. Variation of the dielectric loss factor (tan δ) for bisphenol A polyarylates of different degrees of crystallinity:
1) and 1') with terephthalic acid, non-annealed and annealed; 2) and 2') with isophthalic acid, amorphous and partly crystalline; 3) and 3') with carbonic acid, amorphous and partly crystalline.

TABLE 25. Values of tan δ_{max}, temperature (t_{max}) of maximum dipole-elasticity losses at 60 c/s, and the concentration of aromatic rings (n) in the mixed-polyester chain.

Molar proportions of polyester components	n	tan δ_{max} × × 10²	t_{max}, °C
Terephthalic a. (0.8), adipic a. (0.2), bisphenol A	0.483	1.50	212
Terephthalic a. (0.6), adipic a. (0.4), bisphenol A	0.394	3.35	188
Terephthalic a. (0.6), sebacic a. (0.4), dian (1)	0.317	3.45	151

or only very slightly soluble, in organic compounds. Polycarbonates from dihydric phenols which contain asymmetric or branched radicals between the aromatic rings have considerably higher solubilities [20]. Most of the polycarbonates described are soluble in the usual organic solvents, methylene chloride, *m*-cresol, tetrahydrofuran, etc.[3,20,24].

The polyarylates of mononuclear aromatic dicarboxylic acids and dihydric phenols — poly(resorcinol terephthalate), poly(quinol terephthalate), poly(resorcinol isophthalate), and poly(quinol isophthalate) — are insoluble in organic solvents [31].

The presence of a side-chain in the acid or dihydric phenol molecule increases the solubility of the polyarylate. Thus, the bisphenol A–isophthalic acid polyarylate is soluble in cresol [31], in 1,2,2-trichloroethane and *sym*-tetrachloroethane [46]. The polyarylates of isophthalic acid with 2,2-di(4-hydroxyphenyl)butane and di(4-hydroxyphenyl)-methane are soluble in methyl chloride, 1,2-dichloroethane, 1,2,2-trichloroethane, and tetrachloroethane.

The solubility data for a number of homogeneous and mixed polyarylates of various structures are presented in Tables 11, 13, 14, and 26. [31,33-35,40]

Eareckson [54] presented solubility data for the mixed polyarylates of the bisphenol A–isophthalic acid–terephthalic acid series. He observed that the solubility of the mixed polyarylates was considerably greater than that of the homogeneous polymers. The mixed product of composition 1 : 0.5 : 0.5 possessed the greatest solubility in dioxan, tetrahydrofuran, ketones, chlorinated hydrocarbons, amides, esters, and nitro-compounds. The mixed polyarylates of this series swell considerably in aromatic hydrocarbons. They, however, neither swell nor dissolve in alcohols or aliphatic hydrocarbons.

(f) Molecular weight. Schnell [3] noted that the viscosity number for bisphenol A polycarbonates was not a linear function of the molecular weight, determined by osmometry. The logarithms of these two properties were, however, linearly related (Fig. 20). Schnell [3] expressed the relationship between the viscosity of the polycarbonate and its molecular weight as follows:

$$Z\eta = 1.23 \times 10^{-5} M^{0.83}.$$

Schulz and Horbach [24] have proposed that the molecular weight of bisphenol A polycarbonate may be calculated from the formulae

$$M = 1.03 \times 10^{2} [\eta]^{1.43} \text{ or } M = 2.4 \times 10^{2} [\eta]^{1.22}.$$

The first equation concerns the relationship of the molecular weight of the polycarbonate and the reduced viscosity in tetrahydrofuran solution whereas the second formula refers to a methylene chloride solution.

Eareckson [54] has presented data (Table 27) concerning the molecular weights of mixed polyarylates determined by light-scattering methods, and their reduced viscosities in a mixture of tetrachloroethane and phenol (40/60 w/w) at 30°.

The polyarylate of bisphenol A and isophthalic acid, synthesised by Korshak and coworkers [33-35] by the interfacial method, with a reduced viscosity (in cresol) of 1.0, had a molecular weight (determined by light scattering) of 90 000.

No other information concerning the determination of the molecular weights of polyarylates has been published so far.

TABLE 26. Solubility of the polyarylates of bisphenol A with terephthalic and isophthalic acids in various solvents. [The reduced (inherent) viscosities of the polymers in cresol were 0.50 and 0.54 respectively][40].

Solvent	Solubility, g litre^{-1}	
	polytere-phthalate	polyiso-phthalate
Ethanol	0	0.1
Dioxan	3.9	~20.6
Chloroform	8.2	12.4
***NN*-Dimethylformamide**	1.3	~ 3.8
Ethyl methyl ketone	0.4	0.7
Chlorobenzene	2	~13.3
***p*-Xylene**	0.7	0.9
Benzene	1.0	2.1
Tetrachloroethane	95	19.0
Tetrachloroethylene	0.6	1.1
Carbon tetrachloride	0.3	0.8
Heptane	0	0
Methylene chloride	5.7	~32
Tetrahydrofuran	1.8	5.3

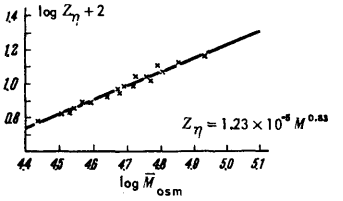


Fig. 20. Relationship between the logarithm of the viscosity number and the logarithm of the molecular weight (determined from osmotic pressure) for bisphenol A polycarbonate.

TABLE 27. The molecular weight and reduced (inherent) viscosity of the mixed polyarylate with the composition bisphenol A:isophthalic acid::terephthalic acid = 1:0.5::0.5.

η^*_{inh}	Reduced viscosity*	$\overline{M}$**
0.77	0.61	24000
1.03	0.89	60000
1.18	1.00	68000
1.51	1.10	88000

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* $\eta_{\text{inh}} = ln\,\eta_{\text{rel}}/c$ determined in solution of tetrachloroethane and phenol (40/60 w/w), where η_{rel} is the relative viscosity and c the concentration (0.5%).

** The molecular weight was determined by the light-scattering method in chloroform solution.

TABLE 28. Steam permeability of polycarbonates[20].

Bisphenol	Steam permeability, g $\text{cm}^{-1}\,\text{h}^{-1} \times (10^{-8}\,\text{mm Hg})^{-1}$
2,2-di(4-Hydroxyphenyl)propane	3.0
1,1-di(4-Hydroxyphenyl)cyclohexane	1.0
1,1-di(4-Hydroxyphenyl)cyclopentane	1.5
Di-(4-hydroxyphenyl)methylphenylmethane	2.4
2,2-di(4-Hydroxy-3-chlorophenyl)propane	0.56
2,2-di(4-Hydroxy-3,5-dichlorophenyl)propane	2.1
1,1-di(4-Hydroxy-3,5-dichlorophenyl) cyclohexane	1.14
2,2-di(4-Hydroxy-3,5-dibromophenyl)propane	2.3

TABLE 29. Gas permeability of bisphenol A polycarbonate[20].

Gas	Gas permeability, g $\text{cm}^{-1}\,\text{h}^{-1} \times (10^{-9}\,\text{mm Hg})^{-1}$, at 20°
Hydrogen	1.35
Carbon dioxide	0.75
Oxygen	0.18
Air	0.04
Nitrogen	0.01

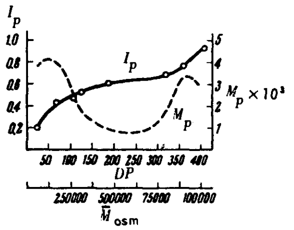

Fig. 21. The integral and differential curves for the molecular-weight distribution in bisphenol A polycarbonate prepared by the interfacial method. I_p—overall weight fraction, $I_p = \int dc/d\overline{M}$; c — weight fraction; $\overline{M}$ — mol. wt.; M_p — $dc/d\overline{M}$.

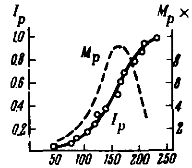

Fig. 22. The integral and differential curves for the molecular-weight distribution in bisphenol A polycarbonate prepared in solution. I_p — overall weight fraction, $I_p = \int dc/d\bar{M}$; c — weight fraction; $\bar{M}$ — mol. wt.; M_p — $dc/d\bar{M}$.

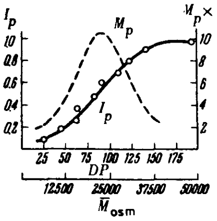

Fig. 23. The integral and differential curves for the molecular-weight distribution in bisphenol A polycarbonate prepared in the melt. I_p — overall weight fraction, $I_p = \int dc/d\bar{M}$; c — weight fraction; $\bar{M}$ — mol. wt.; M_p — $dc/d\bar{M}$.

(g) Other properties. Schnell[20] giving data relating to the steam- and gas-permeability of polycarbonates (Tables 28 and 29).

The molecular-weight distributions of the bisphenol A polycarbonates obtained by both the heterogeneous and homogeneous (in solution or in the melt) polycondensations were compared by Schnell[3]. The integral and differential curves for the molecular-weight distribution in these polymers are shown in Figs. 21–23; there is an anomalous distribution (two maxima) in the polycarbonate obtained by the interfacial polycondensation.

Molecular-weight distribution data for polyarylates of other dicarboxylic acids have not been described so far. There are, however, good reasons to believe that polyarylates produced by the interfacial technique will have different distributions from those produced by homogeneous polycondensation.

IV. USES OF POLYARYLATES

The polycarbonate of bisphenol A currently finds practical application under the trade names Lexan and Makrolon. Lexan was introduced by the General Electric Company of America[21] and Makrolon is produced by the German firm Farbenfabrieken Bayer (Federal German Republic).[26] Articles can be manufactured from this polycarbonate by various methods; under pressure, by extrusion, vacuum moulding, etc.[26] It is used as a building or structural material in a number of technical fields. Lexan is particularly suitable where a high impact stability is required because of its exceptionally high specific impact strength (~ 354 cm kg cm^{-3}), its dimensional stability, and thermal stability. Bisphenol A polycarbonate is used for the manufacture of calculating-machine casings, tubing, moulds, films, sheets, etc. It is widely used in high-precision mechanical engineering[21,26]. It may be possible to utilise Lexan for the production of lenses and inspection windows, and also for the formulation of adhesive compositions which can maintain their stability over a wide temperature range[21].

Polyarylates of other dicarboxylic acids do not yet find practical applications. Since, however, their physicochemical properties (high softening temperatures, thermal stability, resistance to chemical attack, good dielectric properties, etc.) surpass in some respects those of the polycarbonates (*e.g.* thermal and dielectric properties), there are good grounds for believing that their application will not be delayed for long.

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ORGANOMETALLIC COMPLEXES — OLEFINE POLYMERISATION CATALYSTS

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CONTENTS

After the discovery by Ziegler of a new method of synthesising polyethylene, complex organometallic catalysts came to be widely used in macromolecular chemistry.

The most important act in the intricate process of polymerisation, using organometallic complex catalysts, is the formation of the complex. The different aspects of the mechanism of the formation, and the catalytic action of organometallic complexes, have been widely discussed in the literature, including this journal[1]. However, recent work necessitates a reassessment of the concepts regarding the nature of the activity of organometallic catalysts in the polymerisation of unsaturated hydrocarbons.

1. METALALKYLS — OLEFINE POLYMERISATION CATALYSTS

Certain simple organometallic compounds act catalytically in the polymerisation of ethylene, even in a homogeneous phase[2]. However, by no means all partially ionic compounds with a metal–hydrocarbon bond possess such catalytic properties. Thus, the typically ionic alkyls of the alkali metals (sodium to caesium) are not α-olefine polymerisation catalysts and are found to be active only in the polymerisation of diolefines. Organometallic compounds of the alkali-earth metals (calcium to barium) likewise do not display catalytic activity in the polymerisation of ethylene. But aluminiumalkyls (ionic character of the bond 22%) and lithiumalkyls (43%) polymerise ethylene to low-molecular polymers, and give dimers with other α-olefines.

It is evident from a comparison of the behaviour of a few simple metalalkyls that the strongest catalytic action in the polymerisation of ethylene is shown by the alkyls of metals which have the smallest ionic diameters (Li, Be, Al; see Table 1). These metals belong to the first subgroups of the first three groups of the periodic classification and very easily form complexes. However, boron, which also has a very small ionic diameter, forms organometallic compounds which have the lowest catalytic activity. This is explained by the low electropositivity of the metal (2.0 eV on Pauling's scale of electronegativity). Therefore, the most active polymerisation catalysts are the organometallic compounds of strongly electropositive metals with small ionic diameters[3].

Lithiumalkyls are present as dimers in hydrocarbon solvents and are catalysts for the stereospecific polymerisation of isoprene[4], the polymer, formed by catalysis, having the 1,4-*cis*-configuration. In ether solution lithiumalkyl loses its stereospecific effect and forms an atactic polymer by 1,2-combination of monomeric units. The most likely reason for stereospecific 1,4-*cis*-polymerisation is obviously the small $Li^+(CH_2)^-$ spacing and the ability of lithium to form complexes:

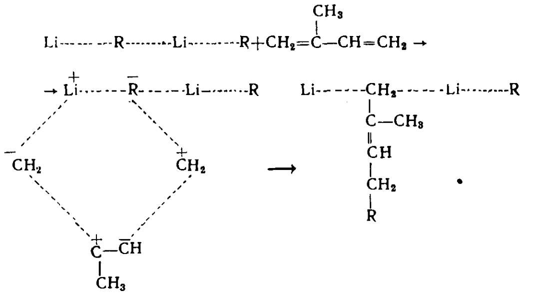
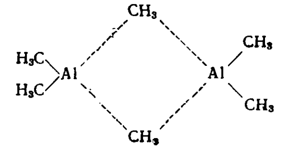


TABLE 1.

Metal	Electro-negativity according to Pauling, eV	Atomic radius, Å	Ionic radius, Å	Metal	Electro-negativity according to Pauling, eV	Atomic radius, Å	Ionic radius, Å
Li	1.0	1.33	0.68	Zn	1.5	1.31	0.74
Na	0.9	1.57	0.97	Ca	1.0	1.74	0.99
K	0.8	2.03	1.33	Ba	0.9	1.98	1.34
Rb	0.7	2.16	1.47	B	2.0	0.88	0.23
Cs	0.8	2.35	1.67	Al	1.5	1.26	0.51
Be	1.5	0.90	0.35	Si	1.8	1.17	0.42
Mg	1.2	1.36	0.66				

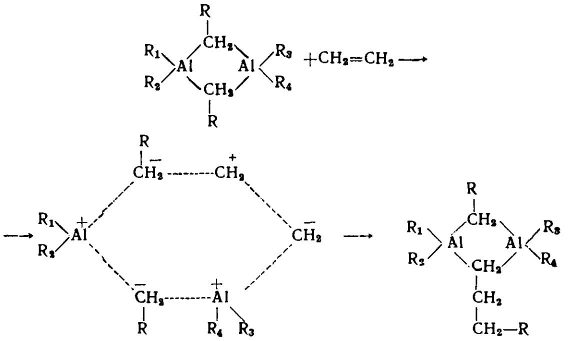
Note. Underlined metals are strongly electropositive and have small ionic radii.

Alkyls of aluminium and beryllium also tend to form complexes. This is confirmed by the fact that they are usually found in dimeric form. By electron-diffraction and X-ray analysis of trimethylaluminium dimer, the C–Al spacing was calculated for both carbon atoms forming the bridge between the two Al atoms, and found to be equal to 2.24 Å, which is far greater than the C–Al spacing in the four terminal bonds (1.99 Å). This is the reason for the much easier dissociation of the bridge bonds.



In this compound the univalent CH_3 group with one unpaired electron is joined to two atoms of aluminium. A tricentric orbital is thus formed, with two electrons revolving in the field of three nuclei. Such a "tricentric" bond has an energy about 10 kcal higher than that of the usual $Al-CH_3$ bond[5]. This feature of aluminium, beryllium, and certain other elements is connected with the fact that the valency of atoms is specified not only by the number of unpaired electrons which an atom can use for the formation of chemical bonds, but also by the presence of unfilled orbitals. Thus, although an aluminium atom has only three electrons available for bond formation, it can supply four orbitals. Therefore, despite the deficiency of electrons, the formation of tricentric orbitals provides sufficiently stable bonding.

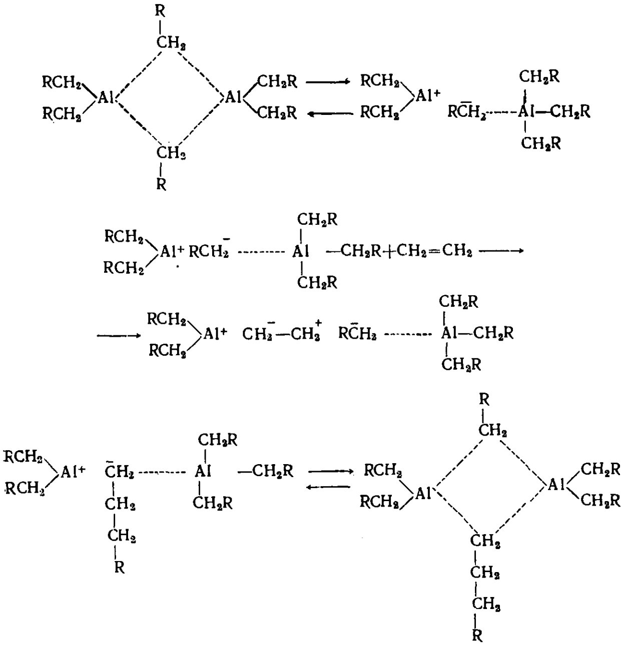
It is characteristic that in molecules of this type the angle between the bonds formed by the carbon atoms and the two metals atoms is equal to 60°–70°, since the two metal orbitals combine with the tetrahedral orbital of the CH_3 carbon. As a result, the two Al atoms are brought closer together. This is hindered if the radius of the metal atom is large. Natta[2] explains the catalytic action of the simple organometallic compounds in the polymerisation of ethylene in terms of the coordination of the electron-rich carbanion (formed by the polarisation of the ethylene molecule, $CH_2=CH_2 \rightarrow {}^-CH_2-CH_2^+$) to the electron-deficient complex. This is accompanied by the dissociation of the bridge metal–alkyl bond:



The solubility of ethylene in heptane and its heat of solution are not increased in the presence of R_3Al, which means that addition of ethylene molecules (by means of their *p* electrons) to the electron-deficient aluminium molecule does not take place with a low activation energy.

In a consideration of the various interpretations of the mechanism of ethylene addition, the electrical conductivity of R_3Al solutions in hydrocarbons cannot be disregarded. Bonitz[6] ascribed this conductivity to ionic dissociation.

When a polarised ethylene molecule is placed between two oppositely charged ions we have:



Even the most active of the simple metal alkyls considered above (alkyls of Al, Be, Li) polymerise ethylene rather slowly by successive (gradual) addition and allow only low-molecular polyethylene to be obtained (average molecular weight below 10 000). The reason for this is probably that at the elevated temperatures at which this reaction takes place (120°–250°), the chain-breaking reaction is very rapid; moreover, when the chain becomes very long, the polymer has a tendency to crystallise, thus blocking the small metal atoms firmly bound to the end of the chain.

2. THE ROLE OF ORGANOTITANIUM COMPOUNDS IN OLEFINE POLYMERISATION

The high catalytic activity of organotitanium compounds in the polymerisation of α-olefines has been demonstrated experimentally. As early as 1956 it was suggested that organotitanium compounds might act as catalysts in the polymerisation of ethylene and propene[7]. Recent work has shown[8] that organotitanium compounds — $RTiCl_3$ and R_2TiCl_2 — which are active catalysts in the polymerisation of α-olefines, can be isolated from mixtures of $TiCl_4$ and aluminiumalkyls. As the equilibrium position is unfavourable[9], special complex-forming compounds must be added to drive the reaction in the required direction. Sodium chloride or diphenyl oxide are used as additives. Methyltitanium trichloride consists of dark-violet crystals, melting at 28°–29° to a yellow liquid. The boiling point, from extrapolation of the vapour pressure curve, lies at about 120°. Other organotitanium compounds ($C_2H_5TiCl_3$ and iso-$C_4H_9TiCl_3$), which are less stable than the methyl derivative, were obtained in the same way.

The author of this work considers that in the polymerisation of ethylene with organotitanium catalysts a monomer molecule is inserted in the Ti – C bond, resulting in the formation of high-molecular organotitanium compounds. This was demonstrated experimentally by allowing the polymers to react with deuterated water or deuterated alcohol, when a deuterated hydrocarbon separated:

$$CH_3(CH_2-CH_2)_n.TiCl_3 + ROD \rightarrow$$
$$\rightarrow CH_3(CH_2-CH_2)_nD + ROTiCl_3.$$

Spectroscopic examination of the polymer in the infra-red absorption region showed that unsaturated groups were present:

$$CH_2=CH_2, \quad -CH=CH-, \quad \text{and} \quad {>}C=CH_2.$$

These may be formed by decomposition of the organotitanium compound, for example, as follows:

$$RCH_2-CH_2-TiCl_3 + CH_3TiCl_3 \rightarrow$$
$$\rightarrow 2TiCl_3 + RCH=CH_2 + CH_4.$$

In the polymerisation of ethylene with the catalyst $RTiCl_3$ + + $TiCl_3$ ($TiCl_3$ is formed in the partial decomposition of $RTiCl_3$) comparatively low-molecular polymers were obtained ($\eta_x = 0.4-1.0$).

At present there is every reason to believe that organotitanium compounds play an essential part in the common Ziegler catalysts, as Ziegler admits[10]. This may explain the previously established effect of aging of the $TiCl_4$ + + R_3Al complex catalysts, *i.e.* the unstable organotitanium compounds have time to decompose and the catalyst activity is sharply reduced. In order that the catalyst may retain its activity, conditions for the continuous formation of organotitanium compounds are required. One successful practical method of accomplishing this is the gradual addition of R_3Al to the $TiCl_4$ in the reaction medium[11]. The activity of the catalyst complex is also preserved by introducing a small amount of oxygen with the ethylene to be polymerised. It has been shown experimentally[12], that there is a definite optimum oxygen content of the ethylene, at which the yield of polymer is substantially higher. This effect was studied by the present authors in the polymerisation of propene[13].

Especially interesting are the experimental data[8] showing that small amounts of oxygen first of all oxidise $TiCl_3$ to $TiCl_4$, despite the presence of R_3Al in the system. Subsequently $TiCl_4$ is again alkylated by R_3Al. Thus the reactivity of the organotitanium compound is continuously regenerated and the high activity of the catalyst complex is maintained.

It is also reported[14] that the most likely active centres of polymerisation are the organotitanium compounds. The formation of the catalyst is obviously least complicated when LiR and $TiCl_4$ are used. This reaction can be represented by the following equation:

$$TiCl_4 + nLiR \rightarrow nLiCl + TiCl_{4-n}R_n,$$

where n = 1, 2, 3, or 4. Ludlum *et al.*[14] suppose that ultimately the organotitanium compound breaks down by a free-radical mechanism with the formation of RTiCl, which appears to be an active form of the catalyst. However, this idea is not supported by experiment and for the present can only be considered as a conjecture.

Study of the change in the activity of the catalyst complex with time showed that the gradual decrease in activity in the course of polymerisation is caused by the active catalytic centres becoming blocked by the adsorbed polymer which is insoluble in the reaction medium. If the polymerisation is conducted under conditions such that a soluble polymer is formed (low molecular weight), then decrease in the rate of polymerisation does not occur.

The data on the application of certain other titanium compounds[15], in particular $C_6H_5Ti(iso\text{-}C_3H_7O)_3$, in the catalytic polymerisation of propene are interesting from a theoretical point of view. In this case only low-molecular oil is formed. The organotitanium compound $TiCl(OC_2H_5)_3$ has higher catalytic activity than the compound which does not contain chlorine but here too there was considerably less polymerisation of propene than when $TiCl_4$ was used.

The $Ti(iso\text{-}C_3H_7O)_4 + TiCl_4$ catalyst system has a high activity in the polymerisation of propene yielding liquid polymers (yield 93–96%). Razuvaev *et al.*[16] have shown that the best results are obtained with a (three–six) fold excess of $TiCl_4$. Unfortunately the results of the polymerisation of propene with pure $TiCl_4$ are not quoted, although it has been known for a long time that $AlCl_3$, $TiCl_4$, and other similar substances can catalyse the polymerisation of propene, yielding low-molecular viscous products.

It has been shown that a very rapid exchange reaction takes place between $TiCl_4$ and $Ti(OR)_4$ with the formation of compounds of the type $TiCl_n(OR)_{4-n}$, where $n = 1-3$;[17] n depends on the molar ratio of $TiCl_4$ and $Ti(OR)_4$. In the present case the reaction

$$3TiCl_4 + Ti(OR)_4 \rightarrow 4TiCl_3OR$$

takes place.

It is believed that the organo titanium compound formed is the catalyst in the polymerisation of propene. It is curious that freshly-prepared catalysts, consisting of the specially synthesised compounds $TiCl_3(iso\text{-}C_3H_7O)$, etc. have low initial activity, which increases on storage. This is accompanied by decomposition with the separation of liquid and gaseous products which were shown to consist of HCl and the corresponding alkyl chlorides. The solid decomposition product is titanium oxychloride, which is obviously responsible for the activity of the catalyst system in propene polymerisation.

3. ORGANOBIMETALLIC COMPLEXES

According to recently published data[18], a necessary condition for the formation of an active catalyst of high-molecular polymerisation of ethylene is the presence of three components in the catalyst system: an alkyl donor, quadrivalent titanium, and an electrophilic reagent. The alkyl donor can be any metalalkyl or its derivative (for example, the hydrides of lithium, aluminium, zinc, tin, and many other metals). Quadrivalent titanium may be represented as $TiCl_4$, $Ti(OR)_4$, or $(C_2H_5)_2TiCl_2$. The electrophilic reagent may be $AlCl_3$, R_2AlCl, $SbCl_5$, etc.

In the polymerisation systems commonly used the necessary electrophilic reagent is formed by reaction between R_3Al and $TiCl_4$:

$$R_3Al + TiCl_4 \rightarrow R_2AlCl + RTiCl_3.$$

In a study of various metalalkyls, Roha *et al.*[18] noted that $Sn(C_4H_9)_4$, for example, does not have a marked ability to reduce $TiCl_4$, but is a good alkyl donor and forms a catalyst of high activity by interaction with $TiCl_4$ in conjunction with the electrophilic $AlCl_3$. This confirms the need for three components to be present in the catalytic systems, including an electrophilic reagent.

A very curious fact is the observation made by the authors[13] regarding the absence of reduction of $TiCl_4$ in their catalytic system. In spite of this the catalyst promoted rapid polymerisation of ethylene to high-molecular polyethylene. Similar observations were made in the investigation of $(iso\text{-}C_4H_9)_2AlCl$. This compound has a very low reducing power but is nevertheless a good alkyl-donor and electrophilic reagent. Here also, on interaction with $TiCl_4$, an active ethylene polymerisation catalyst was formed, which allowed the reaction to be conducted at a steady, easily controlled rate. It is possible that the active catalyst is an organotitanium compound which is formed, but this was not confirmed.

The polymerisation reaction with the usual Ziegler catalyst begins rapidly, but before long the rate falls as reduction of titanium by excess metal alkyl absorbs the necessary Ti^{4+}. Slow continuous addition of an oxidising agent such as O_2,[12] ensures the presence of a sufficient quantity of Ti^{4+} and therefore activates the "dying" catalyst.

Table 2 presents experimental data obtained in the polymerisation of ethylene (in benzene at 50°–60°) with various catalyst systems. The data confirm the idea regarding the three components which are necessary to endow the organometallic complexes with high catalytic activity.

According to the data in Table 2, the character of the alkyl-donor has considerable importance; for example, $(iso\text{-}C_4H_9)AlCl_2$ being a weak alkyl-donor, although also a good electrophilic reagent, does not form an active catalyst complex with $TiCl_4$. On the other hand, a good alkyl donor, such as di-isobutylaluminium acetylacetonate, by itself, also does not form an active catalyst with $TiCl_4$ since it is not electrophilic in character; in combination with enough electrophilic $(iso\text{-}C_4H_9)AlCl_2$ an active catalytic complex is obtained.

Unfortunately the data does not include quantitative characteristics of the catalysts investigated; even the molecular weight and other elementary properties of the polyethylene obtained are not quoted. This eliminates any possibility of estimating with sufficient reliability the activity of the catalysts from the polymerisation rate constant. It should be mentioned that the experimental data discussed above contradict earlier communications[19-25]

TABLE 2. Comparison of the activities of various organometallic catalysts in the polymerisation of ethylene.

Alkyl-donor		Electrophilic agent		$TiCl_4$, mmoles	Activity in ethylene polymerisation
mmoles	compound	mmoles	compound		
12	$(iso\text{-}C_4H_9)_3Al$*	—	—	15.0	very poor
12	»	7.5	$AlCl_3$	15.0	good
5.5	95% $(iso\text{-}C_4H_9)_3Al$ + + 5% $(iso\text{-}C_4H_9)_2HAl$	—	—	11.0	good
5.5	89% $(iso\text{-}C_4H_9)_2HAl$ + + 11% $(iso\text{-}C_4H_9)_3Al$	—	—	11.0	good
	ditto	5.5	$(iso\text{-}C_4H_9)_2AlCl$	11.0	very good
	»	8.25	»	8.25	very good
	»	8.00	»	3.0	good
11.0	63% $(iso\text{-}C_4H_9)$ AlCl + + 34% $(iso\text{-}C_4H_9)_3Al$ + + 3% $(iso\text{-}C_4H_9)_2HAl$		—	11.0	good
		11.0	$(iso\text{-}C_4H_9)AlCl_2$	11 0	very poor
5.5	Aluminiumdi-isobutyl acetylacetonate	—	—	11.0	very poor
5.5	ditto	2.0	$(iso\text{-}C_4H_9)AlCl_2$	11.0	good
11.0	$(iso\text{-}C_4H_9)_2Al\ (iso\text{-}C_4H_9O)$	—	—	11.0	very poor
11.0	»	2.0	$(iso\text{-}C_4H_9)AlCl_2$	11.0	good

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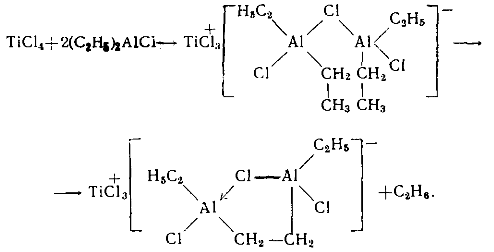
* Carefully freed from hydride.

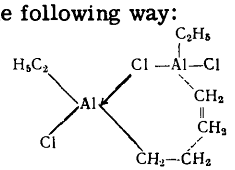
regarding the reducing role of AlR_3 in the formation of an active catalyst complex for ethylene polymerisation.

From this viewpoint, work on the catalytic activity of organometallic complexes in the polymerisation of ethylene [26-27] deserves special attention. It was shown that the interaction of $TiCl_4$ and $2(C_2H_5)_2AlCl$ in benzene solution at 25° in an atmosphere of nitrogen leads to the formation of a brown precipitate, consisting mainly of $TiCl_3$, and gaseous products containing ethane and only small amounts of H_2, C_4H_{10} and C_4H_8. With high values of the $R_3Al:TiCl_4$ ratio, the formation of a small amount of C_2H_4 was also noted. The filtrate consisted of unconverted $(C_2H_5)_2AlCl$ and a certain amount of an organoaluminium compounds of higher molecular weight. The presence of the latter compounds was demonstrated experimentally by oxidation and subsequent hydrolysis to form the corresponding primary aliphatic alcohols with molecular weights of about 400. The catalyst system $(C_2H_5)AlCl_2 + TiCl_4$ was also investigated. Mainly $TiCl_3$ and ethane were formed in the reaction of the components under the above conditions. The polymerisation of ethylene with this catalyst system at -10° gave only a low molecular product (average molecular weight 400).

Helden *et al.*[26-27] consider that ethane appears in the complex-formation reaction as a result of intramolecular disproportionation and hydrogen abstraction. The overall reaction may be represented in the following way:



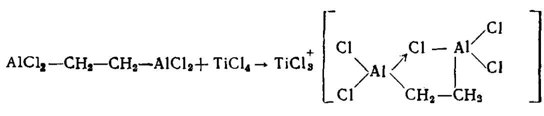
The authors believe that the aluminium compound initiates the polymerisation reaction. The role of $TiCl_3$ formed by the reduction of $TiCl_4$ is not presented clearly enough. It is only shown to "stabilise" the formation of the organoaluminium compound, the structure of which was given above. Chain growth was assumed to take place through the Al–C bond in the following way:



Using the above ideas on the mechanism of the formation and action of organometallic polymerisation catalysts, the same authors proposed a new catalyst system ($AlCl_3$, K, and $TiCl_4$) for ethylene. $AlCl_3$ and K, suspended in heptane (1–2 : 1), react in the presence of ethylene to form a dark-grey solid product. The addition of $TiCl_4$ leads to the rapid polymerisation of ethylene (reaction temperature 65°, atmospheric pressure). It is assumed that in the interaction of $AlCl_3$ and K, the $AlCl_3$ is partly reduced. The subhalide derivatives of aluminium formed (their formation was confirmed by decomposition of the product with water) react with ethylene giving a compound of the type $AlCl_2$-C_2H_4-$AlCl_2$. The structure of this compound was confirmed by the formation of dideuteroethane ($C_2H_4D_2$) on decomposition with deuterated water and also by analogy with the previously known compound with the structure BCl_2-C_2H_4-BCl_2. The compound $AlCl_2$-C_2H_4-$AlCl_2$ was extracted with ether which resulted in the formation of $Al_2Cl_4.C_2H_4.2(C_2H_5)_2O$. The diether derivative obtained was active in the polymerisation of ethylene only in conjunction with $AlCl_3$ (2 moles per mole of diether derivative). The authors consider that this is explained by the following reactions.

$$2AlCl_3 + AlCl_2\text{-}C_2H_4\text{-}AlCl_2.2(C_2H_5)_2O \rightarrow$$
$$\rightarrow 2AlCl_3.(C_2H_5)_2O + AlCl_2\text{-}C_2H_4\text{-}AlCl_2.$$

An active catalyst complex is formed by the interaction of this compound with $TiCl_4$.



Chain growth proceeds in the same way as described above.

In connection with the experimental data and theories of the Dutch investigators it should be noted that the activity of the catalyst $AlCl_3 + LiAlH_4 + TiCl_4$ in the polymerisation of ethylene had been established earlier by us [28]. In this case $LiAlH_4$ is an even better reducing agent than K which was used in the investigations described above. In contrast to the Dutch workers, the present authors believe that the intermediate formation of R_3Al, by the reaction of $AlCl_3$, $LiAlH_4$, and C_2H_4 is more likely. We did not study the reaction mechanism, but established experimentally the high activity of the proposed new catalyst system not only for the polymerisation of ethylene but also for the synthesis of stereoregular polypropylene.

The experimental investigation of the polymerisation of ethylene and propene in the presence of powdered aluminium and $TiCl_4$, described quite recently by Japanese authors [29,30], is extremely interesting. In the polymerisation of ethylene this catalyst leads to the formation of linear polymers with a melting point of 130° and a molecular weight (30–40) × 10^3. It was also established that the addition of $TiCl_3$ to the Al–$TiCl_4$ system considerably affected the properties of the polymer obtained, especially its molecular weight, which in this instance increased to 300 × 10^3. It is interesting that according to the authors' data, turnings may be used successfully instead of powdered aluminium, which of course is of considerable interest from the point of view of possible practical application of the reaction to obtain polyethylene.

In a study of the activities of titanium chlorides, it was shown that the highest activity is displayed by $TiCl_4$ which the authors explain by its high Lewis acidity.

In the polymerisation of ethylene a solid polymer is obtained in good yield only when an alloy of Al and Mg is used. Variation in reaction conditions (temperature, pressure, and proportions of the catalyst components) can affect the properties of the polyethylene in the same way as the polymerisation of ethylene is controlled in the presence of a typical Ziegler catalyst. On the basis of experimental data, the following equation for the rate of polymerisation is proposed:

$$-\frac{dP}{dt} = 4.37\,[TiCl_4]\exp(-4800/RT)P.$$

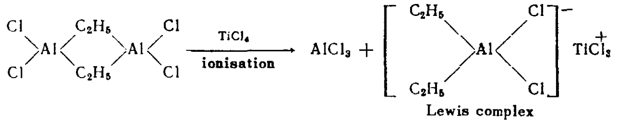
From the equation it is clear that, other conditions being equal, the reaction rate is determined only by the concentration of $TiCl_4$ and does not depend on the amount of Al. On this basis the authors consider a cationic mechanism the most likely and do not give it further consideration. We suggest that in this instance one may expect the formation of an intermediate organoaluminium compound which subsequently yields the active catalyst complex.

In order to obtain reproducible results in polymerisation with the R_3Al + $TiCl_4$ catalyst system, a high degree of purity of the monomer and the solvent in which the polymerisation is carried out is essential[11]. It is also shown that to ensure the formation of an active complex it is necessary to introduce the components of the catalyst system in a sequence which will result in the minimum formation of R_2AlCl as this is less active than R_3Al. However, according to a number of other publications, R_2AlCl has an activity equal to, or even higher than, that of R_3Al in the polymerisation of ethylene and propene.

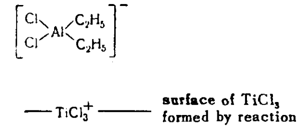
One investigator[31] has proposed the following mechanism for the interaction $(C_2H_5)_2AlCl$, and $TiCl_4$:

$$(C_2H_5)_2AlCl + 2TiCl_4 \rightarrow (C_2H_5)AlCl_2 + TiCl_3' + TiCl_4 + C_2H_5. \quad (1)$$

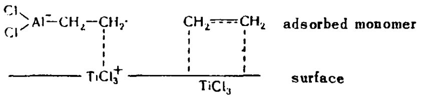
$(C_2H_5)AlCl_2$ exists in dimeric form:



The complex formed is adsorbed on the solid surface of $TiCl_3$ through $TiCl_3^+$ ions:



Later, evidently through intermolecular disproportionation, ethane is evolved and an active centre for the growth of a polymer chain is established:



The monomer is adsorbed on the surface of $TiCl_3$ and is polymerised by means of the ion-radical of the active complex. Although this mechanism is not substantiated by experiment, we believe it to be more probable than the similar idea put forward by Helden and coworkers[26,27] and discussed above.

Several investigators consider that the catalytic activity of R_3Al is directly connected with its reducing power with respect to $TiCl_4$.[32] The authors show that the substitution of one ethyl group by an ethoxy-group leads to the formation of a compound which does not reduce $TiCl_4$ at all. However, no experimental data have been reported, which would suggest that the organometallic compound obtained has no catalytic activity.

It is interesting to note that an excess of $TiCl_4$ in the catalyst system leads to a substantial reduction in the molecular weight of the polyethylene. A similar effect takes place when $(C_2H_5)_2AlCl$ is introduced into the catalyst composition, which agrees well with earlier data[8]. The observed lowering of molecular weight of the polymer is explained in different ways. Some consider[8] that with excess $TiCl_4$ the following reaction occurs:

$$R_3Al + 2TiCl_4 \rightarrow RAlCl_2 + 2RTiCl_3.$$

The compound $RAlCl_2$ causes less decomposition of $RTiCl_3$ with the formation of $TiCl_3$ than does R_2AlCl; since according to these authors the organotitanium compound leads to the formation of a low-molecular polymer, this explains the effect observed with excess $TiCl_4$.

On the other hand[32], it is suggested that the lowering of the molecular weight of the polymer in the presence of excess $TiCl_4$ is due to the breaking of a growing polymer chain by a chloride ion:

$$TiCl_4 \rightleftharpoons TiCl_3^+ + Cl^-,$$

$$M^+-\bar{C}H_2-CH_2-CH_2-CH_2-\sim\sim + TiCl_3^+ + Cl^- \rightarrow$$

$$\rightarrow MCl + TiCl_3-CH_2-CH_2-CH_2-CH_2-\sim\sim.$$

Both explanations are hypothetical as they are not supported enough by experimental data. It may equally well be suggested that the excess $TiCl_4$ (and also the excess R_2AlCl) lead to the destruction of the high-molecular compound formed.

Comparison of the reduction of Ti^{4+} to Ti^{3+} by the action of R_3Al, R_2AlCl, and $RAlCl_2$ on $TiCl_4$ showed that the organoaluminium compound is not fully used up, even with a considerable excess of $TiCl_4$, evidently due to complex formation[33]. The reducing power of organoaluminium compounds increases in the series $(C_2H_5)AlCl_2 < (C_2H_5)_2.AlCl < (C_2H_5)_3Al$, the change from $(C_2H_5)AlCl_2$ to $(C_2H_5)_2.AlCl$ being insignificant, and very marked from $(C_2H_5)_2AlCl$ to $(C_2H_5)_3Al$. It is interesting that under the experimental conditions (80°) the reducing power calculated for one ethyl group remains practically the same for the series of organoaluminimum compounds investigated.

Similar observations were reported by other authors who also studied the interaction of various organoaluminium compounds with titanium halides[34,35]. It was found that in the interaction of $TiCl_4$ with R_3Al there is evidently formed a brown modification of $TiCl_3$ which is very reactive with respect to R_3Al. Unfortunately the conclusions of these authors, like many others, are not reliable enough owing to the fact that the R_3Al used contained other compounds which were not inert to $TiCl_4$. Thus the $(C_2H_5)_3Al$ used by Boldyreva *et al.*[35] contained according to analysis 80% $[(C_2H_5)_3Al + (C_2H_5)_2HAl]$ and 20% $(C_2H_5)_2AlOC_2H_5$. The purest organoaluminium compound was used by Roha and coworkers[18].

In all the papers quoted the interaction between $TiCl_4$ and the organoaluminium compounds is considered as an oxidation–reduction reaction. This is true only when there is a hydride ion in the organoaluminium compound; reduction of titanium and oxidation of the hydride ion then takes place:

$$2R_2HAl + 2TiCl_4 \rightarrow 2TiCl_3 + 2R_2AlCl + H_2.$$

In the other cases titanium tetrachloride is alkylated in the usual way with the formation of organotitanium compounds:

$$R_3AL + TiCl_4 \rightarrow RTiCl_3 + R_2AlCl,$$

$$R_2AlCl + TiCl_4 \rightarrow RTiCl_3 + RAlCl_2,$$

$$RAlCl_2 + TiCl_4 \rightarrow RTiCl_3 + AlCl_3.$$

A paper was recently published which was devoted to the study of a new catalyst system, R_3Al + $CrCl_3$, in the stereospecific polymerisation of propene[36]. Chromium trichloride has a substantial advantage over titanium trichloride as it is inert to air. The experimental data show that the catalyst complex obtained with $CrCl_3$ has a lower activity, but is quite stereospecific. In this system $(C_2H_5)_3Al$ proved to be a more active component of the polymerisation catalyst than $(iso\text{-}C_4H_9)_3Al$ which was studied at the same time. In view of the high activity of $TiCl_2$ in the polymerisation of ethylene reported above, it is interesting that $CrCl_2$ is practically inactive in the polymerisation of propene, as can be seen from the following data:

$CrCl_2 : CrCl_3$ Ratio	0.00	1.0	∞
% conversion of C_3H_6	16.0	9.0	0.0

The product of the interaction of $(C_2H_5)_2Zn$ and $TiCl_4$ was shown to be an active catalyst for the polymerisation of propene to a high molecular solid polymer[37]:

$$TiCl_4 + (C_2H_5)_2Zn \rightarrow TiCl_3 + C_2H_5ZnCl + C_2H_5^{\bullet}$$

The highest percentage conversion of propene to polymeric oil was attained with equimolar proportions of $(C_2H_5)_2Zn$ and $TiCl_4$. With a threefold molar excess of $(C_2H_5)_2Zn$, solid polypropylene, which had a melting point 150°–158° and a molecular weight $(1.0-1.8) \times 10^4$, was formed in 30% yield; with a higher excess of $(C_2H_5)_2Zn$, the yield of solid polymer was appreciably lower. The authors[37] also established that the character of the radical in the organozinc compound had practically no effect on the activity of the catalyst system formed.

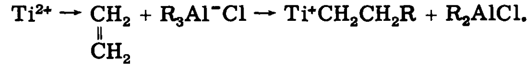
Interesting data were obtained in an investigation of the effect of nucleophilic organic compounds which could interact with both components of Ziegler catalysts[38]. The influence was studied of electron-donor additives (triethylamine, diphenylamine, aniline, and dimethylaniline) in the polymerisation of propene with the $(C_2H_5)_3Al + TiCl_3$ (molar ratio 3 : 1) catalyst system. It was found that the presence of a certain amount of amine led to a considerable increase in the molecular weight of the polypropylene.

The activating influence of amines, leading to a change in the relative rates of the growth and chain breaking processes, was also established. In some experiments, especially when halogen-substituted amines were used, an increase in the overall rate of polymerisation was observed. It is supposed that the electron pair of the amine can interact with the *d* shell of $TiCl_3$ to form bonds; this should be reflected in the electronic state of the adsorbed organometallic molecule and consequently in the energy of the active bond. The value of the latter determines the rate of the chain-propagation reactions and the probability of chain termination at the active bond to a considerable extent. For a fuller explanation of the role of amines, their interaction with R_3Al would also have to be studied, but this was not done.

Addition of small amounts of diphenylamine to the organometallic catalyst $(C_2H_5)_3Al + TiCl_4$ or $(C_2H_5)_2AlCl + TiCl_3$ in the polymerisation of 1-pentene increased the yield of polymer. However, increase in the diphenylamine above a certain amount inhibited the reaction. A similar effect was caused by tolylthiol[39].

It is well known that alkylaluminium forms complexes or co-ordination compounds with amines[40], for example, $Me_3Al^-.N^+Me_3$. It has been found that R_3Al readily forms co-ordination compounds with electron donors; therefore it is quite likely that the initial step in the interaction of R_3Al with $TiCl_4$ is the formation of complexes of the type $Cl_3Ti^+.R_3Al^-Cl$ or $Cl_2Ti^+.(R_3Al^-Cl)_2$.[41] These complexes are then decomposed with rupture of the Ti–Cl and Al–R bonds.

The experimental data of Cooper and Rose[41] are of interest in connection with the elucidation of the nature of the activity of organometallic catalyst complexes. They have shown that the activity of solid products, formed by the reaction of R_3Al and $TiCl_4$, is not reduced on drying in a vacuum. These solid products have a laminated structure, in which the chlorine layer is slightly modified through partial substitution of chloride ions by species such as $(C_2H_5)_3\overline{Al}Cl$, $(C_2H_5)_2\overline{Al}Cl_2$, or $(C_2H_5)\overline{Al}Cl_3$. These ions are formed by co-ordination of $(C_2H_5)_3Al$, $(C_2H_5)_2AlCl$, or $(C_2H_5)AlCl_2$ with chloride ions already present in the lattice. It is supposed that ethylene molecules combine with titanium atoms and then react with complex anions in the lattice:



$$Ti^{2+} \rightarrow \underset{CH_2}{\underset{\|}{CH_2}} + R_3Al^-Cl \rightarrow Ti^+CH_2CH_2R + R_2AlCl.$$

Chain growth then proceeds through introduction of olefine molecules at the Ti–C bond. The mechanism of chain transfer is similar to Ziegler's hypothesis[42] for the interaction of R_3Al with C_2H_4. This mechanism leads to R and $C=CH_2$ terminal groups in the polymer, which was confirmed experimentally by Natta and his coworkers[80]:

$$Ti^+CH_2CH_2R + nC_2H_4 \rightarrow Ti^+CH_2CH_2(CH_2CH_2)_nR,$$
$$Ti^+CH_2CH_2(CH_2CH_2)_nR + C_2H_4 \rightarrow Ti^+CH_2CH_3 + CH_2=CH(CH_2CH_2)_nR.$$

Other mechanism may also be proposed which entails the formation of similar terminal groups. In this case preliminary reduction of ethylene by divalent titanium is supposed, with the formation of a hydride ion which ultimately enters into the lattice:

$$Ti^{2+} + CH_2=CH_2 \rightarrow Ti^{3+}CH=CH_2 + H^-,$$

$$Ti^{3+}CH=CH_2 + nC_2H_4 \rightarrow Ti^{3+}(CH_2CH_2)_nCH=CH_2,$$

$$R_3Al^-Cl, + Ti^{3+}(CH_2CH_2)_nCH=CH_2 \rightarrow Ti^{2+} + R(CH_2CH_2)_nCH=CH_2 + R_2AlCl.$$

Both mechanisms require further experimental study.

Investigation of ethylene polymerisation in the presence of a catalyst complex, formed from $TiCl_4$ and $(C_4H_9)Li$ or $(C_4H_9)_2Zn$,[43] showed that the polymerisation rate was proportional to the amount of $TiCl_4$ and did not depend on the nature or the amount of metal alkyl. With a considerable excess of $(C_4H_9)_2Zn$, the reaction was inhibited. The reaction mechanism proposed, including the preliminary formation of a trivalent titanium alkyl-compound, followed by rupture of the Ti–C bond, was not verified by experiment.

Natta[2] considers that organometallic complex catalysts represent a special type of catalyst as in many cases they allow polymers to be obtained, having structures different from those previously known, even with atactic poly-α-olefines. In fact, investigation of the infra-red spectra showed that the new polymers of α-olefines have more regular structures (especially "head to tail" addition compounds) than the polymers obtained by other methods. Natta attributes this difference to the special co-ordination bonds in the catalyst. He considers that there can be no doubt that the activity of the better stereospecific catalysts in the polymerisation of α-olefines, is connected with the co-ordination activity of atoms of a strongly electropositive transition metal, distributed on the surface of the solid microcrystalline phase, which can chemisorb organometallic compounds.

The electropositivity of the transition metal atom increases as its valency decreases; therefore only low-valency compounds of the transition metals can take part in anionic co-ordination catalysis. Weakly electropositive metals (for example, Pt, Pd, etc.) are inactive even in a low-valency state.

The following arguments are cited in support of the hypothesis of anionic co-ordination catalysis:

1. The regular linear macromolecules of "head to tail" structure, which are formed in the polymerisation of monomers of the type $CH_2=CHR$ may be explained by the greater tendency of the CH_2 group, compared with the CHR group, to give a carbanion which can enter into a co-ordination bond with an organometallic complex.
2. The poly-α-olefine macromolecules have vinylidene groups at one end of the chain, and alkyl groups, with the same number of carbon atoms as the normal chain of the olefine monomers, at the other[44].
3. In the most active catalysts there are at least two different metals, strongly electropositive and with the power to form complexes.
4. The greater catalytic activity of complexes containing metal ions with small radius and high local electric field (ionic radii: Be 0.35 Å, Al 0.51 Å, Li 0.68 Å).
5. The electrical conductivity of the ionic type, with migration of the more alkylated groups to the anode, which is shown by solutions of organometallic compounds (such as R_3Al) and by their catalytically active soluble complexes.
6. The reactivity of the monomers follows a sequence which is the reverse of that in cationic polymerisation. The reactivity of propene and butene is less than that of ethylene because of the presence of the CH_3 group.
7. The nature of chain growth,

   $$\text{(complex)} - CH_2 - CHR - P + CH_2{=}CHR \rightarrow$$
   $$\rightarrow \text{(complex)} - CH_2 - CHR - CH_2 - CHR - P,$$

   and the nature of chain termination, which leads to the formation of a vinylidene bond through transfer of the hydride ion from the CHR group of the last monomer unit to the catalyst complex, which can then initiate a new polymer chain:

   $$\text{(complex)} - CH_2 - CHR - P \rightarrow$$
   $$\rightarrow \text{(complex)} - H + CH_2{=}CR - P,$$
   $$\text{(complex)} - H + CH_2{=}CHR \rightarrow$$
   $$\rightarrow \text{(complex)} - CH_2 - CH_2R.$$

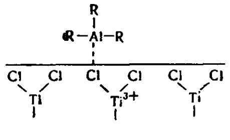
   This transfer takes place more easily, the better an electron donor group R is. In this way it is possible to explain the lower molecular weight of poly-α-olefines compared with polyethylene or polystyrene.
8. The fact that, in contrast to radical polymerisation, the molecular weight does not drop when the polymerisation is conducted in the presence of solvents which are capable of absorbing free radicals (for example, cumene, iso-octane, etc.).
9. The rate of polymerisation is constant when stable catalysts are used. In contrast to radical initiators, a solid catalyst is not used up.
10. The molecular weight is reduced with increase in the concentration of R_3Al.

Our experimental results[13,45] and the published data suggest that radical processes also play a definite part in the stereospecific polymerisation of α-olefines in the presence of complex catalysts. In general, we believe that it is impossible to determine definitely the mechanism by which the very complex reaction of polymerisation takes place in the presence of organometallic catalysts.

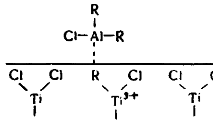
In the interaction of the components of a Ziegler type catalyst, alkylation of $TiCl_4$ first takes place, and then homolytic scission of the organotitanium compound formed:

$$TiCl_4 + R_3Al \rightarrow RTiCl_3 + R_2AlCl,$$
$$RTiCl_3 \rightarrow TiCl_3 + R^{\cdot}$$

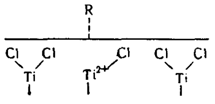
The radicals evolved recombine or disproportionate. The excess R_3Al in the system is adsorbed on the $TiCl_3$ crystal surface:



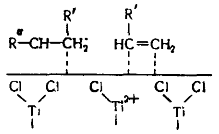
Then an exchange reaction takes place between $TiCl_3$ and aluminiumalkyl:



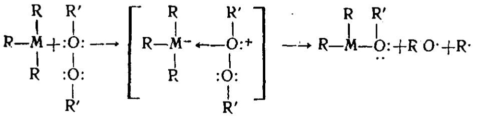
The organotitanium compound formed is decomposed with the formation of a radical, which is adsorbed on the surface:



The radicals adsorbed on the surface will have different properties from ordinary free radicals. They may in fact initiate the polymerisation of monomer, which is adsorbed on the surface as well:



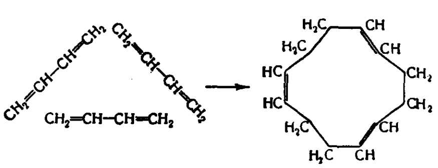
A recently published work by Japanese authors[46], concerning the additional catalytic effect of oxygen compounds on the polymerisation of vinyl monomers initiated by organometallic compounds is of interest. In this work the effect of molecular oxygen, peroxides (organic and inorganic), salts of silver, copper, and other auxiliary catalysts on the catalytic activity of organometallic compounds of boron, cadmium, zinc and aluminium was studied. It was shown that the behaviour of the oxygen compounds was connected with the nature of the central atom in the organometallic compound. A large accelerating effect was observed in polymerisation initiated by triethylboron. It should be noted that molecular oxygen, in an appropriate amount, accelerated polymerisation, but became an inhibitor when present in excess. These results suggest that molecular oxygen can react with organometallic compounds, forming an active radical, which initiates polymerisation. Excess O_2 breaks the radical chain in the same way as in ordinary radical polymerisation. The authors propose the following mechanism. They regard this type of polymerisation as a new form "redox" polymerisation. The organometallic compound may react, for example with a peroxide, as follows:



$$R{-}\underset{R}{\overset{R}{M}}+:\underset{\underset{R'}{:O:}}{\overset{R'}{O}}: \longrightarrow \left[R{-}\underset{R}{\overset{R}{M}}{}^{-}\longleftarrow\underset{\underset{R'}{:O:}}{\overset{R'}{O}}:^{+}\right] \longrightarrow R{-}\underset{R}{\overset{R}{M}}{-}\overset{R'}{O}:+RO\cdot+R\cdot$$

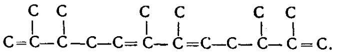
where M may be Al or B. The free radicals formed initiate polymerisation.

The experimental data of Wilke[47] indicating the exceptional selectivity of organometallic catalysts of the Ziegler type are of great theoretical and practical interest. The author showed that a catalyst, consisting of $TiCl_4$ and R_2AlCl, which polymerises ethylene to high-molecular polyethylene, converts butadiene almost exclusively to one specific oligomer. The elucidation of the structure of this oligomer, however, led to a far more important result. The authors had discovered that the ethylene polymerisation catalyst causes cyclisation of three molecules of butadiene into a ring and that the oligomer represents 1, 5, 9-cyclododecatriene.



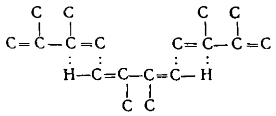
The oligomerisation process, with the catalysts indicated, takes place selectively to form a specific isomer. Thus, $TiCl_4 + R_2AlCl$ gives only *trans, trans, cis*-1, 5, 9-cyclododecatriene. Another cyclododecatriene isomer, for example, *trans, trans, trans*-1, 5, 9-cyclododecatriene, can be synthesised by using the $CrCl_3 + R_3Al$ catalyst system or R_2HAl. The study of the cyclisation of butadiene led the author to investigate the reaction of organometallic catalyst complexes with other conjugated diolefines such as isoprene, piperylene and 2, 3-dimethylbuta-1, 3-diene. In the course of this investigation a new kind of addition mechanism by conjugated diolefine monomers was discovered.

It was shown that 2, 3-dimethylbuta-1, 3-diene reacts with a chromium catalyst; the reaction product is not however, a homologue of cyclodecatriene, but an open-chain trimer of dimethylbutadiene. The structure of this compound was established by means of infra-red spectroscopy:



$$C{=}\overset{C}{C}{-}\overset{C}{C}{-}C{-}C{=}\overset{C}{C}{-}\overset{C}{C}{=}C{-}C{-}\overset{C}{C}{-}\overset{C}{C}{=}C.$$

The oligomer was formed by addition of the H–C = groups of the middle molecule to the double bonds of the two end molecules:



$$\begin{matrix} C{=}\overset{C}{C}{-}\overset{C}{C}{=}C & & C{=}\overset{C}{C}{-}\overset{C}{C}{=}C \\ \vdots & & \vdots \\ & H{-}C{=}\underset{C}{C}{-}\underset{C}{C}{=}C{-}H & \end{matrix}$$

This addition mechanism with hydrogen transfer in the interaction of organometallic catalyst complexes with conjugated diolefines had not been observed until recently. The situation becomes more complicated in the case of isoprene, which reacts partly like butadiene and partly like dimethylbutadiene.

The polymerisation of unsaturated hydrocarbons in the so-called canal compounds[48] offers considerable interest as regards the elucidation of the nature of sterospecific polymerisation and the conditions necessary to effect it. Therefore, although this goes somewhat beyond the scope of the present paper, we shall now turn our attention to the polymerisation of unsaturated hydrocarbons in the presence of such systems. It was found that 2, 3-dimethylbuta-1, 3-diene forms a molecular canal compound with thiourea in which the monomer is polymerised. The rate of formation of the canal compound and the rate of polymerisation depend on the purity of the reagents used.

The canal polymer obtained is in the form of white flakes which on drying in air become grey and melt at 175°–225°. After prolonged water treatment the polymer contained approximately 2.5% S and 2.2% N. It thus appears that every hundredth thiourea molecule participates in the polymerisation. Five high-molecular crystalline polymers, synthesised by irradiating the monomer oriented in urea canal complexes have also been described[49]. These were polybutadiene, polyacrylonitrile, polyacrolein, polyvinyl chloride and a copolymer of vinylchloride and acrylonitrile. Canal polymerisation was studied in the case of 13 different compounds altogether. The authors believe that isotactic and syndiotatic polymers can be obtained in this way. From our point of view the possibility of polymerisation with optically active urea deserves special attention. White and Brown[49] suggested that optically active polymers might be synthesised in this way from inactive monomers. Unfortunately in the last 3–4 years no new data have been obtained in the field of canal polymerisation, and the subject has received little attention.

In recent years, a number of papers, devoted to stereospecific polymerisation of unsaturated compounds containing polar groups have been published. It was shown that under certain conditions the stereospecific polymerisation of a variety of unsaturated compounds, not only of the hydrocarbon series, is practicable. Using the common catalyst system $R_3Al + TiCl_3$ in a saturated hydrocarbon medium, crystalline stereoregular polyvinyl chloride was obtained successfully[50]. It was shown that to form more stable catalyst complexes, it is expedient to use certain complex-forming additives, for example, ethyl ether, dioxane, amines.

4. SOLUBLE ORGANOMETALLIC COMPLEX POLYMERISATION CATALYSTS

The typical Ziegler catalysts considered above are insoluble in the reaction medium. In recent years interest has arisen in the study of completely soluble polymerisation catalysts.

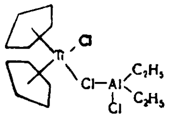
This is because comparison of the catalytic activity of homogeneous and heterogeneous catalysts gives a definite answer to the very important question whether the success of polymerisation depends on the presence of a solid surface. Up to the present, many investigators have held the opinion that Ziegler catalysts owe their high activity to their heterogeneity. Moreover, the presence of a solid surface presents the greatest difficulty in studying the process mechanism. The study of the kinetics in a homogeneous medium makes it possible to avoid this.

Polymerisation by soluble catalysts has also certain practical advantages. Each ionic bond in the soluble complex can react with the monomer and initiate the growth of a polymer chain. With a heterogeneous catalyst, only a small part, directly on the surface, is active. By virtue of this the consumption of a homogeneous catalyst is far less. In addition, unreacted catalyst is not left contaminating the polymer and this considerably eases the cleaning of the polymer – a very laborious step in the manufacturing process. In this case also, there is no danger of deactivating the catalyst through it being blocked by the polymer. Soluble catalysts give a far narrower molecular weight distribution in the polymer since in the course of polymerisation the amount of catalyst remains relatively constant.

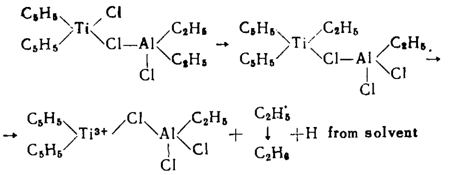
Natta[51] and Breslow[52] first reported the soluble complex compounds which are formed from $(C_5H_5)_2TiCl_2$ and organic aluminium compounds and are active in the polymerisation of ethylene to high-molecular products. It was shown[53] that in a solution of the complex, titanium is present in the trivalent state. Reduction of Ti^{4+} evidently involves three steps: (1) formation of a complex between the "sandwich" dichloride and the aluminiumalkyl compounds; (2) alkylation of the "sandwich" dichloride; (3) homolytic scission of the alkyl–titanium bond. The first stage of complex formation takes place very rapidly:

$$2(C_5H_5)_2TiCl_2 + 2(C_2H_5)_2AlCl \rightleftharpoons 2(C_5H_5)_2TiCl_2 . (C_2H_5)_2AlCl.$$

One possible structure of the complex is



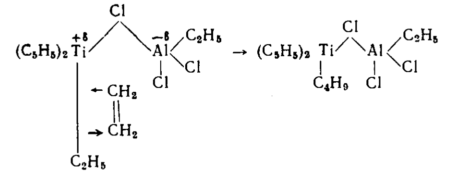
The complex is far more soluble in hydrocarbons than the original "sandwich" compound. This indicates that the bond in the complex is covalent:



The second and third stages are rather complicated. For instance, it is not clear why $(C_2H_5)_3Al$ causes very rapid reduction but $(C_2H_5)_2AlCl$ is slow-acting. Evidently, the stability of the Ti–C bond depends on the type of compound with which complex formation takes place, or it is possible that reduction involves dialkylation, and $(C_2H_5)_3Al$ is a more powerful alkylating agent than $(C_2H_5)_2AlCl$.

The complex of trivalent titanium is a very poor ethylene polymerisation catalyst. This is in keeping with the data of Natta[50] regarding the complex obtained with $(C_2H_5)_3Al$. However, a fresh mixture of $(C_5H_5)_2TiCl_2$ and $(C_2H_5)_2AlCl$ becomes a very active catalyst if the ethylene contains traces of oxygen. In the latter case a change in the colour shows quite definitely that the oxygen leads to the formation of a compound of tetravalent titanium. In this way it was established that in order for the given soluble catalytic system to be highly active, it must contain a certain amount of tetravalent titanium. However, it has not yet been demonstrated whether the presence of Ti^{4+} is the only requirement or whether a mixture of Ti^{4+} and Ti^{3+} is needed for high activity.

The active form of the catalyst is possibly the compound $(C_5H_5)_2Ti^{4+}(C_2H_5)Cl.(C_2H_5)AlCl_2$ or the product of its interaction with ethylene[53,54]. Growth of the polymer chain takes place by the introduction of a monomer molecule between the alkyl group and Ti:



The first stage of the polymerisation evidently includes the formation of a π-complex between titanium and the olefine. All co-ordination potentialities of aluminium are already exhausted and therefore formation of a complex of olefine and aluminium is improbable. The function of R_3Al is to alkylate Ti and by subsequent redistribution of electrons to increase the power of titanium to form complexes.

The second step is the conversion of an ethyl group (or a long alkyl chain in a growing polymer) to ethylene and the formation of a new titanium–carbon bond. Chain growth on a titanium atom seems all the more likely as catalytic polymerisation systems which include only titanium compounds are known. Thus, the products of irradiated $TiCl_4$ can by themselves polymerise ethylene to a high-molecular product[55]. R_3Al may be replaced successfully by other reducing agents, including the alkyls of alkali metals[56–59]. However, additional evidence is required on this point.

With compounds of titanium (or other transition metals) of the lowest valency, a more stable metal–carbon bond is realised. This in turn increases the life of the active centres and consequently leads to polymers of higher molecular weight being obtained.

On the other hand, from what has been said above, the formation of a highly active catalyst requires that a certain amount of Ti^{4+} be present. This was confirmed by a study of the kinetics of ethylene polymerisation by the $(C_5H_5)_2.TiCl_2 + (CH_3)_2AlCl$.[60] The process of chain initiation includes the rapid reaction of the catalyst components to form an inactive complex, which is then transformed into a complex possessing catalytic activity. This process takes place with measurable speed. The rate constant of initiation depends on the Al:Ti ratio, and as this increases, initiation takes place more slowly.

Three types of structure may be postulated for the active complex, differing mainly in the position of the alkyl groups which are involved in the growth of the polymer chain: (1) the alkyl groups bridge the Ti and Al atoms; (2) the alkyl groups are joined only to Ti; (3) the alkyl groups are joined only to Al.

The first two possibilities are the most likely, since, as was already noted in section 2, catalytic systems are known which consist only of titanium compounds, for example: CH_3TiCl_3, $CH_3TiCl_3-TiCl_3$, $(C_5H_5)_2Ti(C_6H_5)_2-TiCl_4$, etc. The function of R_3Al consists of alkylating Ti^{4+}. In addition, R_3Al acts as a Lewis acid, producing a deficit of electrons in the titanium and thus facilitating the complex formation between titanium and ethylene.

The chain-propagation stage includes the formation of a complex by the overlapping of the ethylene π electrons with the 3*d* orbitals in titanium. This is followed by displacement of an alkyl group from Ti to C_2H_4 and conversion of the link between the latter and Ti to a σ bond. All this agrees with the mechanism discussed before[53]. The total activation energy of the polymerisation of ethylene with the catalytic system $(C_5H_5)_2TiCl_2$ + $(CH_3)_2AlCl$ was found to be 11.75 kcal mole^{-1}.

It was shown that on average each methyl group taking part in the initiation of a polymer chain gives one polymer molecule. The number of polymer molecules formed on $(C_5H_5)_2TiCl_2$ is usually greater than unity, and it increases with increasing Al:Ti ratio. Thus it is evident that Ti^{4+}, before it is reduced to Ti^{3+} with homolytic scission of the Ti–C bond, takes part in the initiation and growth of more than one macromolecule. The trivalent titanium complex is not a catalyst for the polymerisation of ethylene at room temperature and atmospheric pressure.

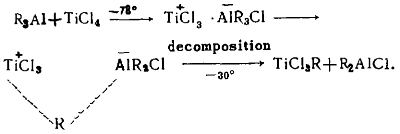
In work with a complex labelled with a ^{14}C atom it was established that rupture of the Ti–C bond is followed by disproprortionation, and not recombination, of the alkyl radicals formed.

Table 3 shows the principal properties of polyethylene, obtained with the soluble catalyst system $(C_5H_5)_2TiCl_2$ + + $(C_2H_5)_2AlCl$. The properties of polyethylene, obtained with a heterogeneous Ziegler catalyst, are given for comparison. It is evident that the soluble catalyst forms a highly linear polymer with a higher melting point and a considerably narrower molecular weight distribution.

In the light of the work on soluble complexes discussed above, it may be concluded that the presence of a solid surface is not a requisite condition for the catalytic polymerisation of ethylene to a high-molecular product.

In an investigation of the soluble catalyst system $(C_5H_5).TiCl_3$ + R_3Al in ethylene polymerisation[61], it was found that the catalyst was only active when a certain amount of HCl was added. Evidently, this is related to the data discussed above, regarding the role of electrophilic reagents in the formation of an active organometallic catalyst. The polyethylene obtained with this catalyst system has practically the same properties as the polymer synthesised with ordinary Ziegler catalysts.

Soluble complexes of $TiCl_4$ and R_3Al formed at low temperatures are also known[62]. It is thought that this occurs by the addition of a chlorine atom to aluminiumalkyl.



$$R_3Al+TiCl_4 \xrightarrow{-78°} \overset{+}{Ti}Cl_3 \cdot \overset{-}{Al}R_3Cl \longrightarrow \overset{+}{Ti}Cl_3 \quad \overset{-}{Al}R_2Cl \xrightarrow[-30°]{\text{decomposition}} TiCl_3R+R_2AlCl.$$

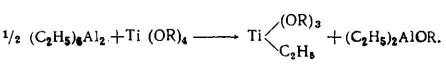
On decomposition of the complex the stable Al–C bond is broken and the less stable Ti–C bond is formed.

TABLE 3.

Properties of polyethylene	Soluble catalyst	Ziegler catalyst
Intrinsic viscosity	2.3	2.3
Melting point, °C	137	132
Crystallinity, %	85	79
$\bar{M}_w/\bar{M}_n$	3.6	7.0
Methyl groups, %	0.05	0.86
Vinyl groups, %	0.036	0.044
Vinylidene groups, %	0.006	0.007

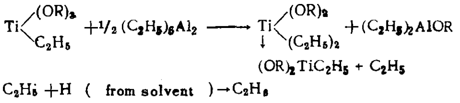
Under these conditions, with the soluble (iso-$C_4H_9)_3Al$ + + $TiCl_4$ catalyst complex, a fairly constant rate of polymerisation of ethylene was observed. Curiously, determination of the valency state of titanium in the soluble complex at -78° showed that about 90% Ti^{4+} was present. Partial reduction might have occurred through small amounts of hydride present in the aluminiumalkyl. It was shown experimentally that it was not necessary for the entire polymerisation process to be carried out at the low temperature, which is needed to ensure sufficient stability of the soluble complex being formed. A low temperature is required only at the beginning of the polymerisation reaction; when chain growth has started on all the catalytic centres (this is observed visually by the disappearance of the dark-red colour from the reaction medium), polymerisation can be continued successfully at room temperature. The polyethylene obtained in this way has a melting point of 128° – 130° and 80% crystallinity. At -75° propene was either not polymerised at all or showed only traces of polymer, but at a higher temperature, -20° to -30°, a polymer was formed. The properties of the product were not determined[62]. Nevertheless the polymerisation of propene in the presence of soluble catalyst complexes is of very great interest in extending our ideas on the nature of stereospecific catalysis and the role of surface effects in it.

In the study of the kinetics of ethylene polymerisation in the presence of R_3Al and s-butyl titanate[63], it was found that the most active catalyst is formed with an $(C_2H_5)_3Al$: : titanium ratio of 3 : 1. The authors explain this by the fact that interaction between the catalyst components takes place in the following way:



$$\tfrac{1}{2}\,(C_2H_5)_6Al_2 + Ti\,(OR)_4 \longrightarrow Ti\begin{matrix}(OR)_3\\ C_2H_5\end{matrix} + (C_2H_5)_2AlOR.$$

Formation of the insoluble titanite $Ti(OR)_3$ was not observed, the catalytic system remaining homogeneous throughout.



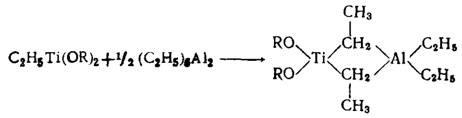
$$Ti\begin{matrix}(OR)_3\\ C_2H_5\end{matrix} + \tfrac{1}{2}\,(C_2H_5)_6Al_2 \longrightarrow Ti\begin{matrix}(OR)_2\\ (C_2H_5)_2\end{matrix} + (C_2H_5)_2AlOR$$

$$\downarrow$$

$$(OR)_2TiC_2H_5 + C_2H_5$$

$$C_2H_5 + H \text{ (from solvent)} \rightarrow C_2H_6$$

Later alkyl titanite is co-ordinated to a third molecule of aluminiumalkyl:

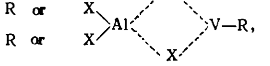


co-ordination compound

The co-ordination compound formed is an active catalyst complex with electron-deficient bonds, which is a general feature of catalyst systems of this type. Inhibition by alkyl halides, alcohols, and other polar molecules is explained by their interaction with the active complex and breakdown of the latter.

The authors[63] assert, albeit without any evidence, that homogeneous co-ordination compounds of this type can behave like the heterogeneous catalyst used in stereospecific polymerisation. However, Natta[64] found that the $Ti(OR)_4$ + + $(C_2H_5)_3Al$ catalyst complex, active in the polymerisation of ethylene, did not catalyse the polymerisation of propene. In our opinion this is due to the fact that reaction conditions (temperature, pressure, etc.) had not been found in which the polymerisation of propene becomes feasible.

According to Carrick's data[65,66], vanadium chloride may be employed instead of $TiCl_4$ in the formation of an active complex for the polymerisation of ethylene. A catalyst complex was formed by the interaction of $AlBr_3$, an organoaluminium compound [$(C_6H_5)_3Al$ or $(iso\text{-}C_4H_9)_3Al$], and vanadium chloride in a cyclohexane medium. The following structure is ascribed to the soluble catalyst complex:



where X—halide, R—aryl or alkyl radical.

Polarographic analysis established that the vanadium is present in the catalytic complex in the divalent state. It is stated that the function of the R_3Al in the formation of the catalyst complex is confined to reducing the vanadium to the divalent state and alkylating it in order to obtain the active form of the catalyst—RVX. These data are in good agreement with the above observations on the polymerisation of ethylene with R_3Al and the halides of titanium[14]. The role of $AlBr_3$ is to dissolve and stabilise the active vanadium part of the complex. In addition the $AlBr_3$ prevents further reduction of the vanadium. The polymerisation of ethylene with the vanadium catalyst complex was carried out at atmospheric pressure at 60°. The polyethylene obtained is highly linear (one methyl group per 1000 C atoms) and contains few double bonds (less than one C = C bond per 5000 C atoms). Propene and other α-olefines are not polymerised with this catalyst.

In order to explain the true nature of the active polymerisation centres in organometallic complex catalysts, Natta[67] and coworkers isolated three complexes in the pure state by crystallisation from solution. These contained titanium and aluminium with the general formula $(C_5H_5)_2.TiCl_2AlR_1R_2$, where R_1 and R_2 are chlorine atoms or ethyl groups. Some physical properties are given in Table 4. All the complexes are easily soluble in aromatic hydrocarbons and can be crystallised from n-heptane.

From a study of the chemical properties of these compounds and X-ray examination of their lattice structure, the authors concluded that two cyclopentadienyl nuclei are joined to a titanium atom whilst the latter is joined to aluminium through two chlorine bridges. The presence of chlorine bridges was also confirmed by reaction with trimethylamine.

All three complexes initiate the polymerisation of ethylene to form high-molecular polymers. However, the complex which does not contain alkyl groups shows extremely low activity. With the complexes containing ethyl groups, it was found by means of ^{14}C labelled alkyl groups, that each polymer chain contains one ethyl group originally present in the complex. Similarly with the complex containing four chlorine atoms in the molecule, $(C_5H_5)_2TiCl_2.AlCl_2$, it was established by means of labelled cyclopentadienyl groups that these groups were present in the polymer chains. Therefore, polymerisation of ethylene by the above complexes takes place *via* an anionic co-ordination mechanism through the introduction of monomer molecules at the organometallic bonds Al—C or Ti—C.

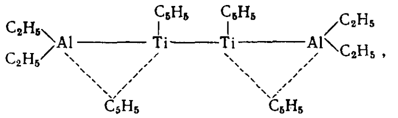
TABLE 4.

Complex	M.p., °C	Magnetic moment*
$(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	126—130	1.70
$(C_5H_5)_2TiCl_2AlC_2H_5Cl$	88—92	1.57
$(C_5H_5)_2TiCl_2AlCl_2$	155—160	1.72

* Trivalent titanium has one unpaired electron in the *d* orbital and this is the cause of the paramagnetic properties of the complexes.

With increase in the number of alkyl groups in the complexes, their cationic activity is increased and they become capable of initiating the stereospecific polymerisation of vinyl ethers[68]. The complex $(C_5H_5)_2TiCl_2(C_2H_5)AlCl$ is an example of a catalyst capable of initiating stereospecific polymerisation by two different mechanisms, cationic and anionic, depending on the capacity of the monomers to be polymerised by one or other of the mechanisms.

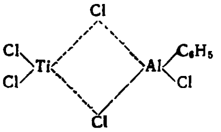
By interaction of $(C_5H_5)_2TiCl$ in benzene at 80° with excess $(C_2H_5)_3Al$, a red crystalline product was obtained, which dissolved readily in aromatic hydrocarbons and melted (with decomposition) at 169°—171°. Chemical analysis and molecular-weight determination indicated that the compound had the formula $[(C_5H_5)_2Ti(C_2H_5)_2Al]_2$,[69] in which two cyclopentadienyl rings are joined to an atom of titanium. X-Ray examination showed that two types of cyclopentadienyl groups were present in this compound, two being joined to Ti atoms by means of σ, π-bonds and two joined to Al by σ, σ-bonds. The position of the latter two cyclopentadienyl groups suggests that they may be connected by a bridge both to Ti and to Al and in addition by π-bonds to Ti. The complex possesses diamagnetic properties owing to the presence of the Ti—Ti bond. Each Ti atom, moreover, gives up an electron pair to an Al atom, forming a dative Ti—Al bond.



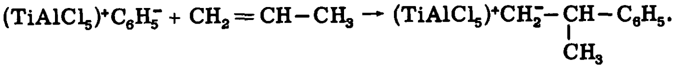
The tricentric electron-deficient bonds are denoted by broken lines.

The complex is a catalyst for the polymerisation of ethylene to high-molecular products and in conjunction with α-$TiCl_3$ forms a catalyst system, which initiates highly stereospecific polymerisation of propene (the polypropylene contains far more isotactic molecules of high molecular weight than with the ordinary catalyst system $(C_2H_5)_3Al$ + + α-$TiCl_3$). The higher stereospecificivity and the higher degree of polymerisation may be attributed to the fact that here chain transfer between the growing polymer chain and alkyl groups present in the catalyst system is more restricted.

The complex with the general formula $Al_2TiCl_8C_6H_5$ [70] was also obtained by reaction of $TiCl_4$, $AlCl_3$, Al and benzene on heating to 80° for 7 h. This complex melts at 110°—115° (with decomposition), is easily dissolved in benzene and toluene, and is slightly soluble in aliphatic hydrocarbons. In the presence of oxygen and moist air it gives off HCl and phenol and with water in the absence of oxygen it yields benzene. This indicates that the phenyl group is joined to metal by a σ-bond. By decomposing the complex with dilute HCl and titrating with iron sulphate it was established that the titanium is in the trivalent state. On treating the complex with compounds containing a free electron pair, such as tetrahydrofuran, dibutyl ether, pyridine, or trimethylamine at room temperature, the loss of one molecule of $AlCl_3$ was observed. This accords with the formula $[AlTiCl_5C_6H_5].AlCl_3$:



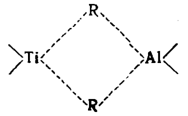
This complex, suspended in heptane, catalyses the polymerisation of ethylene, with the formation of a low-molecular fraction along with crystalline polymers of high molecular weight. The solid microcrystalline complex $AlTiCl_5C_6H_5$ polymerises ethylene at a higher rate than does $[AlTiCl_5C_6H_5].AlCl_3$. In this, only high-molecular polymers are obtained. The complex is also an active catalyst in the polymerisation of propene. The polypropylene formed contains isotactic, stereo-block, and atactic fractions. The following mechanism is proposed for polymer chain growth in the presence of the complex $AlTiCl_5.C_6H_5$:



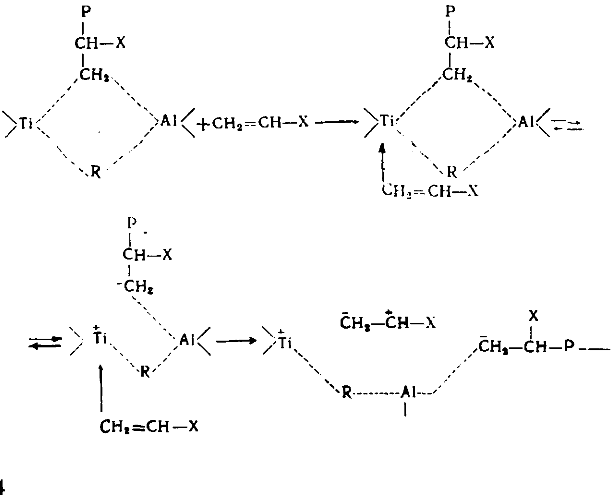
$$(TiAlCl_5)^+C_6H_5^- + CH_2{=}CH{-}CH_3 \rightarrow (TiAlCl_5)^+CH_2^-{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}C_6H_5.$$

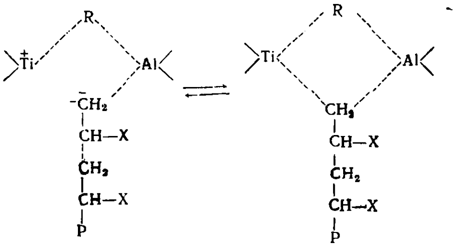
The presence of phenyl groups in the polymer chains was confirmed by infra-red spectroscopic analysis.

From the above discussion, a definite conclusion may be reached: all active polymerisation catalysts are electron-deficient organometallic complexes, which contain at least two metal atoms in their molecules, and polymerisation takes place by introduction of a monomer molecule in the bridge formed by alkyl groups between Ti and Al by means of tricentric bonds:



In this case it is difficult to determine whether the chain grows on the Ti or on the Al atom.





The first stage in monomer addition to the complex is determined by the high electron density in the double bond and a deficiency of electrons in the transition-metal complex.

However, until now the question of the valency of the transition metal in the active form of the catalyst complex remains unsolved. Some investigators[43] think that the catalyst owes its activity to trivalent titanium: others[14] quote experimental data showing that the most active valency state of titanium in the formation of a catalyst complex is Ti^{2+}; a third group[53] points to the necessity for heterovalent titanium (a mixture of Ti^{3+} and Ti^{4+}) to be present.

All the same, it is evident that it is not the valency state of titanium which is responsible for the catalytic activity but the presence of an electron-deficient bridge bond between Ti and Al. The valency state of the transition metal exerts a substantial effect on the stability of the metal–carbon bond. A reduction in valency leads to the formation of a more stable bond[17] and consequently to a longer life of the active centres.

It has been established that even stereospecific polymerisation, with the exception of polymerisation of α-olefines, does not necessarily require the presence of a solid phase. Thus isotactic and syndiotactic polymers were obtained from diolefines using soluble catalysts, formed by reaction between chromium acetylacetonate and R_3Al.[72]

Soluble catalysts are also known for the stereospecific polymerisation of alkyl vinyl ethers[68]. These compounds, such as $(R_2AlCl)_2$, $TiCl_2(OR)_2$, products of the reaction between $(C_5H_5)TiCl_2$ and R_3Al, etc. have weak cationic activity.

When the monomer contains two electron-rich groups (two double bonds in diolefines or one double bond and one oxygen with a pair of free electrons in vinyl ethers), then before addition of the monomer to the growing polymer chain, it associates with the electron-deficient catalyst, even if the catalyst does not contain a heterogeneous phase capable of adsorbing the monomer. This explains the stereospecific nature of the process in the presence of soluble catalyst complexes.

TABLE 5. Properties of methylmethacrylate polymers.

Type of solvent	Polymer properties		Density of Polymer at 30°(amorph) g ml^{-1}	Suggested chain configuration
	vitrification temp., °C	M.p., °C		
Strongly solvating	115	>200	1.19	isotactic
Weakly solvating	45	160	1.22	syndiotactic
Moderately solvating	60—95	170	1.20—1.22	stereo-block polymer

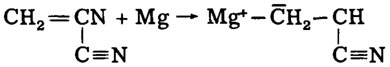
In the homogeneous catalytic polymerisation of methyl methacrylate with butyllithium or other organolithium compounds polymers of regular structure were also obtained (reaction temperature -50° to -80°).[73] It was shown that the nature of the reaction medium exerts a considerable influence on the stereospecific nature of the polymer. Thus, with a weakly solvating medium (toluene or hexane), isotactic polymethacrylate is formed but in a pyridine medium a syndiotactic polymer is obtained. In moderately solvating medium a stereo-block polymer is formed.

As was shown for the stereospecific polymerisation of methyl methacrylate, it is possible to use not only organolithium compounds, for example lithium fluorenyl, but also, apparently, other homogeneous catalyst systems[74]. Various types of stereoregular polymers were obtained in solvents of different solvating power.

5. THE ROLE OF PREVIOUS ORDERING OF THE MONOMER IN THE FORMATION OF THE POLYMER CHAIN MICROSTRUCTURE

Work carried out in recent years by Soviet investigators has demonstrated the role of previous ordering of the monomer in the formation of the polymer chain microstructure. The initiating power of certain metals in molecular mixtures with monomers[75] was investigated by applying for the first time the method of molecular beams in the polymerisation reaction. It was found that rapid low-temperature block polymerisation took place in molecular mixtures of metallic magnesium with a series of monomers (acrylonitrile, methyl methacrylate, methyl acrylate).

Polymerisation of acrylonitrile in the presence of magnesium in a frozen molecular mixture was studied by means of electron spin resonance[76]. It was shown that in this system polymerisation takes place by a radical mechanism. The formation of radicals, so the authors presume, occurs by interaction of the monomer vapour and magnesium:



$$CH_2{=}\underset{\substack{|\\ C\equiv N}}{C}N + Mg \rightarrow Mg^{+}-\bar{C}H_2-\underset{\substack{|\\ C\equiv N}}{C}H$$

These radicals together with excess of the monomer are condensed on a surface cooled by liquid nitrogen, and initiate polymerisation in the frozen mixture. However, we think that this hypothesis has not yet been supported by enough experimental data and the mechanism of this very interesting reaction should be investigated further. The fact that the polymethylmethacrylate obtained by this method has an isotactic structure deserves special attention. Until now only a syndiotactic polymer could be obtained from methacrylate by ordinary radical polymerisation.

Interesting data were also obtained in the study of the polymerisation of styrene with the $R_3Al + TiCl_3$ catalyst by the molecular-beam method[77]. It was found that $TiCl_3$, which does not usually act as a catalyst in the polymerisation of vinyl compounds, on being dispersed in polystyrene rapidly initiates polymerisation to form a non-stereoregular polymer. In a joint condensation of molecular beams of styrene, $TiCl_3$, $(C_2H_5)_3Al$ and solvent rapid non-stereospecific polymerisation occurs, as it does also in the absence of $(C_2H_5)_3Al$. This, evidently, is explained by the high rate of polymerisation of styrene by $TiCl_3$ which exceeds the rate of formation of the catalyst complex $TiCl_3 + (C_2H_5)_3Al$. The authors of this work presume that the polymerisation rate with these complexes is very small at low temperatures. Slow stereospecific polymerisation of styrene takes place only when the monomer is introduced into the reaction after the formation of $TiCl_3$ crystals. The low-temperature polymerisation of styrene with the $(C_2H_5)_3Al + TiCl_4$ catalyst system was also studied by means of an original method, developed by Kabanov *et al.*[77], based on microscopic observation of the polymerisation process in a glass capillary. It was shown that stereospecific polymerisation was possible only when interaction between $(C_2H_5)_3Al$ and $TiCl_4$, with the formation and crystallisation of $TiCl_3$, occurred in the absence of the monomer. When the $TiCl_3$ crystals are formed, it loses the power of initiating rapid non-stereospecific polymerisation.

The role of crystal defects in the initiation of polymerisation was observed in the polymerisation of crystalline acrylate salts and methacrylic acid[78]. In the study of the sodium acrylate–LiCl and sodium acrylate–$MgCl_2$ systems, it was found that rapid polymerisation of the acrylate began on adding just enough of a 50% aqueous C_2H_5OH solution to wet the crystals. In this case the process of polymerisation depends on a heterogeneous exchange reaction between the salts which takes place the moment the mixture is moistened. As a result of this reaction a new crystalline phase (NaCl) emerges and forms nonequilibrium crystallisation catalysts with the crystals of the monomer salt. In the opinion of the authors, defects in the crystal structure, forming at the points of contact, serve as the centres of initiation, for example, "excess" ions stuck in the monomer lattice.

Effective initiation of the polymerisation of crystalline acrylates and methacrylates also occurs on mechanical dispersion of these salts, when defects in the monomer structure are created.

A whole series of monomers (styrene, methyl methacrylate) were polymerised when subjected to intense mechanical grinding with inorganic substances (quartz, graphite, sodium chloride), which in the ordinary state are not polymerisation catalysts[79]. In mechanical dispersion, continuous splitting of particles of the crushed substance takes place with the formation of new solid surfaces which in the first moment are free of adsorbed layers and by virtue of this possess considerable reactivity.

It is interesting that in the grinding of quartz, not only initiation of polymerisation takes place but also chemical grafting of the polymer being formed to SiO_2. This is not difficult to imagine, if it is borne in mind that in the dispersion of the quartz, radicals of the type Si–O– or Si– emerge and introduction of the inorganic substance into the polymer may occur.

The authors think that the mechanism of polymerisation on the exposed solid surface of the inorganic substance depends on the nature of the chemical bonds in the dispersed material and on the nature of the monomer. Thus the polymerisation of styrene by crushed NaCl evidently has ionic character and the polymerisation of styrene by quartz takes place with the participation of free radicals (the existence of free radicals during the dispersion of quartz has been shown experimentally).

In every case where dispersed inorganic substances were used as polymerisation initiators, the polymers formed had comparatively low molecular weights (of the order of 20 000–30 000). In the authors' opinion this is due to the fact that the concentration of active centres, initiating polymerisation, is rather high. As a result of this, the role of the recombination and disproportionation of the growing polymer radicals increases sharply. Another reason is that polymerisation is accompanied by destruction of the polymer chains.

The experimental data discussed in this paper and the theories evolved from them show, on the one hand, that full use has not yet been made of the possibilities of complex organometallic catalysts in polymerisation, and on the other hand, the large number of unsolved problems connected with the mechanism of stereospecific polymerisation. It is to be hoped that in the next few years we shall see new advances in the application of complex catalysts to the polymerisation of unsaturated compounds of different classes and structure.

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METHODS OF PREPARATION AND PROPERTIES OF SUBSTITUTED VINYL ETHERS AND SULPHIDES

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CONTENTS

INTRODUCTION

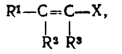
From the 'thirties onwards a large number of papers were published on the methods of preparation and the reactions of vinyl ethers[1-3], which, by virtue of their high chemical reactivity, have been used extensively in organic syntheses. Vinyl ethers[1-3] and vinyl sulphides[4,5] became easily accessible, especially after the industrial application of the Favorskii–Shostakovskii method of preparation:

$$CH\equiv CH + RXH \xrightarrow{\Delta,\ KOH} CH_2{=}CHXR,$$

where X = O, S, N, Si; R = alkyl, aryl.

With the growth in the industrial production of acetylene homologues, there is now a possibility of the latter being applied in the synthesis of substituted vinyl compounds.

Unlike unsubstituted vinyl ethers and vinyl sulphides, substituted ethers and sulphides of the general formula



$$\underset{\substack{|\\R^2}}{R^1{-}C}{=}\underset{\substack{|\\R^3}}{C}{-}X,$$

where R, R^1, R^2, R^3 = alkyl, aryl, halogen, and X = O, S, cannot easily be obtained and as a result are little known. Substituted vinyl ethers and sulphides are of considerable interest in preparative organic chemistry. Like their unsubstituted analogues[2,3], they can, in the presence of acid catalysts, add on a compound containing a mobile hydrogen atom; in this reaction the nature of the substituent has a considerable effect on the rate, yield, and stability of the product. Besides additions to the double bond, they are capable of a number of reactions which are brought about by the presence in the molecule of another reactive centre, such as an alkoxy or mercapto group, or a halogen atom.

The present review deals with the methods of preparation and the basic reactions of substituted vinyl ethers and sulphides and compares them with the like reactions of their unsubstituted analogues. For convenience, the reactions of ethers and sulphides are treated in separate sections.

The review does not cover diene ethers, which can be considered as substituted vinyl ethers containing unsaturated radicals R^1 or R^3, whose double bond is conjugated with that of the vinyl group. Methods of preparation of diene ethers were reviewed by Petrov[6] and Nazarov *et al.*[7]

I. PREPARATION OF SUBSTITUTED VINYL ETHERS

1. Preparation from α-Haloalkenes

Substituted vinyl ethers were first obtained by Butlerov[8] and El'tekov[9] by the reaction of alkenyl bromides with sodium alcoholates. In 1870 Butlerov synthesised β,β'-dimethylvinyl ethyl ether by the following reaction:

$$(CH_3)_2C{=}CHBr + C_2H_5ONa \rightarrow (CH_3)_2C{=}CHOC_2H_5.$$

This method[1-3] has found wide application in the synthesis of unsubstituted vinyl ethers from vinyl chloride. It is of limited value in the synthesis of alkyl-substituted ethers, owing to difficulties involved in the preparation of the starting α-haloalkenes. So far only a few papers have been published on the preparation of alkyl(aryl)-substituted ethers by this method[8-16]. Of note is the work of Niederl and Storch[12], who obtained isopropenyl aryl ethers by heating 2-bromopropene with potassium phenolate at about 48°:

$$CH_2{=}CBr{-}CH_3+ArOK \rightarrow CH_2{=}C(CH_3){-}OAr+KBr.$$

The authors of this review have been unable to reproduce these results. The experimental conditions are far too mild for the reaction to take place. The similar reaction of 2-chloropropene with sodium ethylate requires heating at 180° for several hours in an autoclave[13,14].

The Butlerov method is applied extensively in the preparation of the halogen derivatives of vinyl ethers from the easily obtainable polyhaloethylenes[17-26]. For instance, heating dibromoethyelene with potassium phenolate in an autoclave gives β-bromovinyl phenyl ether[17-19]:

$$CHBr{=}CHBr+C_6H_5OK \xrightarrow[-KBr]{} CHBr{=}CHOC_6H_5,$$

while trichloroethylene yields a series of β,β'-dichlorovinyl ethers[20-25].

2. Vinylation

Favorskii[27] discovered vinylation in 1887, in his attempt to prepare isopropenyl ethyl ether from methylacetylene and ethanol:

$$CH_3C{\equiv}CH+C_2H_5OH \xrightarrow{\Delta, KOH} CH_2{=}C(CH_3)OC_2H_5.$$

This reaction was later used for the preparation of unsubstituted vinyl ethers from acetylene. Its application in the preparation of substituted ethers from acetylene homologues is limited by the tendency of acetylenic hydrocarbons to isomerise under the action of the alcoholic alkali into disubstituted acetylenes and allenes[28,29], which are unable to react with alcohols. Those acetylenes which do not isomerise under the conditions of vinylation are used successfully for the preparation of substituted vinyl ethers. Thus, phenylacetylene reacts easily in alkaline solution with alcohols to form β-alkoxystyrenes[16,30-35]:

$$C_6H_5C{\equiv}CH+ROH \xrightarrow{KOH} C_6H_5CH{=}CHOR,$$

where R = CH_3, C_2H_5, C_3H_7, C_4H_9.

Trifluoromethylacetylene reacts with ethanol on merely mixing in an alkaline solution[36]:

$$CF_3C{\equiv}CH+C_2H_5OH \xrightarrow{KOH} CF_3CH{=}CHOC_2H_5.$$

Chloroacetylenes also react with alcohols[37,38], for example,

$$C_6H_5C{\equiv}CCl+C_2H_5OH \rightarrow C_6H_5CH{=}CClOC_2H_5.$$

Vinylation also includes the reaction of alcohols with diacetylene[39] and vinylacetylene[40]. They all yield β-substituted vinyl ethers as a result of the electron-withdrawing power of the acetylene substituents[34]. On the other hand, reaction of alcohols[41-43] and phenols[44] with methylacetylene yields α-substituted vinyl ethers. It should be noted that under the conditions of vinylation, namely in alkaline solution and at high temperatures, methylacetylene is in equilibrium with the isomeric allene:

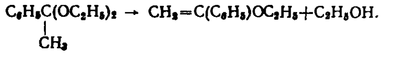
$$CH_3C{\equiv}CH \rightleftarrows CH_2{=}C{=}CH_2.$$

Physicochemical calculations[45] show that at high temperatures the equilibrium is shifted towards methylacetylene. This is consistent with the data on the isomerisation of allene at high temperatures to methylacetylene[46,47]. Consequently[44], allene, methylacetylene, or a mixture of the two, can be used in the synthesis of isopropenyl aryl ethers.

Preparation of alkyl(aryl)-substituted vinyl ethers by this method is limited by the impossibility of using alkylacetylenes in the reaction. For the preparation of vinyl ethers containing functional groups (COOH,[48] OR,[49] etc.), however, vinylation has great possibilities.

3. Decomposition of Ketals and Acetals

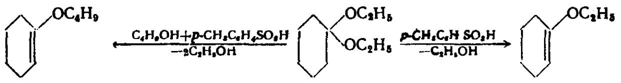
In 1896 Claisen[50,51], in a study of the properties of the ketals he had synthesised, discovered a method for preparing substituted vinyl ethers by the decomposition of ketals. Ketals were shown to eliminate readily a molecule of alcohol, sometimes merely on distillation. By distilling acetophenone ketal Claisen obtained α-ethoxystyrene[50]:



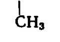
$$C_6H_5C(CH_3)(OC_2H_5)_2 \rightarrow CH_2{=}C(C_6H_5)OC_2H_5+C_2H_5OH.$$

Later he used catalysts to decompose ketals, for example, phosphorus pentoxide and quinoline (as in the preparation of isopropenyl ethyl ether)[51].

In further studies of the preparation of α-substituted vinyl ethers by this method, various other catalysts were used, in particular, p-toluenesulphonic acid[52,53], volatile mineral acids (in the vapour phase)[54], and catalysts containing noble metals of Groups I–VIII of the Periodic Table[55,56]. Of special interest is the work of Johanissian[52] and Nieuwland[53] who used the reversiblity of the decomposition of ketals in the presence of acid catalysts for the synthesis of substituted vinyl ethers. Johanissian, the first to use p-toluenesulphonic acid as a catalyst, carried out the synthesis according to the following scheme:



Similarly, Nieuwland synthesised a series of α-alkylvinyl ethers[53], from 2,2-dimethoxyalkanes, which, after his discovery of the reaction of alkylacetylenes with methanol in the presence of mercury and boron fluoride etheradduct[68], had become readily available:



$$RC{\equiv}CH+2CH_3OH \rightarrow R{-}C(CH_3)(OCH_3)_2$$

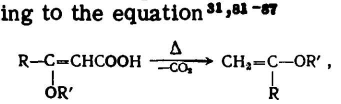
$$RC(CH_3)(OCH_3)_2+R'OH \xrightarrow{p\text{-}CH_3C_6H_4SO_3H} CH_2{=}C(R)OR'+2CH_3OH,$$

where R = CH_3, C_4H_9, C_5H_{11}, C_6H_5; R′ = CH_3, C_2H_5, C_3H_7, C_4H_9.

Under similar conditions acetals of type $RCH(OCH_3)_2$ do not yield unsaturated ethers derived from the alcohol used in the reaction. This is due to the harsher reaction conditions required for the decomposition of acetals[69-80]. Such decomposition is best carried out in the vapour phase, *e.g.* Sigmund and Uchann[62] passes acetal vapours over hot alumina. Noble metals deposited on asbestos, kieselguhr, etc., also act as catalysts in this reaction[55,56,69,70]. Nazarov and his collaborators[58] described a new catalyst ($MgHPO_4$, NaH_2PO_4), which yields 60–75% of ethers when acetal vapour is passed over it at 325°. This method is of considerable importance for the preparation of α- and β-substituted vinyl ethers.

4. Decomposition of Substituted α,β-Unsaturated Acids

Certain, mainly α-substituted, vinyl ethers have been prepared by thermal decomposition of unsaturated alkoxy-acids, according to the equation[31,81-87]



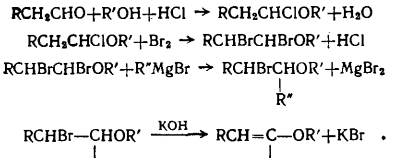
$$\mathrm{R{-}C(OR'){=}CHCOOH \xrightarrow[-CO_2]{\Delta} CH_2{=}C(R){-}OR'},$$

where R = CH_3, C_5H_{11}, C_6H_{13}, C_6H_5; R′= CH_3, C_2H_5, C_3H_7, C_6H_5, $C_6H_4CH_3$, $C_{10}H_7$.

This method has no preparative significance, as the alkyl-substituted vinyl alkyl ethers can be obtained more simply by the decomposition of acetals and ketals. But it is the only one for the preparation of ethers of the general formula $CH_2{=}C(Ar){-}OAr$.

5. Preparation from Halogen Derivatives of Ethers

(a) Elimination of the hydrogen halide from β-halo-ethers. Lauer and Spielman[88-89] were the first to prepare α,β-substituted vinyl ethers from β-halo-ethers[88-105], according to the scheme



$$\mathrm{RCH_2CHO+R'OH+HCl \rightarrow RCH_2CHClOR'+H_2O}$$
$$\mathrm{RCH_2CHClOR'+Br_2 \rightarrow RCHBrCHBrOR'+HCl}$$
$$\mathrm{RCHBrCHBrOR'+R''MgBr \rightarrow RCHBrCH(R'')OR'+MgBr_2}$$
$$\mathrm{RCHBr{-}CH(R'')OR' \xrightarrow{KOH} RCH{=}C(R''){-}OR'+KBr}\ .$$

The first three steps had been worked out earlier[90]. The particular value of this method lies in the fact that it yields ethers substituted in both the α- and β-positions, while nearly all the other methods mentioned above yield ethers substituted in either one or the other. α,β-Dibromo-ethers required for the preparation of α-substituted vinyl ethers can be obtained from vinyl alkyl ethers[92-94].

$$\mathrm{CH_2{=}CHOR+Br_2 \rightarrow CH_2BrCHBrOR.}$$

The hydrogen halide can be eliminated not only from β-bromo-ethers, but also from β-iodo-ethers[95] and β-chloro-ethers[96,97]; however, these cannot be so readily obtained.

A modification of this method is the elimination of hydrogen chloride from β-chloro-ethers by means of finely granulated metals (Cu, Al, Mg)[98]. The yield of α-propylvinyl methyl ether obtained by this method from 1-chloro-2-methoxypentane can reach 60%. Hydrogen chloride and the metal chlorides formed in the reaction can cause polymerisation and hydrolysis of vinyl ether, thereby lowering the yield. The use of excess alkali as in the Lauer method stops such processes and gives better yields.

(b) β-Alkylvinyl ethers from α-chloroalkyl ethers. A number of papers have recently appeared on the synthesis of vinyl ethers from α-chloro-ethers[106-108], which are readily obtainable from aldehydes and alcohols in the presence of hydrogen chloride. It has been shown[109] that the reaction of dimethylaniline with α-chloroethyl alkyl ethers hydrogen chloride splits off and vinyl ethers are formed. A number of β-alkylvinyl ethers was obtained by using organic bases to remove hydrogen chloride from α-chloroalkyl alkyl ethers[106-108]:

$$\mathrm{RCH_2CHClOR' \xrightarrow[HCl]{} RCH{=}CHOR'},$$

where R = CH_3, C_2H_5, C_5H_{11}; R′ CH_3, C_3H_7, C_4H_9, C_7H_{15}. The bases used were dimethylaniline[106] or triethylamine[107]. Unfortunately, in many cases the yields of ethers were not larger than 20–30%.

Erickson[108] prepared β-alkylvinyl ethers by the conversion of α-chloro-ethers into 1-alkoxyalkyl acetates, followed by pyrolysis:

$$\mathrm{RCH_2CHClOR'+CH_3COONa \xrightarrow[-NaCl]{} RCH_2CH(OCOCH_3)OR'}$$
$$\mathrm{RCH_2CH(OCOCH_3)OR' \rightarrow RCH{=}CHOR'+CH_3COOH},$$

where R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}; R′ = C_2H_5, iso-C_4H_9, $CH_2CH(C_2H_5)_2$, $CH(C_2H_5)C_4H_9$. The vinyl ethers formed can easily combine with acetic acid, which clearly makes the separation of the final products somewhat difficult.

(c) Some methods for the preparation of halogen derivatives of vinyl ethers. The difference in the chemical behaviour of halogen atoms in the α- and β-positions is used, in the same way as in the two preceding methods, for the preparation of β-halovinyl ethers from α,β-dihalo-ethers. It was shown in a number of papers[110-117] that under the action of organic bases (dimethylaniline, diethylaniline, pyridine) α,β-dihalo-ethers split off a molecule of hydrogen halide forming β-halovinyl ethers in good yields:

$$\mathrm{RCHX{-}CHXOR' \xrightarrow[-HX]{} RCHX{=}CHOR'},$$

where R, R′ = alkyl, X = Cl, Br.

The reaction of α,β-dihalo-ethers with inorganic bases does not yield vinyl ethers[110,118]; nonetheless, ethers of type $CCl_3CHClOC_2H_5$,[119] $CHClBrCClBrOC_2H_5$,[120] or C_6H_5.$CHBrCHBrOR$[121] split off hydrogen halide in the presence of alkali yielding the halogen derivatives of vinyl ethers, for example:

$$\mathrm{C_6H_5CHBrCHBrOR \xrightarrow{KOH} C_6H_5CBr{=}CHOR},$$

where R = CH_3, C_2H_5.

The mobility of the α-halogen atom is also utilised in the preparation of dihalovinyl ethers from tetrahaloalkyl ethers[79,122,123]:

$$\mathrm{CCl_3CHClOR \xrightarrow{Zn, alcohol} CCl_2{=}CHOR},$$

where R = CH_3, C_2H_5.

A variation of this reaction is the synthesis of β-halovinyl ethers from dibromo-acetals[124,125]:

$$\mathrm{CHX_2CH(OR)_2 \xrightarrow{Zn} CHX{=}CHOR},$$

where R = alkyl, X = Cl, Br.

Mention may be made of the interesting synthesis of α-methyl-β,β-dichlorovinyl alkyl ethers by the reaction of α,β,β,β-tetrachloroethyl alkyl ethers with Grignard reagents[126]:

$$\mathrm{CCl_3CHClOR+CH_3MgCl \longrightarrow CCl_2{=}C(CH_3)OR},$$

where R = CH_3, C_2H_5, C_3H_7. Unfortunately, no data on the yield of this reaction are available.

6. Miscellaneous Methods of Preparation

In addition to those described above, there are a number of special reactions which also lead to the formation of substituted vinyl ethers.

Favorskii and Shchukina[110,127] synthesised a number of alkoxyacetylenes from unsubstituted vinyl ethers, which reacted with hydrogen chloride to give α-chlorovinyl ethers:

$$HC\equiv COR \xrightarrow{HCl} CH_2=CClOR,$$

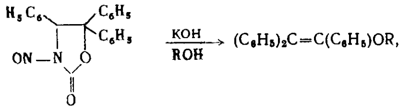
where R = C_2H_5, C_3H_7, C_4H_9.

It should be noted that, in contrast to the chlorine atom in α-chloroalkyl ethers, the α-chlorine in α-chlorovinyl ethers is inert in substitution reactions, *i.e.* it behaves in a way characteristic of a halogen atom attached to a double bond.

Arens[116] established the experimental conditions for the preparation of alkoxyacetylenes, and from them, β-chloro- and β-bromovinyl ethers. Of special note is the method whereby substituted vinyl ethers are obtained after the migration of the double bond in certain hydrocarbons under the action of potassamide in liquid ammonia. For instance, after the migration of the double bond, 3-butoxy-2-methylpropene yields β,β-dimethylvinyl butyl ether[129]:

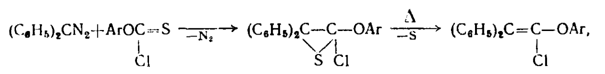
$$CH_2=C(CH_3)CH_2OC_4H_9 \xrightarrow{KNH_2} (CH_3)_2C=CHOC_4H_9.$$

Newman[130] described the preparation of some vinyl ethers, otherwise difficult to obtain, by the decomposition of substituted oxazolidones in alcoholic alkali:



where R = CH_3, C_2H_5.

Schönberg[131] obtained α-chloro-β, β-diphenylvinyl ethers by the following scheme:



$$(C_6H_5)_2CN_2+ArOC(Cl)=S \xrightarrow[-N_2]{} (C_6H_5)_2C\underset{S}{—}C(Cl)—OAr \xrightarrow[-S]{\Delta} (C_6H_5)_2C=C(Cl)—OAr,$$

where Ar = C_6H_5, 2,4,6-$Cl_3C_6H_2$.

There are a number of other papers[132-140] dealing with the formation of substituted vinyl ethers, but they are of little preparative significance.

II. PREPARATION OF SUBSTITUTED VINYL ALKYL-(ARYL) SULPHIDES

1. Preparation from Alkenyl Halides

The reaction of vinyl halides with mercaptides yields vinyl sulphides[3,141]; in the same way, substituted vinyl halides give substituted vinyl sulphides[142,143]:

$$RCH=CHBr+C_2H_5SNa \rightarrow RCH=CHSC_2H_5,$$

where R = CH_3, C_5H_{11}.

Trichloroethylene reacts with thiophenoxide to give α,β-dichlorovinyl aryl sulphides[144,145]:

$$CCl_2=CHCl+ArSNa \rightarrow CHCl=CClSAr.$$

However, in reactions of trichloroethylene with sodium ethylmercaptide[114] and of tetrachloroethylene with p-methylphenylmercaptide[146], instead of the expected chlorovinyl sulphides, products are obtained in which chlorine atoms are substituted further by ethylthio and p-tolylthio groups, respectively. Under similar conditions trichloroethylene and t-butylmercaptide react to form α,β-dichlorovinyl t-butyl sulphide[147], according to the equation

$$ClCH=CCl_2+NaSC(CH_3)_3 \xrightarrow[-NaCl]{} ClCH=CClSC(CH_3)_3.$$

2. Vinylation of Thiols

A number of papers by Truce and his collaborators[148-152] deal with the reactions of thiols with substituted acetylenes in alkaline solutions. They established this to be a stereospecific reaction involving nucleophilic addition, and yielding, as a rule, the *cis*-isomers, *e.g.* *cis*-β-p-tolylthiostyrene:

$$C_6H_5C\equiv CH+p\text{-}CH_3C_6H_4SNa \rightarrow p\text{-}CH_3C_6H_4SCH=CHC_6H_5.$$

In the main, the authors used acetylenes containing electron-withdrawing substituents such as C_6H_5, COOR, COC_6H_5, which facilitate the addition of thiols yielding in alkaline solution β-substituted vinyl sulphides[148-153]. These products are inconsistent with the Markownikoff rule. If acetylenes which do not contain an electron-withdrawing group are used, the addition results in "normal" reaction products. Thus, the authors showed that methylacetylene reacts with thiols giving α-methylvinyl sulphides:

$$CH_3C\equiv CH+RSH \xrightarrow{KOH} CH_2=C(CH_3)SR,$$

where R = C_2H_5, C_3H_7, C_4H_9, C_6H_5. These products are consistent with the Markownikoff rule.

A series of α,β-dichlorovinyl aryl sulphides was prepared by the reaction of dichloroacetylene with thiophenols[154]:

$$CCl\equiv CCl+ArSH \xrightarrow{C_2H_5ONa} ArSCCl=CHCl.$$

3. Decomposition of Mercaptoles

This method can be used in principle for the preparation of different vinyl sulphides containing substituents in the vinyl radical[155-157]. However, as regards alkyl sulphides only isopropenyl ethyl and isopropenyl butyl sulphides could be obtained in this way[158-160], namely by thermal decomposition of acetone mercaptoles:

$$(CH_3)_2C(SR)_2 \xrightarrow{80-120^\circ} CH_2=C(CH_3)SR+RSH,$$

where R = C_2H_5, C_4H_9.

Difficulties involved in the decomposition of mercaptals and mercaptoles may be accounted for not only by their greater stability as compared with that of acetals and ketals[157], but also by the different course of the thermal decomposition of sulphur compounds from that taken by the corresponding oxygen compounds. For instance, compounds of type $Ar_2C(SCH_2C_6H_5)_2$ decompose to yield $Ar_2C=S$, $(C_6H_5CH_2)_2S$, $C_6H_5CH_2SH$, and resinous products[161].

4. Decomposition of Substituted α,β-Unsaturated Acids

Thermal decomposition of unsaturated acids according to the equation

$$RC(SR')=CHCOOH \xrightarrow[-CO_2]{\Delta} RC(SR')=CH_2,$$

where R = CH_3, C_6H_5, R' = C_2H_5, yields α-substituted vinyl alkyl(aryl) sulphides[155,162,163]. This method is of greater preparative significance in the sulphur than in the oxygen series, despite the complicated preparation of the starting unsaturated acids.

5. Preparation from the Halogen Derivatives of Sulphides

As in the oxygen series, this method is based on the ability of the halogen atoms in α-position to split off under the action of bases. By varying the starting components in the first stage,

$$\mathrm{RCH_2CHO + R'SH + HCl \rightarrow RCH_2CHClSR'},$$

various β-substituted vinyl sulphides can be obtained[164]:

$$\mathrm{RCH_2CHClSR' \xrightarrow{C_6H_5N(C_2H_5)_2} RCH{=}CHSR'}.$$

α,β-Dibromo sulphides, obtained by the bromination of α-chloro-sulphides, can split off hydrogen bromide to form β-bromovinyl sulphides[165]:

$$\mathrm{RCH_2CHClSR' \xrightarrow{Br_2} RCHBrCHBrSR' \xrightarrow{C_6H_5N(C_2H_5)_2} RCBr{=}CHSR'}.$$

In the presence of inorganic bases polyhalogeno-sulphides[166] or α,β-dibromoethyl vinyl sulphide[167] split off hydrogen halide, for example:

$$\mathrm{CCl_3CHClSR \xrightarrow{KOH, NaOCH_3} CCl_2{=}CClSR},$$

where R = CH_3, C_2H_5, C_6H_5, $CH_2C_6H_5$.

Mention may be made of the interesting fact that the same differences in the action of various bases are observed here as in the oxygen series (see p. 209).

6. Preparation of β-Halovinyl Sulphides

The addition of sulphenyl chlorides to acetylenes can be used for the synthesis of β-chlorovinyl aryl sulphides[150,154,168,169]:

$$\mathrm{RC{\equiv}CR + ArSCl \rightarrow RCCl{=}C(R)SAr},$$

where R = H, alkyl, aryl.

By this method α-chloroethyl and β-chloroethyl-β-chlorovinyl sulphides were prepared[170,171] from α-chloroethyl- and β-chloroethyl-sulphenyl chlorides, respectively.

The simplest β-chlorovinyl alkyl sulphides can probably be obtained by the method described in the preceding section, but the β-chlorovinyl sulphides described in the literature were obtained in more complicated ways. Thus, β-chlorovinyl methyl sulphide was obtained in small yield as a final product in the following reactions[172]:

$$\mathrm{CH_3SSCH_3 \xrightarrow{Cl_2} 2CH_3SCl}$$
$$\mathrm{CH_3SCl + CH_2{=}CH_2 \rightarrow CH_3SCH{=}CHCl}.$$

Other members of the β-chlorovinyl sulphide series were isolated from the products of the chlorination of saturated sulphides[173,174].

A number of β-chloro- and β-bromo-vinyl aryl sulphides were obtained by the following reaction scheme[175,177]:

$$\mathrm{ArSCH{=}CHCOOH \xrightarrow{Br_2} ArSCHBrCHBrCOOH \rightarrow ArSCH{=}CHBr}.$$

The acid obtained decomposes on mixing with water to yield β-halovinyl sulphide.

The same authors described the preparation of α,β-dibromovinyl sulphides[177]:

$$\mathrm{C_6H_5SC{\equiv}CH \xrightarrow{Br_2} C_6H_5SCBr{=}CHBr}.$$

7. Miscellaneous Methods of Preparation

The following method of preparation of propenyl alkyl(aryl) sulphides, which is specific for sulphur compounds, is of interest. The Claisen rearrangement, which is typical of allyl ethers[182], does not proceed with allyl aryl sulphides[178-181]. Boiling allyl phenyl sulphide, with or without alcoholic alkali, yields propenyl phenyl sulphide, not allyl thiophenol:

$$\mathrm{C_6H_5SCH_2CH{=}CH_2 \xrightarrow{\Delta} C_6H_5SCH{=}CHCH_3}.$$

Allyl alkyl sulphides isomerise in the same manner. Since allyl alkyl(aryl) sulphides can easily be prepared from allyl bromide and a mercaptide, and the isomerisation proceeds with satisfactory yields, this method can be used for the preparation of various propenyl alkyl(aryl) sulphides.

α-Chloro-β,β-diphenylvinyl sulphide, which is difficult to obtain by other methods[131], was prepared by the same method as the similar oxygen compounds (see p. 210).

III. REACTIONS AND PROPERTIES OF SUBSTITUTED VINYL ETHERS

1. Physical Properties

Substituted vinyl ethers are colourless, transparent liquids, sometimes with a pleasant ethereal smell; the polyhalo-ethers are lachrymatory. The higher ethers, oily liquids or solids, are easily soluble in the usual organic solvents. The lower ones have anaesthetic properties[183,184].

Substituted vinyl ethers, like the unsubstituted derivatives[185,186], form azeotropic mixtures with alcohols. The azeotropic mixture of an ether and an alcohol has a lower boiling point and a lower refractive index than the pure ether. For example, impure isopropenyl ethyl ether has a boiling point of 52.5°–53.5° and the refractive index n_D^{20} 1.3805, whereas the pure ether has b.p. 61° and n_D^{20} 1.3918. To purify ether from alcohol, which is usually present as a result of the method of preparation, it should be washed several times with aqueous alkali and then water, dried over potassium hydroxide, and distilled. For further purification, the ether should be treated in the cold (a diethyl ether solution may be used) with sodium. (This method of purification is not suitable for α- and α,β-halo-ethers, which are unstable).

2. Chemical Properties

Hydrolysis. Vinyl ethers have a pronounced unsaturated character and rapidly decolorise bromine water and permanganate solution. Their ability to hydrolyse readily and quantitatively in aqueous acid is used in the laboratory to determine their structure. On hydrolysis, α- and α,β-substituted vinyl ethers yield ketones[41,42,83,89,176], and β- and β,β-substituted ethers give aldehydes[9,10,88,89,95]:

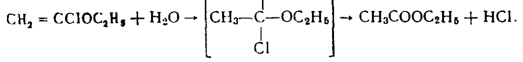
$$RCH{=}C(OR)R' \xrightarrow[-ROH]{H^+, H_2O} RCH_2COR'$$

$$RR'C{=}CHOR'' \xrightarrow[-R''OH]{H^+, H_2O} RR'CHCHO.$$

The structure of the ether can be established by determining the physical constants of ketones or aldehydes obtained by hydrolysis, or those of their derivatives (hydrazones, semicarbazones, etc.). The hydrolysis of alkyl-substituted vinyl ethers proceeds quantitatively in dilute acid solutions or on passing the ether–water vapour mixture over acid catalysts (WO_3 on Al_2O_3,[188] W_2O_5 on Al_2O_3,[189] aluminosilicates, silver oxide,[190] $Ca_3(PO_4)_2$ [191]). The resulting aldehyde or ketone can be determined quantitatively, and from it the quantity of hydrolysed ether can be calculated; in this way the purity of the starting vinyl ether can be determined.

The rate of hydrolysis depends on the structure of the unsaturated radical which is bound directly to oxygen, and on the number and nature of the substituents in the vinyl group. Since the acid-catalysed hydrolysis proceeds through the addition of a proton to the double bond of the molecule[112], the effect of the substituents on the hydrolysis rate depends on the way in which they polarise the molecule, *viz.* on whether they facilitate or hinder the addition of a proton. The structure of the final product of the hydrolysis of unsaturated ethers depends on the course of the decomposition of the intermediate hemiacetals, which in its turn depends on the nature and position of the substituents. This can be verified on the example of the hydrolysis of β-methyl vinyl ethers. The introduction of an electron-withdrawing substituent in α-position causes a certain amount of polarisation, which facilitates the addition of a proton and consequently accelerates the hydrolysis compared with that of unsubstituted ether. In fact, as is apparent from the data on the hydrolysis of vinyl phenyl and isopropenyl phenyl ethers, other conditions being equal, it is the latter compound which is the more completely hydrolysed[191]. Substituted vinyl aryl ethers[44] are more difficult to hydrolyse than the substituted vinyl alkyl ethers. A similar difference is observed in the case of unsubstituted ethers.

In view of the foregoing, the difference in the hydrolysis of α- and β-halo-ethers is noteworthy. α-Chlorovinyl ethyl ether reacts vigourously with water, giving ethyl acetate[127]:



$$CH_2{=}CClOC_2H_5 + H_2O \rightarrow \left[CH_3{-}\overset{OH}{\underset{Cl}{C}}{-}OC_2H_5\right] \rightarrow CH_3COOC_2H_5 + HCl.$$

A β-halovinyl ethyl ether does not hydrolyse in water even on boiling[110], and in acid solution it decomposes upon long heating into the haloacetaldehyde and alcohol[110,113,125]; thus, β-halo-ethers are more difficult to hydrolyse than the substituted vinyl ethers, let alone α-chloro-ethers:

$$XCH{=}CHOC_2H_5 + H_2O \rightarrow [XCH_2CH(OH)OC_2H_5] \rightarrow CH_2XCHO + C_2H_5OH,$$

where X = Cl, Br.

Like α-chlorovinyl ethyl ether, α,β-dichloro- and α,β,β-trichlorovinyl alkyl ethers hydrolyse forming chloro- and dichloroacetates[192-195]. α-Chloro-β,β-diphenylvinyl phenyl ether, however, yields diphenylacetic acid on hydrolysis[131]. β,β-Dichlorovinyl ethyl ether hydrolyses in the same way as β-chlorovinyl ethyl ether, giving dichloroacetaldehyde[138].

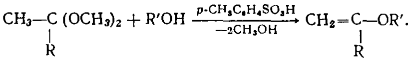
Addition of alcohols. In a number of papers dealing with unsubstituted vinyl ethers it was shown that the ethers react vigorously and exothermically with alcohols, and that the reaction proceeds both in the presence of catalysts (metal chlorides, acids) and without them on heating. Acetals of a wide variety of structures are thereby formed: symmetrical dialkyl-[1,196] and diaryl acetals[197], unsymmetrical dialkylacetals[1,196] and alkylarylacetals[197-201]. Since unsubstituted vinyl ethers can easily be prepared by vinylation, and the reaction of alcohols with the ethers is almost quantitative, this is a good preparative method for acetals.

Although the reaction of alcohols with substituted ethers proceeds as readily as with the unsubstituted ones[42], with the former it has less importance as they themselves are often obtained from acetals and ketals. Moreover, as will be shown later, the reaction of alcohols with α-substituted ethers has a number of features which limit its preparative value.

Acetals, as we know, have a tendency to disproportionation[1,196], whereby a mixed acetal yields, on simple distillation, the two symmetrical acetals:

$$2CH_3CH(OR)(OR') \rightarrow CH_3CH(OR)_2 + CH_3CH(OR')_2.$$

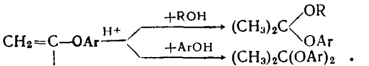
Disproportionation is easier, the greater the difference in the molecular weight of R and R'.[201-203] This tendency is much stronger in ketals[205-206]. For instance, by virtue of the greater mobility of alkoxy groups in ketals, alkyl-substituted ethers can be prepared from dimethyl ketals and alcohols[53]:



$$CH_3{-}\underset{R}{C}(OCH_3)_2 + R'OH \xrightarrow[-2CH_3OH]{p\text{-}CH_3C_6H_4SO_3H} CH_2{=}\underset{R}{C}{-}OR'.$$

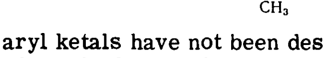
Under similar conditions dimethyl acetals, $RCH(OCH_3)_2$, do not yield the vinyl ethers derived from the reacting alcohol. The tendency to disproportionation is obviously the reason why mixed dialkyl ketals are almost unknown[205].

In view of what has been said above, the results of studies[206] on the addition of alcohols and phenols to α-methylvinyl ethers as a method of preparation of acetone dialkyl and diaryl ketals are of interest:



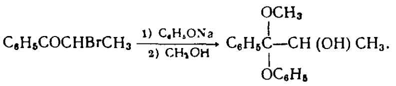
$$CH_2{=}\underset{CH_3}{C}{-}OAr \xrightarrow{H^+} \begin{cases} \xrightarrow{+ROH} (CH_3)_2C\begin{smallmatrix} OR \\ OAr \end{smallmatrix} \\ \xrightarrow{+ArOH} (CH_3)_2C(OAr)_2 \end{cases}.$$

Acetone diaryl ketals were obtained in good yields, but alkyl aryl ketals could not be obtained owing to their decomposition into phenols and isopropenyl alkyl ethers:



$$(CH_3)_2C\begin{smallmatrix} OR \\ OAr \end{smallmatrix} \rightarrow ArOH + CH_2{=}\underset{CH_3}{C}{-}OR.$$

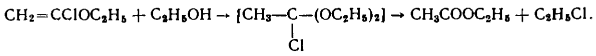
Mixed alkyl aryl ketals have not been described except for methyl phenyl ketals derived from aliphatic-aromatic α-keto-alcohols[207-209]; they were first prepared by Temnikova and Myukhyurdari[207] by the following scheme:



$$C_6H_5COCHBrCH_3 \xrightarrow[2)\ CH_3OH]{1)\ C_6H_5ONa} C_6H_5\overset{OCH_3}{\underset{OC_6H_5}{C}}{-}CH(OH)CH_3.$$

These mixed ketals are stable by virtue of the presence in them of the electron-withdrawing phenyl and hydroxyl groups.

Finally, some features of the addition of alcohols to halogen-substituted vinyl ethers are considered. α-Chlorovinyl ethyl ether reacts vigorously with alcohol, forming an acetate[127]:

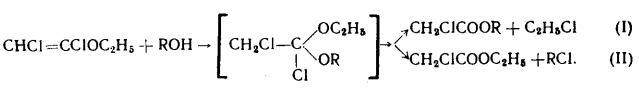


$$CH_2{=}CClOC_2H_5 + C_2H_5OH \rightarrow [CH_3{-}\underset{\displaystyle Cl}{\underset{|}{C}}{-}(OC_2H_5)_2] \rightarrow CH_3COOC_2H_5 + C_2H_5Cl.$$

β-Chlorovinyl ethyl ether adds on one molecule of alcohol in the presence of acids (sulphuric and hydrochloric)[113,125]:

$$CHCl{=}CHOC_2H_5 + C_2H_5OH \xrightarrow{H^+} CH_2ClCH(OC_2H_5)_2.$$

Dichloro-acetal was obtained by heating β,β-dichlorovinyl methyl ether with alcohol at 100° for 3 h in the presence of hydrochloric acid[79]. As in the case of α-chlorovinyl ethyl ether, the alcoholysis of α,β-dichlorovinyl ethyl ether yields acetates[22,23]; their structure depends on the course of the decomposition of the intermediate acetal[23]:



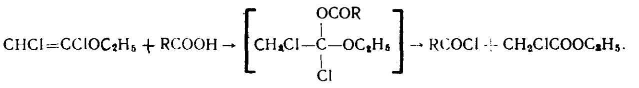
$$CHCl{=}CClOC_2H_5 + ROH \rightarrow \left[CH_2Cl{-}\underset{\displaystyle Cl}{\underset{|}{C}}\begin{matrix}OC_2H_5\\OR\end{matrix}\right] \rightarrow \begin{cases} CH_2ClCOOR + C_2H_5Cl & \text{(I)}\\ CH_2ClCOOC_2H_5 + RCl. & \text{(II)}\end{cases}$$

The reaction with methanol proceeds predominantly by the second pathway, but that with other alcohols and phenols by the first. The reaction of alcohols with α,β-dichloro-β-bromovinyl ethyl ether is more difficult than with α,β-dichlorovinyl ethyl ether[120]:

$$CClBr{=}CClOC_2H_5 + ROH \rightarrow CClBrCOOR + C_2H_5Cl,$$

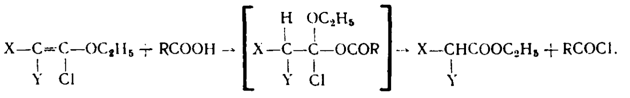
where R = alkyl, aryl.

Addition of acids. The reaction of organic acids with alkyl-substituted vinyl ethers has not been described. It can be assumed, however, that it should differ in the same way from the corresponding reaction with unsubstituted vinyl ethers as in the case of alcohols. Halogen-substituted ethers react in the same manner with acids as with alcohols. For instance, acetic, chloroacetic and benzoic acids combine with α,β-dichlorovinyl ethyl ether in the following way[23]:



$$CHCl{=}CClOC_2H_5 + RCOOH \rightarrow \left[CH_2Cl{-}\overset{\displaystyle OCOR}{\underset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}}{-}OC_2H_5\right] \rightarrow RCOCl + CH_2ClCOOC_2H_5.$$

Reactions with naphthoic and anisic acids are accompanied by the evolution of ethyl chloride. The general reaction of halogen-substituted ethers with organic acids can be represented by the following scheme:



$$X{-}\underset{\displaystyle Y}{\underset{|}{C}}{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}OC_2H_5 + RCOOH \rightarrow \left[X{-}\overset{\displaystyle H}{\underset{\displaystyle Y}{\overset{|}{\underset{|}{C}}}}{-}\overset{\displaystyle OC_2H_5}{\underset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}}{-}OCOR\right] \rightarrow X{-}\underset{\displaystyle Y}{\underset{|}{CH}}COOC_2H_5 + RCOCl.$$

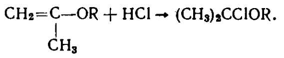
where (1) X = H, Y = Cl;[23] (2) X = H, Y = H;[210] (3) X = Br, Y = Cl.[120] This reaction may be used as a preparative method for acid chlorides. For instance, Heslinga and Arens[211] prepared peptides in that way:

$$CH_2{=}CClOC_2H_5 + YNHCHRCOOH \rightarrow [CH_3CCl(OC_2H_5)OCOCHRNHY] \rightarrow CH_3COOC_2H_5 + YNHCHRCOCl;$$

$$YNHCHRCOCl + HCl\cdot NH_2CHR'COOC_2H_5 \rightarrow YNHCHRCONHCHR'COOC_2H_5 + 2HCl,$$

where Y = benzyloxycarbonyl or YH = phthaloyl radical.

Addition of hydrogen halides. The addition of hydrogen halides to unsubstituted vinyl alkyl or vinyl aryl ethers has been thoroughly studied and can be used as a preparative method for α-chloro-ethers[1]. Only a few cases of additions to substituted ethers have been described. To obtain α-chloroisopropyl alkyl ethers the authors of this review reacted hydrogen halides with α-methylvinyl alkyl ethers:



$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}OR + HCl \rightarrow (CH_3)_2CClOR.$$

However, only the decomposition products of the α-chloro-ether were isolated:

$$(CH_3)_2CClOR \rightarrow CH_3COCH_3 + RCl.$$

Similar decomposition was observed earlier by a number of workers[204,212].

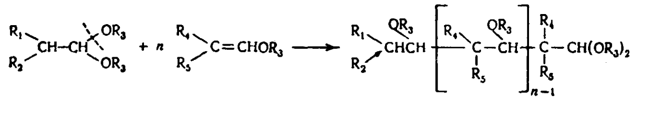
Hydrochlorination of isopropenyl aryl ethers gave α-chloroisopropyl aryl ethers[213]; they are more stable than α-chloroisopropyl alkyl ethers, but not so stable as the α-chloro-ethers obtained by the hydrochlorination of vinyl phenyl ether[214].

The tendency to decomposition of α-chloro-ethers containing the α-chloroisopropyl group was also observed by Hall and Sirel[215]. These authors failed to isolate even traces of the α-chloro-ethers in their attempt to chlorinate di-isopropyl ether by the same method as that which had been used earlier for the preparation of bis(α-chloroethyl) ether by the chlorination of diethyl ether.

The reaction of hydrogen halide with α-halovinyl alkyl ether yields the very stable α,α-dihaloethyl alkyl ether[128,211], which can be distilled and kept without decomposition. The addition of hydrogen chloride to β-chlorovinyl ethyl ether has also been described[216].

Addition of halogens. The addition of halogens to the double bond in substituted ethers has not received much attention. The cases described are the addition of bromine to α-ethylvinyl methyl ether[101], of chlorine to α,β-dichlorovinyl phenyl ether[24,25], and of bromine and chlorine to α,β,β-trichlorovinyl ethyl ether[217]. This reaction is exothermic, and is carried out with cooling under conditions analogous to those described for the halogenation of unsubstituted ethers[1].

Reactions with acetals and ketals. Hoaglin and Hirch[218] studied the addition of vinyl ethers to acetals in the presence of boron fluoride etheradduct, and found it to proceed as follows:

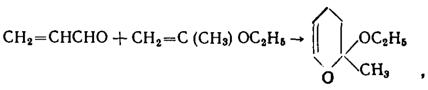


This reaction was subsequently used in a great many syntheses involving the lengthening of the chain in polyenic aldehydes and ketones[219]. Acetals can be condensed with β-substituted vinyl ethers (for instance propenyl methyl and propenyl ethyl ethers[218,220], β-ethylvinyl and β-ethyl-β-butylvinyl ethyl ethers[218], and β-bromovinyl ethyl ether[221]) as well as with α-substituted ones, the latter being less reactive[59,220,223]. Unlike unsubstituted and β-alkyl-substituted vinyl ethers, which form acetals, α-alkyl-substituted ethers yield ketals on condensation with acetals, which on hydrolysis give ketones; for instance, crotonaldehyde acetal[223] reacts with isopropenyl ethyl ether to give 4-ethoxyhept-5-en-2-one ketal, which hydrolyses into hepta-3,5-dien-2-one:

$$CH_3CH{=}CHCH(OC_2H_5)_2 + CH_2{=}C(CH_3)OC_2H_5 \xrightarrow{ZnCl_2}$$

$$\rightarrow CH_3CH{=}CHCH(OC_2H_5)CH_2C(OC_2H_5)_2CH_3 \xrightarrow{H^+, H_2O} CH_3(CH{=}CH)_2COCH_3.$$

Diene synthesis. Vinyl ethers have been used as dienophiles in reactions with cyclopentadiene[224,225], cyclones[226,227], hexachlorocyclopentadiene[228], acrolein and crotonaldehyde[228,229]; they were found, however, to be less reactive than α,β-unsaturated carbonyl compounds. As regards substituted vinyl ethers, β-substituted ethers are inactive in diene synthesis[187], while α-substituted ethers give much smaller yields than the unsubstituted ones[187,229]. Diene synthesis with acrolein and α-alkyl-substituted ethers (isopropenyl ethyl and n-butyl cyclohexenyl ethers)[229]:



and the reactions of α-methyl- and α-phenylvinyl ethers with cyclones[187] have been described.

Polymerisation of vinyl ethers, like their addition reactions, proceeds as a result of the formation of carbonium ions in the presence of acid catalysts ($SnCl_2$, $SnCl_4$, $FeCl_3$, $AlCl_3$, BF_3) with or without solvents. In the presence of these catalysts α-alkyl-substituted ethers form many polymers[230-232]. α-Methylvinyl ethers were shown[206,233] to be more reactive in polymerisation than unsubstituted vinyl ethers; this is reflected in the fact that, under the most favourable conditions, they polymerise at lower temperatures than the corresponding vinyl alkyl ethers[1]. The reason for this difference in behaviour, the authors ascribed to the different stability of oxonium complexes formed by the reaction of the oxygen atom in the ethers with ionic catalysts.

β-Halovinyl ethers also polymerise in the presence of ionic catalysts[110,112,125], although not so easily as the unsubstituted vinyl ethers. α-Chloro(bromo)vinyl ethyl ether polymerises spontaneously on standing[113,125].

Miscellaneous reactions of substituted vinyl ethers. In addition to the above-mentioned reagents, various other compounds can be added on to the double bond in substituted vinyl ethers, for example, hydrogen[57,74,84], ozone[57,102,107], amines[112], organic acid chlorides[101,104], and mercury salts[92].

By virtue of the ease with which alcohols react with the double bond and form ketals, α-substituted ethers can be used instead of ketals and ketones. For instance, the condensation of isopropenyl ethyl ether with the ester of oxalic acid[234] has been described:

$$CH_2{=}C(CH_3)OC_2H_5 + (COOC_2H_5)_2 \xrightarrow{C_2H_5OK}$$

$$\rightarrow C_2H_5OOCCOCH_2COCH_2COCOOC_2H_5.$$

Acetone can be used in this reaction under the same conditions, instead of isopropenyl ethyl ether. In this connection the preparation of isoprene from ethylene and isopropenyl ethyl ether or acetone diethyl ketal may be noted[235].

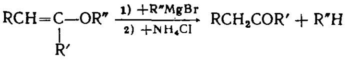
Reactions of substituted vinyl ethers with Grignard reagent have recently been studied[102,105,107]. Arylmagnesium bromides react with α-phenyl-substituted ethers forming substituted ethylenes[105]:

$$RCH{=}C(C_6H_5)OC_2H_5 + ArMgBr \rightarrow RCH{=}C(C_6H_5)Ar + C_2H_5OMgBr,$$

where R = alkyl, aryl. Olefinic hydrocarbons have been prepared by the same method from β-alkyl-substituted vinyl ethers and alkylmagnesium bromides[107]:

$$RCH{=}CHOR' + R''MgBr \rightarrow RCH{=}CHR'' + R'OMgBr.$$

α,β-Dialkylvinyl ethers[102] react differently. The Grignard reagent cleaves them at the C–O bond, yielding ketones:



$$RCH{=}\underset{\displaystyle R'}{\underset{|}{C}}{-}OR'' \xrightarrow[2)\ +NH_4Cl]{1)\ +R''MgBr} RCH_2COR' + R''H.$$ †

α-Phenyl-substituted ethers are characterised by their tendency to thermal rearrangement[50,89,236]:

$$CH_2{=}C(C_6H_5)OR \rightarrow RCH_2COC_6H_5$$

and β-bromovinyl ethers by their ability to split off hydrogen halide upon heating with potassium hydroxide[33,112,115,116,124-125,127].

$$RCBr{=}CHOR' \xrightarrow[-HBr]{KOH} RC{\equiv}COR'.$$

IV. REACTIONS AND PROPERTIES OF SUBSTITUTED VINYL SULPHIDES

1. Physical Properties

Vinyl sulphides are unpleasant-smelling liquids insoluble in water but miscible with the usual organic solvents. They turn yellow on standing in air, especially in the light, and should be kept in the dark, in sealed tubes.

2. Chemical Properties

Vinyl sulphides are stable in alkaline media, but decompose in acid media. They decolorise bromine water. Their reactions are similar to those of vinyl ethers, but they do not enter into addition reactions quite so readily; it is therefore supposed that their double bond is less nucleophilic than that of vinyl ethers[237]. On the other hand, they take part more readily in reactions involving a radical mechanism[3,4,5,238], such as those involving the addition of mercaptans, contrary to Markownikoff's rule, and in radical polymerisations[237]. These conclusions were reached following systematic study of unsubstituted vinyl sulphides. Owing to difficulties involved in obtaining substituted vinyl sulphides, there is little information in the literature concerning their reactions, but what is available is consistent with the principles stated above.

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† The stoichiometry of this reaction is not clear (Ed. of Translation).

In the present chapter sections on polymerisation and diene synthesis[237,239,240] are omitted, as these reactions have not been described for substituted vinyl sulphides.

Halovinyl sulphides have a number of specific properties which do not exist in their oxygen analogues. Some characteristic properties of sulphides concern the sulphur atom (oxidation to sulphoxides and sulphones, desulphurisation, decomposition by an alcoholic solution of mercuric chloride) and naturally have no equivalents among oxygen compounds.

Hydrolysis. Vinyl sulphides react less vigorously with water in acid solution than vinyl ethers. For instance, in the hydrolysis of $CH_2{=}CHSCH_2CH_2OCH{=}CH_2$ [241] and $C_2H_5SCH{=}CHOC_2H_5$ [242] by dilute hydrochloric acid, the ether group hydrolyses first, and $CH_2{=}CHSCH_2CHO$ and $C_2H_5SCH_2.CHO$ are formed respectively. Only by using harsher conditions is the hydrolysis of the alkylmercapto group achieved. In contrast to the oxygen analogues, the hydrolysis is complicated by the formation, in acid media, of mercaptals and mercaptoles from α-substituted sulphides, which, unlike acetals and ketals, are stable in aqueous solution. Thus, in the hydrolysis of isopropenyl ethyl sulphide, acetone diethyl mercaptole was isolated in addition to acetone:

$$2\,CH_2{=}C(CH_3)SC_2H_5+H_2O \xrightarrow{H^+} CH_3COCH_3+(CH_3)_2C(SC_2H_5)_2.$$

The formation of by-products naturally precludes the use of hydrolysis for the quantitative determination of vinyl sulphides. It can, however, be used both for their qualitative determination and in structure determination[179]. If there is no formation of mercaptals and mercaptoles, hydrolysis yields thiols and carbonyl compounds. Thus, by hydrolysis of isopropenyl and propenyl phenyl sulphides we obtained acetone and propionaldehyde respectively, and identified them as the 2,4-dinitrophenylhydrazones. Böhme and Gran[173] obtained 80–90% of chloroacetone and thiols by hydrolysing β-chloro-α-methylvinyl sulphides:

$$CHCl{=}C(CH_3)SR+H_2O \xrightarrow{H^+} CH_3COCH_2Cl+RSH,$$

where R = CH_3, C_6H_5.

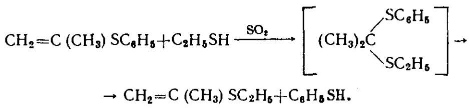
Addition of alcohols and thiols. Vinyl sulphides react with alcohols in the presence of acid catalysts[238] to yield monothioacetals, *e.g.* $CH_3CH(OC_2H_5)SC_2H_5$, which are unstable and have a greater tendency to disproportionation and transetherification than the mixed acetals[1,196]. There is no information in the literature on the addition of alcohols to substituted vinyl sulphides, but, in the case of α-substituted vinyl sulphides, the products (mixed monothioketals) should presumably be less stable than monothioacetals.

Vinyl sulphides react with mercaptans in the presence of acid catalysts according to the Markownikoff rule[4,237]. Addition to α-methylvinyl sulphides[4,237] occurs similarly:

$$CH_2{=}C(CH_3)SR+RSH \xrightarrow{HCl} (CH_3)_2C(SR)_2,$$

where R = C_2H_5, C_3H_7, C_4H_9.

Isopropenyl phenyl sulphide combines with ethanethiol also in accordance with the Markownikoff rule, but the resulting ethyl phenyl mercaptole decomposes in the same way as acetone alkyl aryl ketals[206], to give isopropenyl ethyl sulphide and thiophenol:



$$CH_2{=}C(CH_3)SC_6H_5+C_2H_5SH \xrightarrow{SO_2} \left[(CH_3)_2C\begin{matrix}\diagup SC_6H_5\\ \diagdown SC_2H_5\end{matrix}\right] \rightarrow$$
$$\rightarrow CH_2{=}C(CH_3)SC_2H_5+C_6H_5SH.$$

Unlike their oxygen analogues, vinyl sulphides undergo free-radical reactions, such as the addition of mercaptans. Shostakovskii and Prilezhaeva[4,5,238] showed this reaction to proceed by a free-radical mechanism, the presence of the merest traces of peroxides being sufficient for the reaction to be completed quantitatively simply on mixing the reagents. They studied the addition of mercaptans to isopropenyl alkyl sulphides and observed that the reaction is more difficult owing to the presence of an α-methyl group:

$$CH_2{=}C(CH_3)SR+RSH \longrightarrow RSCH_2CH(CH_3)SR,$$

where R = C_2H_5, C_3H_7, C_4H_9.

Thus, to prepare 1,2-dibutylmercaptopropane, a radical catalyst should be added (azoisobutyric dinitrile) and the mixture heated, while 1,2-dibutylmercaptoethane can be prepared merely by mixing the components[5]. The authors allowed thiols to react with isopropenyl and propenyl phenyl sulphides in the presence of azoisobutyric dinitrile and obtained the isomeric sulphides:

$$CH_2{=}C(CH_3)SC_6H_5+C_2H_5SH \longrightarrow C_2H_5SCH_2CH(CH_3)SC_6H_5$$
$$CH_3CH{=}CHSC_6H_5+C_2H_5SH \longrightarrow C_2H_5SCH(CH_3)CH_2SC_6H_5.$$

Addition of hydrogen halides. The reaction of vinyl alkyl sulphides with hydrogen halides proceeds under the conditions already described for the hydrohalogenation of vinyl ethers, namely on stirring at low temperatures, and the resulting products are consistent with the Markownikoff rule[238]. The hydrochlorination of α-methylvinyl sulphides was studied:

$$CH_2{=}C(CH_3)SR+HCl \longrightarrow (CH_3)_2CClSR,$$

where R = alkyl, aryl. It was shown that α-chloroisopropyl alkyl sulphides are less stable than α-chloro-sulphides of the general formula RCHClSR [167,173,238,243] and that at temperatures below zero they decompose into a complex mixture of products, from which a thiol can be isolated.

α-Chloroisopropyl aryl sulphides are more stable than the corresponding alkyl sulphides, but they also partly decompose on distillation.

Hydrogenation of sulphides. Hydrogenation of organic sulphides over oxides or sulphides of heavy metals at high temperatures is usually accompanied by hydrogenolysis (rupture of the C–S bond). Hydrogenation of unsaturated sulphides without the rupture of the C–S bond can be carried out rapidly and quantitatively in the cold over a palladium–charcoal catalyst[178,179,244]. For instance, β-alkylvinyl sulphides are hydrogenated quantitatively in 2–4 h by vigorous shaking in an atmosphere of hydrogen[244]:

$$CH_3(CH_2)_5CH{=}CHSR \xrightarrow{H_2Pd/C} CH_3(CH_2)_7SR,$$

where R = CH_3, C_2H_5.

Oxidation to sulphones. The oxidation of sulphides to sulphones is widely used in the chemistry of substituted vinyl sulphides for their identification (sulphones are crystalline compounds) as well as for the activation of the vinyl double bond by the electron-withdrawing SO_2 group; the resulting unsaturated sulphones can be used in further reactions (*e.g.* in diene synthesis or in polymerisation). Sulphones are usually prepared by oxidation with 30% hydrogen peroxide in glacial acetic acid in the cold (as in the oxidation of alkyl sulphides[147,150]), or by heating (as for aryl sulphides[145,149,154,180,245,246]. Good results were obtained in oxidations by monoperoxyphthalic acid in ether solution in the cold[164,173,178]. For instance α-methyl-β-chlorovinyl sulphides were oxidised to sulphones in 70–80% yields by monoperoxyphthalic acid[163,173]:

$$CHCl{=}C(CH_3)SR \xrightarrow{2(O)} CHCl{=}C(CH_3)SO_2R,$$

where R = CH_3, C_6H_5.

If the oxidation is carried out under milder conditions, sulphoxides are obtained. Thus, at 28°–30° hydrogen peroxide oxidises α,β-dichlorovinyl t-butyl sulphide into sulphone, whereas at 0° it yields sulphoxides[147].

Miscellaneous reactions of β-halovinyl sulphides. Like β-halovinyl ethers, β-halovinyl sulphides split off a molecule of hydrogen halide in the presence of alkalis and form alkyl(aryl)mercaptoacetylenes[165,175]:

$$RSCH{=}CHX \longrightarrow RSC \equiv CH,$$

where R = alkyl, aryl; X = Cl, Br.

It is interesting that when R is an aryl group, the elimination of hydrogen halide proceeds extremely easily at comparatively low temperatures[175]. By virtue of the mobility of substituents in the β-position with respect to the sulphur atom, the β-chlorine atom in β-chlorovinyl sulphides is very reactive to nucleophilic exchange reactions. In alkaline media the β-chlorine atom can be substituted by alkylmercapto[165], arylmercapto[143 146 247], naphthoxy[174], and amino groups[248]. The ease of the substitution of β-chlorine is especially pronounced in the reaction of polychloroethylenes with thiophenols in alkaline media. Thus, the main product in the reaction of tetrachloroethylene with p-toluenethiol is not α,β,β-trichlorovinyl tolyl sulphide, but α,β-dichloro-α,β-bis(p-tolylmercapto)ethylene[146]:

$$CCl_2{=}CCl_2 + ArSNa \xrightarrow[-NaCl]{} ArSCCl{=}CCl_2$$

$$ArSCCl{=}CCl_2 + ArSNa \xrightarrow[-NaCl]{} ArSCCl{=}CClSAr.$$

The nucleophilic reactivity of the β-chlorine atom in β-chlorovinyl sulphones is even higher than in β-chlorovinyl sulphides[248].

Reactions of sulphides involving the rupture of the C–S bond. Substituted vinyl sulphides undergo desulphurisation on boiling over Raney nickel[180,245]. The hydrocarbons formed in the process can be used as an indication of the structure of the sulphide.

The reaction of vinyl sulphides with alcoholic mercuric chloride solution leads to the rupture of the C–S bond; in contrast, mercury salts combine with the double bond in vinyl alkyl ethers to yield a mercuri-derivative of an aldehyde or ketone[92]. In vinyl sulphides the action of mercury is directed towards a different reactive centre — the sulphur atom — and the reaction proceeds by the elimination of the thiol group. Shostakovskii and Prilezhaeva showed[4,5,237,238,249] that the decomposition of vinyl sulphides by alcoholic mercuric chloride solution proceeds at room temperature:

$$CH_2{=}CHSR + 2\,HgCl_2 + C_2H_5OH \longrightarrow RSHgCl + CH_3CH(OC_2H_5)_2 + HCl.$$

This reaction is quantitative and can be used for the analysis of vinyl sulphides.

α-Methylvinyl sulphides are decomposed by alcoholic mercuric chloride solution. For the quantitative decomposition of isopropenyl alkyl and aryl sulphides the reaction mixture has to be heated, *i.e.* harsher reaction conditions are required than in the case of unsubstituted vinyl sulphides. Decomposition of the isomeric propenyl and isopropenyl phenyl sulphides proceeds at different rates. Thus, after mixing the mercuric chloride solution with isopropenyl phenyl sulphide the phenylmercury chloride precipitate separates in 30 sec, while in the case of propenyl phenyl sulphide it separates in 10–15 sec. Karaulova and collaborators[181] also observed the slow and incomplete decomposition of propenyl phenyl sulphide. According to the available date[173], the decomposition of various sulphides gets progressively more difficult in the order vinyl alkyl > isopropenyl alkyl > vinyl phenyl > isopropenyl phenyl > propenyl phenyl.

We conclude that the substituted vinyl compounds containing oxygen, sulphur, and nitrogen are capable of reacting with various compounds containing a mobile hydrogen atom in the molecule; they can be used in high-polymer chemistry and in polymerisations and copolymerisations, and their significance is bound to grow with the further development of these fields.

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MODERN VIEWS ON GELATION IN POLYMER SOLUTIONS AND ON THE STRUCTURE OF GELS

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CONTENTS

1. INTRODUCTION

The problem of gelation in polymer solutions is of great theoretical and practical interest. The practical importance of the study of gelation is due to the fact that it is necessary to obtain gels having definite physicochemical properties in several branches of industry (*e.g.* in the food, soap, paint, and other industries); but in several other cases the formation of gels is, on the contrary, an undesirable phenomenon and to be avoided (in the manufacture of artificial fibres, adhesives, tanning solutions, etc.). Polymeric gels are interesting also from a theoretical point of view, since they represent a variety of three-dimensional structures possessing many of the properties of a solid, but containing very little solid material.

In spite of the great number of papers concerned with gelation[1-3], several problems still remain to be fully cleared up, including particularly questions of the mechanism of gelation, the nature of the bonds, the equilibrium state of gels, etc. The aim of the present paper is to examine the main present-day views on processes of gelation in polymer solutions. We will confine ourselves to an examination of gels formed when solutions set on cooling, without giving special consideration to gels obtained by the swelling of a polymer in some solvent.

2. GENERAL DEFINITION OF THE CONCEPT OF GELATION AND OF A GEL, AND FUNDAMENTAL CONDITIONS FOR GELATION

By the phenomenon of gelation is meant a process of continuous increase in viscosity of a polymer solution with time, depending on the nature of the polymer and the solvent and on the temperature, accompanied by a continuous growth of elastic properties, and leading to solidification of the whole system into a uniform non-fluid mass – a jelly or gel.

While it is quite easy to give a definition of the process of gelation or setting, based on the phenomenology of the process, the definition of the concept "gel" presents considerably greater difficulties. As early as 1926 Lloyd[4] began his paper on gels with the words: "The colloidal state – a gel – is a state which is easier to observe than to define". In its most general form a gel can be defined as a disperse system consisting of two components – polymer and solvent – uniformly distributed in a space, and exhibiting the mechanical properties of solids.

Polymer gels can be obtained both by the setting of solutions and by the swelling of a polymer in a solvent in which its solubility is limited. According to modern views a general condition for gel formation is the limited solubility of the polymer in the particular solvent. The work of Kargin *et.al.*[5] has shown the applicability of the phase rule to polymer solutions and has established that the formation of gels is associated with the separation of the system into two phases when the solubility of the polymer in a given solvent is limited. Consequently the condition of limited solubility is a necessary condition for gelation. This necessary condition – a partial diminution in the solubility of the polymer, or more correctly of its functional groups, in the given solvent[6] – can be achieved either by changing the temperature, by changing the nature of the solvent at a given temperature, or by making specific additions to the solution. Thus the first stage in gelation is supersaturation of the solution with respect to definite functional groups in the polymer chain. When solutions are supersaturated with substances of low molecular weight, the system usually begins to separate rapidly into two phases. A peculiarity of polymer solutions is that, when solubility is lost and supersaturation occurs, under certain conditions the system does not separate into two phases. The definition of a gel as a system with incomplete separation into layers, given by Papkov[7], is applicable here. The fact that loss of solubility does not lead to separation into layers is due to the precipitation of the polymer from the solution in microvolumes[8], the polymer molecules being linked to one another to a certain extent. We consider that such incomplete formation of layers occurs when the polymer molecule contains groups differing in chemical nature, usually polar and non-polar groups. In such a case the difference in partial solubility[9] of these groups, when present in a definite ratio, results in one part of the molecule being, as it were, in a dissolved state, while the other part tends to precipitate out of the solution. This obviously explains the fact that almost all known gels (gelatin, agar, poly(vinyl alcohol), cellulose nitrate, etc.) consist of molecules containing groups which are different in chemical nature.

The view that formation of intermolecular bonds in solutions of polymers during gelation occurs by the interaction of groups in the polymer which are sparingly soluble in the given solvent has been developed in papers by Lipatov[8,9] Bresler[10], and Morawetz[11], and can be accepted as fully proved. These ideas follow also from the papers by Kargin *et.al.*[5] mentioned above. The specific effect of the solubility of the polymer on the ability of a solution to set is shown also in the fact that gelation can be observed both when the temperature is lowered and when it is raised. Thus although the classical examples of polymeric gels – those of gelatin – are formed when the temperature of the solution is lowered, with solutions of cellulose nitrate in ethanol, in which the solubility falls rapidly with rise in temperature, gelation occurs on heating[12]. It can be stated, in conformity with the work of Kargin *et al.*[3] that, if the solubility diminishes as the temperature falls, gelation occurs on lowering the temperature, and conversely. With solutions of cellulose acetate in dibutylcarbitol benzene phosphonate, where the solubility diminishes on heating, gelation occurs on heating, but for solutions in the same solvent of cellulose acetate containing a certain proportion of propionate groups the temperature coefficient of solubility is positive, and gelation occurs on cooling[13].

However, a diminution in solubility of the polymer is not in itself sufficient for gelation to ensue. Another important condition is the achievement of a definite concentration in the solution, characteristic of each polymer–solvent system. The existence of a critical concentration is due to the fact that gelation occurs when the ratio of intramolecular and intermolecular bonds formed as the solubility decreases reaches a definite value. For dilute solutions it is known that the probability of formation of intramolecular bonds is independent of the concentration of the solution, whereas the number of intermolecular bonds rises sharply with increase in concentration. Thus the critical concentration at which gelation begins corresponds to the start of preferential formation of intermolecular bonds with a decrease in solubility. This concentration was roughly estimated by Ferry[2] for gelatin solutions on the assumption that the structure of the gel is a three-dimensional network formed by joining together the ends of the macromolecules. In spite of the admitted crudity of such a view, the value of 1% found by Ferry for the critical concentration corresponds in fact to the concentration of gelatin solutions at which gelation is possible.

Above we have considered the main cause of gelation to be a reduction in the solubility of a polymer in a given solvent. Gelation may also be produced, however, by introducing certain additives into polymer solutions. These questions have been elucidated in detail in papers by Zubov *et al.*[14-16] In the presence of added compounds of multivalent elements gelation is most often due to the formation of bonds between the polymer molecules in the solution as a result of chemical reaction between the additive and some functional groups in the polymer (*e.g.* gelatin in the presence of alum[17], copolymers of methacrylic acid and methyl methacrylate in the presence of salts of bivalent metals[18], etc.). When stable chemical bonds are formed, gelation leads to irreversible changes in the system. Such systems can no longer be brought into solution by changing the temperature. When compounds of univalent elements are added, there is no possibility of chemical bonds being formed and only the usual type of intermolecular bonds are formed[18].

The solubility of a polymer can be easily varied by adding to the solutions small quantities of a poor solvent, which impair the dissolving power of the solvent. Such additions, too, can lead to gelation. For example, introduction of only 2% of water into solutions of poly(acrylonitrile) in dimethylformamide results in setting occurring even at room temperature, whereas in the absence of water these solutions set only at temperatures below 2°. [19]

The effect of the polydispersity of the polymer on the gelation of its solutions is also readily explained in terms of the general condition for gelation, namely partial loss of solubility. Polydispersity results from a difference in solubility between individual fractions of a polymer in a given solvent, in spite of their identical chemical composition. Since molecules having different molecular weights can take part in forming the three-dimensional structure of the gel, it is obvious that readily soluble fractions will make gelation more difficult. Detailed consideration of these questions has been given in papers by Lipatov[9] and Zubov[16]. Thus it has been shown[9] that a concentrated solution of cellulose acetate will take 24 h to set, whereas a solution of this material freed from readily soluble fractions forms a gel very rapidly. A similar effect is observed with gelatin solutions[16].

Finally, we must note the effect on gelation of the structure of the macromolecule itself. As will be shown below, gelation is observed to involve the formation of secondary structures from molecules which are arranged in a regular manner relative to one another. Walker[20] remarks that the capacity of a polymer for gelation in solution is related to its ability to crystallise. If a change in solubility of a polymer in a solvent involves too great an ordering of the molecular distribution, a precipitate comes down instead of a gel being formed. This explains, for example, the fact that the jellies formed on cooling polyethylene solutions[21] are quite distinct in character from ordinary jellies, *e.g.* of gelatin. An increase in the randomness of interacting groups along the chain leads to a diminution in the ordering of the molecules relative to one another, and decreases the tendency for a deposit to separate out, thus favouring gelation. Some regularity in the mutual arrangement of the molecules is necessary, however, since it favours the formation in the solution of the secondary structures which precede gelation. The structure of the macromolecule also determines its ability to gel because the latter depends on the flexibility of the macromolecule. The conformation of a polymer chain in solution depends on the flexibility of the chain and on its interaction with the solvent. In the case of flexible molecules the viscosity of dilute solutions will be lower, and that of concentrated solutions higher, in a thermodynamically poor solvent than in a good solvent[22]. With rigid molecules, according to Tager[22], the viscosity of solutions will be lower in a good solvent than in a poor solvent, since the uncoiled form of the chain in the poor solvent favours the formation of intermolecular bonds. Hence it follows that the critical concentation for gelation should be lower with rigid polymers than with flexible polymers [*e.g.* gelation in solutions of gelatin and of poly(methacrylic acid)[23]].

The fundamental conditions for gelation considered above also enable other features of the process, *e.g.* the rate of setting, to be understood. If gelation occurs when the temperature is lowered, the velocity of the process will, of course, decrease with rise in the latter; at a given temperature an increase in the rate of setting will be observed when the concentration of the solution is increased[24]. If, however, the concentration of the solution is equal to that of the gel, obtained by syneresis, gelation will occur instantaneously when the temperature is lowered[9].

The following conclusions concerning the fundamental conditions for gelation can be drawn from what has been said above. It occurs only when there is limited solubility of a polymer in a solvent. Therefore all factors affecting the solubility of the polymer also influence the process of gelation. However, gelation is not related solely to the loss of solubility. A necessary condition for it is the formation of a continuous spatial network of macromolecules interacting with one another. As a result of this, it is gelation and not precipitation which occurs when the solubility is decreased. Any additive in the solution which favours the formation of intermolecular bonds will promote gelation. Finally, the capacity for gelation is closely linked with the chain structure of the polymer molecules, which is a ncessary condition for the production of the continuous three-dimensional gel network covering the whole volume of the system.

3. THERMODYNAMICS OF GELATION

The setting of a gel resulting from a change in the external conditions is a spontaneous process accompanied by a decrease in the free energy of the system: $\Delta F < 0$. Since bonds are formed between individual macromolecules in the polymer in solution, producing relatively ordered secondary structures, the process of gelation involves both a decrease in the heat content and a decrease in the entropy of the system. The latter is enlarged also by the reduction in the flexibility of the chains due to the formation of intermolecular bonds, which results in a decrease in the number of possible configurations available to the macromolecule.

At the present time sufficient experimental evidence has accumulated to support the occurence of heat effects during gelation. Such results have been obtained by Lottermoser[25], Fischer[26], and Lipatov[27,28]. Recently this question has been resuscitated in the literature in connection with work[29] in which no heat effects were observed to accompany setting. We consider, however, that the assumptions underlying this work cannot be valid, although they start from a purely thermodynamic consideration of the question.

The experimental determination of heats of gelation involves several difficulties. It has been shown[30] that the magnitude of the heat effect accompanying setting depends on several factors, the most important being the homogeneity of the original polymer and its purity. Fractionation and careful purification of the polymer result in greater heat effects being observed during gelation and the gel passing into solution over a narrower temperature range on heating than when these criteria are not observed. Another factor making it difficult to determine exact values of heats of setting is the possibility that bonds which differ both in nature and in stability are formed during the process. It is also necessary to remember that the process takes time to occur, and the evolution of heat occurs gradually[31]. In view of the experimental difficulties associated with the direct determination of heats of setting, other methods were employed.

Eldridge and Ferry[32] have estimated heats of gelation for gelatin gels. They deduced an equation linking the melting point of the gels (the temperature at which the gel passed into a solution on heating) with the concentration of the gel, its final form being

$$\log C = -\Delta H/RT + \text{const},$$

where ΔH is the heat of gelation, T the melting point, and C the concentration. This equation was derived by regarding gelation as analogous to processes of polycondensation of bi- and multi-functional monomers, which under certain conditions form a continuous spatial structure. ΔH is regarded as a heat of reaction:

2 moles of cross-linking points → 1 mole of cross-links.

The formation of cross-links is likened to a process of binary association:

$$m_1 + m_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} m.$$

In the case of gelation at low temperatures, the forward reaction takes place, so that $k_1 > k_2$ and $K = k_1/k_2 > 1$. When the temperature is raised the reverse reaction takes place, and $K < 1$, *i.e.* the value of K decreases with rise in temperature, and the equilibrium is displaced causing rupture of the bonds formed at the lower temperature. Values of ΔH = 73 and 220 kcal mole^{-1} were found for gels of gelatin which had been kept at 0° and 15° before melting. It is evident from these data that the conditions of preparation of the jelly and its aging have a considerable effect on the magnitude of ΔH, which these workers ascribe to differences in stability of the bonds which are formed. Thus the estimate of the heats of rupture of the structural lattice of the gel using the method suggested by Ferry is quite indefinite in character, which in our opinion is due to jellies being investigated while in a non-equilibrium condition.

If it is supposed, as was done in the work referred to, that the bonds which are formed are hydrogen bonds, it turns out that each cross-link is formed by 10–45 hydrogen bonds. This, of course, is physically impossible, and can only mean that, at the intersections of the three-dimensional network of the gel, there are secondary structures formed by the polymer molecules and having a definite degree of order.

Meerson and Lipatov[28] estimated the heats of fusion of the gels by using Flory's equation[33] for the heats of fusion of crystalline polymers in the presence of solvents. This method gave values of 61 kcal mole^{-1} for dilute gelatin gels and 90 kcal mole^{-1} for the concentrated gels. These values are somewhat lower than those found by Ferry[32], obviously because of the factors already discussed. A direct determination has been made[28] of the heat of fusion of a gel by determining its heat of solution in urea solution at 20° and the heat of mixing of the (polymer) solution with urea solution at 70°. The difference in the heats of solution at these temperatures gives the heat of fusion of the jelly, provided, of course, that the heats of solution of the gel and of mixing of the solutions are independent of temperature. The method suggested by Ferry[32] for determining heats of gelation has been also employed[34] for aqueous and hydrochloric-acid solutions of poly(methacrylic acid).

In view of all the work reported above, it is obvious that we can strictly speak of a definite melting point of a gel, or of a temperature at which it passes into solution, only in the case of dilute gels, in which rupture of the bonds in the structural network occurs quite rapidly. The passage of more concentrated gels into solution usually occurs over a certain range of temperature. Here both the heat of gelation and the temperature of the transition depend not only on the nature of the bonds in the gel but also on the conditions of gelation. During the aging of gels the heat of disintegration of the network structure increases and the temperature of fusion rises, as has been shown by Zubov and Kargin[14,15] in the case of gelatin gels and by Walter[35] for poly(vinyl chloride).

Gels are characterised by a lack of agreement between the temperatures at which they set and those at which they melt. According to Zubov[16], this is explained by the occurrence, during the aging of concentrated gels, of extremely slow processes of stress relaxation, which affect the gel structure as a whole. Another cause of variation in the transition temperatures of gels into solutions may be the increase in stability of intermolecular bonds occurring during aging[32], which, however, can be regarded as a result of the relaxation process.

The applicability of several thermodynamic relationships to the melting of gels and the occurrence of a heat effect in this process raise the possibility of regarding the melting of jellies as a phase transition. Several experimental data provide grounds for such a view. Thus the dependence of the specific volume of gels on temperature is characterised by the occurrence of a point of inflection coinciding with the melting point determined visually. In several cases such a curve has a shape characteristic of crystalline polymers[28]. The view that the melting of jellies involves a phase transition is developed by Boedtker and Doty[36] in a long paper concerned with gelation in gelatin. The concept of phase transitions occurring in gels on fusion has been developed also by Flory[37]. He regards the relationships which he has observed for the change in specific volume with temperature in the collagen–glycol and gelatin–water systems as criteria for the occurrence of a phase transition of the first kind. This conclusion is supported by the applicability to the fusion of gels of the equation for the melting points of crystalline polymers. The occurrence of changes in the volume of a gel on melting[38,39] also indicates the possibility of phase transitions.

In spite of this work, the question of the occurrence of phase transitions in the fusion of gels cannot be regarded as settled. It is quite obvious, however, that the melting of a gel cannot be compared with the fusion of a crystalline polymer, where the phase transition is accompanied by a sharp change in the degree of order of the system, the melting point and the heat of fusion being completely definite thermodynamic quantities. Consequently the melting of gels cannot be regarded as a phase transition of the first kind. On the other hand, it is clear that the disintegration of the structural network of a gel leads to a definite change in the heat content of the system and to a certain change in its degree of order. Therefore the question of the thermodynamic nature of the conversion of a gel into a solution requires still further investigation.

The question of the occurrence of phase transitions in gels is closely linked to the question, repeatedly discussed in the literature, as to whether a polymeric gel represents a one- or a two-phase system. The work of Kargin *et al.*[5] was the first to show clearly the applicability of the phase rule to polymer solutions, and it has been established that under certain conditions two phases are formed in solution, namely a solution of the polymer in the solvent and a solution of the solvent in the polymer, *i.e.* a gel. It is known from Lipatov's papers[9,40] that setting occurs *via* a series of successive stages, with the system finally undergoing syneresis, *i.e.* separation into two equilibrium phases, represented by the gel and a solution of the polymer above the gel. Syneresis has been shown[30] to yield a gel having the same composition as that obtained when the polymer swells in the solvent. Only a gel which can be obtained by independent paths from different sides, *i.e.* by swelling and by setting, can be in thermodynamic equilibrium. The gel formed when a system separates into two phases satisfies this condition, and is consequently an equilibrium gel. In this case, since we have a two-phase system consisting of two components with two degrees of freedom (temperature and pressure), it is obvious that the equilibrium gel is a single-phase, two-component system.

But how must we regard gels which, owing to the extreme slowness of the changes, do not exhibit syneresis on setting? Since the phase rule is inapplicable to non-equilibrium systems, the number of phases in such systems can be judged only indirectly. According to Papkov[7,41] a gel is formed when a single-phase system, a polymer solution, passes into a region of separation into layers. Below the critical solution point, when separation has not yet occurred, we obviously have a two-phase system. The concept of a two-phase structure for jellies has been developed also by Sharkov[42]. It can be concluded from the published results that a non-equilibrium gel is a two-phase system, but an equilibrium gel is a thermodynamically stable single-phase two-component system. Formation of equilibrium gels is accompanied by a definite change in the thermodynamic parameters characterising the system. However, the possibility of applying a series of thermodynamic relationships describing phase transitions to gels does not yet provide grounds for regarding the melting of gels as a phase transition of the first kind accompanied by a sharp change in the order of the system and characterised by rigorously defined thermodynamic parameters.

4. MECHANISM OF GELATION

The process of gelation, *i.e.* the transition from a solution to a jelly, can be arbitrarily divided into two stages. The first is characterised by a considerable increase in the viscosity of the system, but on the whole the system still retains the inherent properties of solutions. The second stage begins from the moment of the appearance of elasticity, *i.e.* the start of the development of the properties of a solid. Subsequently the elasticity gradually increases and reaches a limiting value, determined by the conditions of gelation. From this point of view gelation can obviously be described as a process of the gradual arrangement of the macromolecules in solution into secondary structures with subsequent interaction between the latter to form a continuous three-dimensional structure.

Papers published during recent years have examined the transition from solution to gel by analogy with the formation of three-dimensional structures in the polycondensation of bi- and multi-functional molecules or with the cross-linking of linear molecules. Such a view has a definite physical meaning. This question is discussed quantitatively in papers by Flory[43] and Stockmayer[44]. It is assumed in these papers that combination of the macromolecules with one another is initially accompanied by a change in viscosity, and then, at the gel point, all the molecules combine to form a single three-dimensional structure. This instant corresponds to the appearance of elastic properties. The position of the gel point is determined by the presence of the minimum number of intermolecular bonds which are sufficient for the formation of the three-dimensional structure. When the gel point is reached, further growth occurs in the number of intermolecular bonds in the system, leading to an increase in the strength of the network.

In spite of the great similarity between processes of gelation and the formation of three-dimensional structures during polycondensation, the Flory–Stockmayer theory can be employed only for a qualitative description of the former process. This is because gelation is accompanied by the formation of both intra- and inter-molecular bonds, and the character of the process depends on their relative proportions. Further, it is supposed that the bonds between the molecules are local in character: there are bonds between two active groups (*e.g.* hydrogen bonds). The knowledge now available concerning the structure of polymers in solution and in the solid phase, obtained thanks to the work of Kargin and his school, enables an explanation to be given also for the existence of bonds which are not localised at a single point. The existence of such non-localised bonds had been pointed out by Ferry[2].

An experimental demonstration of the two stages into which gelation can be divided has been given in the work of Lipatov and Lapin[45] and has been shown[46] by means of heating and cooling curves. The presence of two maxima on the curves when setting occurs was explained by the initial formation of weaker bonds followed by that of stronger bonds, actually responsible for gel formation. The presence of two types of bonds differing in strength has also been pointed out in other papers[2,28]. These results can be interpreted as due to the formation of secondary structures from macromolecules arranged in a definite fashion during the early stages of gelation. It is perfectly obvious that the creation of such structures, in the form of stable clusters or groups of molecules, is necessary for gelation from dilute solutions. The existence of such structures is confirmed by early work on the turbidity of solutions during setting[47,48] and by the work of Boedtker and Doty[36], who showed from light scattering measurements that molecular aggregates in gelatin solutions exist even at great dilutions, their size and number increasing continuously with increase in the concentration of the solution. It was shown that these aggregates do not break down even at great dilutions or when the solutions are slightly heated. It was also observed that the change in light scattering ceases appreciably before the structural network of the gel is formed. On this basis it was concluded that the initial stage of gelation involves the formation of aggregates, which then link together to form a continuous three-dimensional structure. The stability of the aggregates at great dilutions has been shown also by Beyer[49]. Electron-microscopic investigations[50] have provided a direct demonstration of the existence of secondary structures, in the form of globules or bundles of uncoiled chains, even in dilute solutions. It was shown that the presence of such secondary structures in solutions was a consequence of the bundle structure of amorphous polymers. Thus these papers make it possible to establish some link between the structure of solid polymers and that of concentrated and dilute polymer solutions.

It is reasonable that the processes producing the secondary structures in solution (or aggregates according to Doty) should be affected by the same factors as those governing gelation. According to Doty[36] the formation of such aggregates involves a certain degree of order in the arrangement of the macromolecules in the aggregate. In this sense he speaks of an analogy between the processes of gelation and of crystallisation. Such an analogy, however, is completely without substance. The work of Kargin and Slonimskii[51,52] has firmly established the differences between crystallisation in high polymers and order–disorder processes, and has shown that even a very high degree of order in the molecular chains does not give grounds for regarding a polymer as crystalline. It is still less possible to speak of the existence of crystalline structures in polymer solutions and gels.

According to Doty[36], the second stage of gelation consists in the linking of the aggregates together in the course of their growth to form a three-dimensional structure. In conformity with this he considers that the melting of gels involves the simultaneous occurrence of two processes: (1) rupture of the bonds in the three-dimensional network of the gel, resulting in the aggregates being set free, and (2) rupture of the bonds between the molecules within the aggregates. Such a view is confirmed by the presence of molecular aggregates in solutions obtained by the melting of gels.

The nature of the bonds responsible for gelation has been discussed in the literature in particularly great detail in connection with gels of gelatin, owing to the complex chemical character of this material. In fact, the formation of different types of bonds – electrostatic, bonds between non-polar groups, bonds between polar groups, hydrogen bonds involving peptide groups in the chain, etc. – is possible in gelatin. It has been established that electrostatic forces play a negligible part in the setting process, since the temperature at which gelatin solutions set is independent of pH.[53]

The marked effect of such additives as urea and acetamide[54] on the melting point of gelatin gels, and the slight effect of introducing non-polar additives[15,16] led to the conclusion that intermolecular interaction in gelatin gels is due to the formation of bonds primarily between polar groups in the macromolecules[15]. According to another point of view[9,55] gelatin gels are formed by the interaction of macromolecules through their non-polar groups, since polar groups react with water, and the formation of bonds between them would presuppose that desolvation occurs, for which there is no evidence[31]. The formation of bonds between polar groups may be assumed even in a polar solvent, but this would require that the bonding energy of the polar groups of the macromolecules among themselves should be greater than the bonding energy of these groups with solvent molecules. These differences in viewpoint are associated with the extremely complicated chemical nature of gelatin. The formation of gelatin gels is probably due to various types of bonding, including bonds between several of the polar groups present in gelatin. In this connection particular interest attaches to an investigation[56] of the effect of various additives (salts of inorganic and organic acids) on the melting point of gelatin gels which have been chemically modified in a definite manner. It was shown that a chemical change in the gelatin molecules entailing bonding to polar groups (acetylation of amino-groups, nitration of guanidino-groups, sulphonation and acetylation of hydroxyl groups, and esterification of carboxyl groups) has no appreciable effect in changing the melting point of the gel of the modified gelatin. It was concluded from this that the above groups play no essential part in gelation. Therefore the action of the additives investigated is associated either with their effect on the non-polar parts of the molecule (in the case of additions of organic ions) or with that on the links between the peptide groups. It is assumed that formation of hydrogen bonds between peptide groups in different chains is the main cause of gelation in the case of gelatin.

Doty[36] also regards the formation of hydrogen bonds between gelatin molecules as the main cause of the formation of aggregates, but he assumes that in gelation the intersections of the network are not local bonds but ordered portions of the chains linked by hydrogen bonds. Thus an examination of existing views as to the mechanism of gelation in polymer solutions leads to the conclusion that this process consists in the formation of stable intermolecular bonds of both localised (*e.g.* hydrogen) and non-localised (*e.g.* van der Waals) types. Here the essential part in the formation of a three-dimensional network is played not by the mutual interaction of individual molecular chains but by the interaction of secondary structures – aggregates of molecules or bundles of molecular chains – existing in concentrated solutions.

5. DEGREE OF ORDERING OF MACROMOLECULES IN GELS

When considering the mechanism of gelation we have already remarked that a necessary condition for the process is the formation in solution of secondary structures, in which the polymer molecules are arranged in a definite manner relative to one another. In addition, we emphasised that such ordering cannot in any way be confused with crystallinity. The occurrence of highly ordered regions in supersaturated solutions leads, as already noted, to precipitation.

Furthermore X-rays have repeatedly demonstrated the presence of definite regions of ordered arrangement of macromolecules in gels, such data being given in the review by Ferry[2]. We feel that the cause of such regularity is the presence in solution of secondary structures, the existence of which has been demonstrated recently by Kargin *et al.*[57,58] They have established that these bundles of uncoiled molecules are stable structures, characterised by a quite definite degree of order in the arrangement of the polymer molecules in them. Kargin *et al.*[57] have put forward the hypothesis that amorphous polymers have a bundle structure. The ideas developed in these papers allow us to make a fresh approach to several aspects of the problem of gelation, and in particular to explain how equilibrium gels of identical structure can be obtained by swelling and by setting. Until recently it was supposed that molecules in solution are irregularly arranged relative to one another, and that in amorphous polymers also there is complete disorder in the mutual entanglement of the chains. On swelling, *i.e.* on penetration of solvent into the polymer, the entropy of mixing of the polymer with the solvent increases and the entropy of the polymer network decreases owing to deformation of the chains and their transition to more extended conformations. At the instant at which these quantities are in equilibrium, the process of swelling ceases. Such a picture, which is valid for cross-linked polymers, cannot be extended to all polymers. In the discussion mentioned above it was obscure in what way, in the formation of the equilibrium gel by setting, transition occurs from the coiled configurations of molecules in solution to the uncoiled configurations with the formation of an extended network, similar to that obtained on swelling. Only with the development of ideas on the bundle structure of polymers does it become possible to explain these phenomena. Polymers in a condensed state are supposed[57] to represent a system of entangled bundles able under certain conditions, *e.g.* on stretching, to change their shape, to uncoil and to straighten out. On the basis of these ideas we may suppose that the swelling of a polymer involves rupture of the bonds between individual bundles of molecules, a change in their shape, and the establishment of a new arrangement of the bundles in the swollen polymer, with the individuality of the bundles to some extent preserved. On the other hand, since the molecular bundles may exist also in solution, it is easy to imagine that, on setting, bonds will be formed between them, leading to a structure similar to that obtained on swelling. On such a view we must remember that a change in the shape of the molecules with a change in the nature of the solvent will not always lead to the same effects in concentrated as in dilute solutions, since in the former the intermolecular interaction may greatly impede a change in shape of the molecules, as will also the entry of a molecule into a bundle. It may therefore be accepted that, when the solvent deteriorates, *i.e.* in the process of gelation, molecules are not displaced, as occurs in dilute solutions, but interaction between the chain bundles is intensified, leading ultimately to the production of a continuous three-dimensional network.

Papkov[41] regards the structure of a non-equilibrium gel consisting of two phases as analogous to that of an emulsion in which the low-viscosity phase (*i.e.* the solvent) forms spherical particles in the high-viscosity phase (*i.e.* the polymer). In the light of the ideas considered above, it is impossible to agree with such a view. The structure suggested by Papkov for a gel does not explain either the fact that a gel can be obtained by two independent paths, or the similarity in mechanical properties of jellies formed by intermolecular and by chemical bonds. Nor does this scheme explain the complex of relaxation properties of jellies, and takes no account of the possibility of obtaining single-phase equilibrium gels. Finally, these concepts disregard thixotropic systems, in which the bonds between the molecules are similar in nature to those in ordinary, thermally reversible gels.

Thus existing views as to the structures of amorphous polymers and of gels lead us to conclude that there is an appreciable degree of order in the arrangement of molecules in gels. This regularity is due to the existence in solution of stable secondary structures of the type of aggregates or bundles of molecules having a definite degree of order, which, however, cannot be compared with the order characteristic of crystalline polymers.

6. RELATIONSHIP BETWEEN STRUCTURE AND MECHANICAL PROPERTIES OF GELS

The views considered above as to the nature of gels are confirmed by existing knowledge of their mechanical properties.

The formation of three-dimensional network structures involves the creation of a sufficient number of stable intermolecular bonds. Consequently the physical properties of gels will depend on the number and nature of the intermolecular bonds, as well as on the nature of the polymer and the solvent. In their most general form the mechanical properties of polymer gels are analogous to those of cross-linked polymers, and are determined by the deformations of the portions of the chain molecules situated between intersections in the three-dimensional network of the gel. The elastic properties of gels are explained by a change in shape of portions of the chains on deformation, *i.e.* they have the character of rubberlike elasticity. The nature of deformations occurring in polymer gels has been studied in detail[14-16]. It has been shown that the elasticity of jellies involves a change in entropy. However, whereas in the case of polymers having a purely rubber-like elasticity a rise in temperature is accompanied by an increase in the equilibrium modulus of the system, with gels a change in temperature immediately leads to a change in the number and strength of the intermolecular bonds, as a result of which the rigidity of the system diminishes (with gels which melt on heating). The analogy between gels and the three-dimensional networks of cross-linked polymers gives us some idea of the effect of the number of bonds in the network on the mechanical properties of gels. These ideas are based on the kinetic theory of elasticity, which links the extent of deformations and the corresponding stresses with the temperature and the number of bonds in a network of flexible polymer chains[59]. However, the kinetic theory can give only a qualitative description of gels, since the three-dimensional network of a gel is more imperfect than a cross-linked polymer, owing to the greater number of intramolecular bonds formed on gelation in dilute solutions. In addition, the lower strength of bonds in gels leads to their rupture and redistribution, also disregarded by the kinetic theory. Further, whereas in cross-linked polymers the flexibility of the chains in the network is determined solely by their chemical nature and the temperature, in gels an important part is played also by the nature of the solvent, on which depend both the strength of the intermolecular bonds and the flexibility of chain segments which are not linked together.

Polymer gels are able to exhibit true elastic deformations, *i.e.* to obey Hooke's law right up to the melting point[60]. True elastic properties are associated with the presence of strong intermolecular bonds and with weak interaction between unlinked portions of the chains. Gels are always more elastic than solutions of equal concentration, since in the latter the possible elasticity is masked by flow. With respect to mechanical properties it is difficult to draw a sharp boundary line between a gel and a solution, since many solutions exhibit elastic properties below the limiting shear stress. An example of this is provided by thixotropic solutions, which possess a structure formed by unstable bonds which are broken on mechanical treatment. It is interesting that, at the start of gelation, immediately after the appearance of elasticity, all jellies possess thixotropic properties[61]. This points to a close relationship between thixotropic and ordinary (thermally-reversible) setting.

The presence of elastic properties allows gels to be characterised by their modulus of rigidity. Most papers on the mechanical properties of jellies have been concerned with elucidating the dependence of this modulus on various factors. These questions have been investigated in detail by Zubov[16,15,54], Ferry[62,63], Sheppard[60], and Hirai[64,65]. The laws observed to govern the changes in mechanical properties confirm to a considerable extent the views of the structure of polymer gels which we have examined above. It is important to note here that the magnitude of the modulus of rigidity of a gel depends also on the method of preparation if it is not an equilibrium gel. Thus, at any instant before equilibrium is reached, the modulus of gels obtained from solutions by cooling is lower than that of a gel heated to the given temperature. This phenomenon is due to the slow establishment of equilibrium in gels with change in temperature. Whereas the cooling of a solution involves a slow process of the formation of bonds of different strengths with the selection of those characteristic of the given temperature, heating a gel formed at a lower temperature involves merely the rupture of those bonds which are unstable at the given temperature. A detailed investigation of the dependence of the mechanical properties of gelatin gels on the conditions under which they have been aged has been carried out by Rebinder and Ivanova-Chumakova[66].

We have discussed above the effect of various additives on gelation. Those additives which govern the process of setting also have a substantial effect on the mechanical properties of the gels[15,19,35,54,60,67,68]. The effect of adding a non-solvent on the rigidity of gels is governed by the fact that, when the solvent deteriorates, the total number and strength of the intermolecular bonds in the gel increase. On the other hand, successive replacement of the solvent in gels may be accompanied by a considerable increase in rigidity, obviously not due to a change in the number of bonds, since the volume of the gel remains unchanged during such replacement[69]. This is obviously due to a change in flexibility of the segments of the polymer chain between the intersections of the network, as the solvent deteriorates. On passing to a worse solvent these segments tend to contract, but this is prevented by the previously formed bonds in the network; as a result, these portions of the molecules are in a strained condition, which hinders their deformation.

The most interesting feature of the mechanical properties of gels is their relaxation behaviour, first studied thoroughly in the work of Zubov and Kargin already mentioned. The relaxation behaviour of gels differs from the behaviour of a polymer in a condensed state. There is a great difference in the character of the relaxation in dilute and in concentrated gels. The former obey Hooke's law over a wide range of rates of deformation, the magnitude of the deformation being independent of the time during which the forces have acted. This indicates that in dilute gels the free portions of the macromolecules between the joints in the network structure do not interact with one another. In contrast, concentrated gels exhibit a greater dependence of the extent of deformation on the rate of action of the forces the higher the concentration. In this case Hooke's law is no longer obeyed. Such behaviour is explained by an intensification of the intermolecular interaction of the portions of the chains situated between intersections in the three-dimensional network. A detailed characterisation of the properties of gels can be obtained also by investigating the relaxation of tension[61]. In the case of gelatin gels it has been shown that, under static conditions of investigation, the bonds in the gel do not break down under loads of short duration. But when the mechanical action is prolonged, a permanent set appears in gels, and appreciable stress relaxation is observed[66]. The relaxation of stresses at constant deformation and the presence of irreversible deformations can be due only to a relative displacement of the molecules of secondary structures forming the gels, which is possible only as a result of the rupture of the bonds between them. Obviously these effects are associated not so much with the relaxation of stresses by a change in shape of the chains, as with processes of relaxation of the bonds. The different rates of stress relaxation in gelatin gels under different conditions indicates the existence of bonds of different strengths. According to Ferry's data[63] the bonds in 6% gelatin gels are characterised by a set of relaxation times between 10^3 and 10^6 sec. Every temperature then has its own set of relaxation times, and a rise in temperature shifts the relaxation spectrum towards lower values. The concept of a set of bonds in gels is being developed at the present time also by Trapeznikov[70]. Stress relaxation in gels accompanied by the rupture of bonds between molecules and the resulting displacement of the latter is similar in character to the chemical relaxation of stress in cross-linked elastomers[71]. The relaxation properties of gels greatly depend on their methods of preparation. If the bonds are of great strength, they are characterised by great times of relaxation, and all factors promoting an increase in bond strength lengthen relaxation times.

An interesting feature of the relaxation behaviour of gels is that their rigidity remains unchanged during relaxation, *i.e.* that the total number of bonds does not change: in the place of the bonds which have been broken in the displacement of the molecules or structural units in the gel, new bonds of the same type are formed, but with different arrangements of the molecules. These bonds have the same distribution of relaxation times as those in the original gel[63].

Data on the mechanical properties of gels bring out their two peculiarities – the presence of reversible elastic deformations and their dependence on the conditions of formation of the gels, and the exhibition by gels of relaxation properties depending on the concentration of the gel. Data on the mechanical properties support the views of the structure of gels obtained in other ways, and enable these concepts to be considerably supplemented.

The main task in the study of concentrated solutions and their conversion into the gelatinous state is to investigate their structure in order to be able to control the properties of the solutions and gels, which is of great practical importance. The great advances made in the investigation of the structure of polymers in solution and in the condensed phase, and the discovery of the bundle structure of amorphous polymers, enable a fresh approach to this problem, which has not yet been completely solved, *i.e.* the structure of concentrated polymer solutions and gels. Although many questions have still to be cleared up, at the present time, conditions are suitable for a more complete investigation into the structure and properties of polymer gels, one of the most interesting systems formed by polymers.

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SODIUM NITROPRUSSIDE AND ITS USE IN ANALYSIS

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CONTENTS

INTRODUCTION

Sodium nitroprusside, first prepared in 1850[1], has been used for over a century as a reagent in the qualitative and quantitative analysis of organic and inorganic compounds. Its use is not yet fully developed, however, and has been increasingly investigated by analysts in recent years. The compound and its analytical applications feature little in Soviet and foreign literature; it is still not widely enough used in analysis, although it is cheap and available in any analytical laboratory, being manufactured in quantity in the Soviet Union. A review of problems connected with the increased analytical use of known reagents is of considerable scientific and practical interest[2], and in this connection a survey is presented of sodium nitroprusside and its analytical applications.

I. PREPARATION

Most of the preparative reactions described are between sodium ferro- or ferri-cyanide and nitric acid[3-7] or sodium nitrite[8-13]. Present-day preparations[14] likewise involve passage of oxides of nitrogen through sodium ferro- or ferri-cyanide solution[8], and the reaction between sodium nitrate and potassium ferrocyanide solution in the presence of sulphuric acid and ferric chloride[15]. Nitroprussides are formed when potassium ferrocyanide and potassium chlorate interact[16], and when potassium ferricyanide and calcium hypochlorite are heated together in solution[17]. Instead of the hexacyanoferrate complex, mercury[18], sodium[19], and potassium[9] cyanides may be used as starting materials, together with various iron compounds. Sodium nitroprusside was originally prepared from gaseous thiocyanates, formed by heating a mixture of tar and sulphur[20]. Electrolysis of potassium ferrocyanide solution also yields nitroprussides[17].

II. STRUCTURE

The accepted general formula $R_2[Fe(CN)_5NO]$ is based on many studies[4,8,9,15,21-33], but the structure is not clear. Some authors consider the NO group to be charged negatively[34], others positively[35]; this is considered in recent monographs on co-ordination compounds[36,37]. Bailar[37] considers the possibilities of the NO group bearing positive, negative, or zero charge, and suggests that it is doubly bonded to the metal atom. Grinberg[38] relates nitroprussides to the pentacyanomonoammines, and suggests that the molecule NO is covalently bonded to the iron(III) atom. Sas[39] considers the iron atom to be divalent, one CN group being bonded to it through nitrogen and the rest through carbon. There is clearly no firm indication yet of the structure of the ion, the valency of the ion, or its bonding with the ligands.

III. PROPERTIES OF SODIUM NITROPRUSSIDE

The compound crystallises readily from aqueous solutions as ruby-red prisms of specific gravity 1.71, which dissolve in water (1 : 2.5) at 16° to give a dark red solution, but are not soluble in absolute ethanol[1,14]. They belong to the bipyramidal class of orthorhombic symmetry[40], and their crystallographic parameters, coefficient of expansion, hardness, refractive index, and magnetic susceptibility are known[21]. Sodium nitroprusside has two molecules of water of crystallisation and the crystals do not deliquesce in air[1]. At 98°–99°, 1.5 water molecules are lost at first, and the rest gradually. In air at 15°–17°, the anhydrous salt readily reverts to the dihydrate[21]. The dihydrate is also reported[14] not to lose water at 100°, to lose half of it at 115°, and to decompose on further heating[21]. Hofmann[24] considers loss of water to be complete after 6 h at 110°, further loss of weight at 160° being due to decomposition. At 200° cyanogen and oxides of nitrogen are evolved, leaving a residue of the ferrocyanide type[41]. Heating to 440° in a sealed vessel causes yellow-brown crystals of formula $Na_2Fe(CN)_4$ to be formed[25].

The absorption spectra of sodium nitroprusside solution have two maxima in the ultra-violet[21], and one in the infra-red[42]. From values of cryoscopic constants[21,32] and the conductivity of solutions at different temperatures, the mobility of the nitroprusside ion has been calculated[21].

The colour of solutions kept in colourless and brown bottles changes to dark blue in sunlight, but does not change in darkness[21,43,44]. Investigations of the mechanism of this change have led to varying results; the products are considered by some authors to be Prussian blue and oxides of nitrogen[44], by others to be Prussian blue and hydrogen cyanide[21,45], or sodium cyanide, nitric oxide, and Prussian blue[46]. The photosensitivity of sodium nitroprusside solution is twenty times greater than that of potassium ferricyanide solution, and may be increased about another twenty times by the addition of ferric chloride; the products of photo-decomposition in the latter case have been shown to be diverse[46-47]. The sensitivity to sunlight of the nitroprussides of uranium, silver, iron, and mercury has been studied[48]. Crystals of sodium nitroprusside decompose to sodium nitrate and cyanide, hydrogen cyanide and ferrous cyanide[49].

Chlorine attacks sodium nitroprusside solutions at room temperature, slowly in darkness, but more rapidly in sunlight to give cyanogen chloride, ferric chloride, sodium chloride, and hydrochloric acid[50]. Hydrogen peroxide and sodium nitroprusside react to give oxygen[51] and sodium pentacyanoaquoferrate(III)[52]. Alkaline potassium permanganate solution gives ferric cyanides and nitrates[53]. Bromine at 120°–140° gives hydrogen cyanide, carbon dioxide, sodium bromide, and ferrous and ferric pentacyano-complexes[15].

Boiling aqueous solutions of sodium nitroprusside evolve nitric oxide at a rate sharply increased by the passage of a stream of oxygen[54]. Thus, oxidants decompose sodium nitroprusside entirely or cause other pentacyano-complexes of iron to be formed.

Hydroxylamine converts sodium nitroprusside to complexes of composition dependent on the pH and temperature[24,55,56]. Sodium nitroprusside is reduced by alkaline phenylhydrazine solution to sodium pentacyanoaquoferrate(II), by sodium bisulphite to sodium pentacyanomonoammineferrate(II)[24], and by metallic sodium in alkaline media to a compound resembling a ferrocyanide in its composition[15]. The products from sodium nitroprusside and sodium amalgam and the zinc–copper couple have been studied[15,57]. Hydrogen does not affect sodium nitroprusside[15]; attempts to hydrogenate it in the presence of platinum black gave no definite results[58]. The successive reactions between sodium nitroprusside and hydrogen sulphide have been studied[21,59,60]. Reducing agents usually lead to the formation of other complex compounds.

Inorganic acids, and their mixtures with ethanol or potassium permanganate, decompose sodium nitroprusside[57,61]. Caustic alkalis and alkaline-earth hydroxides cause an intense yellow colour, due to $Na_4[Fe(CN)_5NO_2]$;[21,62]

the corresponding silver salt has been studied[61]. Spectroscopic study of the reaction with sodium hydroxide indicates the equilibrium[63]:

$$[Fe(CN)_5NO]^{2-} + 2OH^- \rightleftharpoons [Fe(CN)_5NO_2]^{4-} + H_2O.$$

On heating solutions containing sodium nitroprusside and sodium hydroxide, iron and sodium cyanides, nitrates, and other decomposition products are formed[1,15,22,23]. Masal'skii[64] showed that ferrous complexes are formed, of composition depending on the temperature and the concentration of alkali. The yellow coloration is not produced by solutions of ammonia, bicarbonates, or carbonates[62]; ammonia gives sodium cyanamide[65,66], sodium pentacyanomonoammineferrate(II)[67,68], or disodium ammonium pentacyanomonoammineferrate(II)[67]. Sodium nitroprusside rendered anhydrous at 160° takes up two molecules of ammonia[69].

Sodium nitroprusside reacts with potassium cyanide to give potassium ferro-[15,24] or ferric-cyanide[8], but does not react with phosphites, hypophosphites, or antimonites[24].

Potassium, silver, copper, iron, zinc, calcium, and ammonium nitroprussides were first prepared and studied by Playfair[1]. Cadmium, mercury, cobalt, and nickel nitroprussides were prepared later[70], and the product of the reaction between sodium nitroprusside and mercuric oxide was studied[71]. The reactions between sodium nitroprusside and copper, nickel, and cadmium salts in the presence of pyridine yield the compounds[72]:

$$[CuPy_2][Fe(CN)_5NO],\quad [NiPy_4][Fe(CN)_5NO],$$
$$\text{and}\quad [CdPy_2][Fe(CN)_5NO].$$

Methyl, ethyl, and propyl nitroprusside derivatives have been prepared and studied[61]. Tetramethyl and tetraethyl nitroprussides, prepared from the corresponding amines, form sparingly soluble ruby-red prisms[73]. The alkylation of nitroprussic acid yielded tetramethylammonium, diethyl, pyridinium, and benzidinium nitroprussides[74]. The mechanism of formation, and the properties, of compounds from sodium nitroprusside and arylhydroxylamines[75], methylamine, ethylenediamine, and pyridine in the presence of ammonia[76] have been studied. Compounds of sodium nitroprusside with barium formate[77], hexamethylene tetramine[78], and urea[79] are described. The properties have been studied of crystalline compounds formed from nitroprussides and the potassium salts of alkynes[80].

IV. ANALYSIS OF SODIUM NITROPRUSSIDE, AND ITS USE AS AN INDICATOR

The nitroprusside ion may be detected by various microchemical reactions[81]. Sodium nitroprusside is estimated volumetrically with cadmium nitrate[82], and its argentimetric estimation is used for potentiometric titration[83]. Mercurimetric estimation is used[84], and a determination based on the reaction between sodium nitroprusside and sodium tetracyanonickelate is described[85]. Polarography has been applied successfully[86-88].

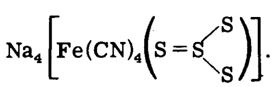
Sodium nitroprusside is used as an indicator in the volumetric determinations of halides[89,90], cyanides[89], and nitroprussides of alkali metals[82], the titration of ammonium mercaptide with potassium ferricyanide[91], and the estimation of mercuric acetate in non-aqueous solvents[92]. Its use as an indicator is proposed in the mercurimetric estimation of chloride formed on the hydrolysis of chlorobutanol[93], and it is used in conjunction with certain dyes as an indicator in the estimation of reducing sugars[94].

V. ANALYSIS OF INORGANIC COMPOUNDS

The cyanide ion may be detected through the formation of the nitroprusside ion[95]. Very sensitive microchemical tests for zinc[96] and palladium[97] depend on the precipitation of the nitroprussides with sodium nitroprusside, the zinc salt forming characteristic crystals. The formation of metal nitroprussides is used for the volumetric estimation of nickel[98] and copper[99] and the gravimetric estimation of silver[100]. Errors are avoided in the conductimetric titration of heavy metal ions with nitroprusside if ethanol is present[101].

The intense yellow colour given by sodium nitroprusside and caustic alkalis or alkaline-earth hydroxides serves to indicate the presence of these compounds[21]. At room temperature, arsenious oxide dissolved in 20% sodium hydroxide solution gives an intense dark red colour with sodium nitroprusside, although sodium arsenite gives no colour under these conditions[102,103].

A year before nitroprussides were first synthesised, Gmelin[21] observed the colour given by sulphides with the product from nitric acid and "red blood salt" [presumably potassium ferricyanide (Ed. of Translation)], so that the formation of the sulphide – nitroprusside colour was called Gmelin's reaction. Playfair described this reaction in the first description of the synthesis of nitroprussides[1]. Conditions for the analytical use of the reaction were later studied in detail; the optimum concentrations of the reactants were established, the reaction was studied in neutral, alkaline, and acid solution, and in the presence of glycerol, ethanol[104], and phosphates[105], and the influence of respective concentrations was investigated[106]. The colour is given by hydrogen sulphide only with alkaline solutions[104], so that to test for this gas in air, filter paper moistened with ammoniacal sodium nitroprusside solution has been proposed; a purple-violet colour is produced[107]. The sulphide – nitroprusside colour is given in the presence of not only caustic alkalis and ammonia, but also carbonates, borates, silicates, and phosphates, so that it may be used to indicate alkalinity[108]. The colour given by hydrogen sulphide and sodium nitroprusside in the presence of magnesium or calcium carbonate is used to detect sulphides in mineral water[109]. Alkaline solutions of polysulphides mixed with sodium nitroprusside transmit purple light, but reflect blue light[10]. The sensitivity of the sulphide – nitroprusside reaction has been recorded[21,110,111]. The mechanism of the reaction has been much studied; Scagliarini and his coworkers[112-116] investigated it, as well as the products of the decomposition of the coloured complex, the composition of which they showed to accord with the formula $Na_4[Fe(CN)_5NOS]$. Other workers[33,117] studied the reaction mechanism, and suggested the structure[117]:



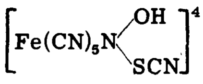
Scagliarini confirmed the theoretical basis for this structure[118]. Later work[119] showed the coloured complex of Gmelin's reaction to be $(Na_6[Fe_2(CN)_8S_2])_n$. Gmelin's colour reaction is used for the potentiometric estimation of sulphides[112,120] or the spectrophotometric estimation of small quantities of sulphide ion[121].

The rose colour given by sulphites and sodium nitroprusside is intensified by ferrocyanides and zinc salts[122]. The effects on this reaction of reagent concentrations, pH, and other cations have been studied in detail[123]. The detection of sulphur dioxide in gases has been described[124], using zinc nitroprusside suspension on a glass rod. The sulphite – sodium nitroprusside colour is used to detect sulphur dioxide in drops of sulphite cellulose extract[125], and for the photometric estimation of small amounts of sulphite[121]. The additive formation of the coloured ion $[Fe(CN)_5(NO)(SO_3)]^{4-}$ has been suggested[116,126].

Mixtures of sodium thiosulphate and nitroprusside solutions remain colourless in darkness, but direct sunlight produces a dark blue colour[21], used to detect thiosulphates[95]. A drop method for this detection has been proposed, so that sodium nitroprusside may be used for the consecutive drop analysis of a mixture of sulphide, thiosulphate, and sulphite ions in the presence of sulphate[127].

A yellow colour results from sodium nitroprusside and sodium tetrathionate in the presence of alkali metal carbonates, becoming green after several hours; the change is more rapid in sunlight, while the colour disappears again in darkness[128]. Sodium nitroprusside and alkaline sodium hydrosulphite solutions give a red colour[129].

The colour reaction between potassium thiocyanate and sodium nitroprusside has been studied in alkaline and acetic acid solutions; formation of the ion



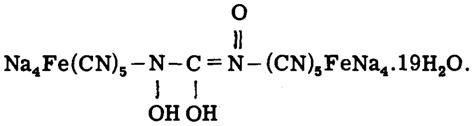
was suggested by Tarugi[130]. Data concerning the reaction mechanism were reviewed critically in the light of the part played by the NO group in the nitroprusside ion[131], but the criticism was refuted by Tarugi, who had investigated the mechanism[132].

The literature indicates that the use of sodium nitroprusside for the qualitative and quantitative analysis of cations is based on the formation of insoluble nitroprussides. A series of anions, all sulphur-bearing, give colorations with sodium nitroprusside, sometimes only after exposure to sunlight. Studies of reaction mechanism indicate that the anions become attached to the NO group, or replace it.

VI. ANALYSIS OF ORGANIC COMPOUNDS

Sodium nitroprusside is widely used as a reagent for organic analysis. Copper nitroprusside, obtained from it, was used in 1857 to detect artificial essential oils, particularly turpentine[133]. Small quantities of pyruvic acid are detected and estimated colorimetrically with sodium nitroprusside[134]; in alkaline solution the latter undergoes a colour reaction with cyclic hydrocarbons, suggested as due to co-ordination of these to the nitroprusside ion[135]. Isophorone is estimated colorimetrically by means of its colour reaction with sodium nitroprusside[136]. Halogen derivatives of some aliphatic amines are detected by means of the colour formed on successive addition to their solution of sodium nitroprusside, caustic alkali, hydrochloric acid, and ferric chloride[137]. An alkaline solution of cane sugar and sodium nitroprusside becomes yellow-brown on boiling, while glucose and invert sugar give this colour at room temperature or at 50°–60°.[138] Sodium nitroprusside is used in the microanalysis of organic compounds containing reactive methylene groups[139]. Sodium nitroprusside solution, hydrogen peroxide, and benzene react in sunlight to give a green colour in the benzene layer, due to $o\text{-}C_6H_4(OH)(NO)$.[140]

The use of sodium nitroprusside as a reagent for aldehydes and ketones has been studied in detail. Alkaline formaldehyde solution gives an amber colour[7], due to the compound[129]:



$$\underset{\displaystyle OH}{\overset{}{Na_4Fe(CN)_5-\underset{|}{N}}}-\underset{\underset{\displaystyle OH}{|}}{C}=\overset{\overset{\displaystyle O}{\|}}{N}-(CN)_5FeNa_4.19H_2O.$$

If alkaline formaldehyde solution is treated with sodium nitroprusside and phenylhydrazine in hydrochloric acid, a blue coloration appears which becomes red on addition of ferric chloride and concentrated hydrochloric acid, and then orange[141]; formaldehyde is estimated in this way[142]. A colour reaction was later demonstrated between sodium nitroprusside and formaldehyde in the presence of hydroxylamine[143]. Legal[144] discovered the colour given by acetone and sodium nitroprusside in alkaline or acetic acid solution, and Bitto[145] showed that many aldehydes and ketones may be detected thus; acetyl compounds are also detected[146], but compounds in which the carbonyl group is directly bonded to $-OH$, $-OR$, $-OM$, $-NH_2$, and $-Cl$ groups give a negative reaction[147]. Cambi[148,149] separated and examined the product from sodium nitroprusside and acetone, and suggested that acetone and some other ketones form coloured compounds by addition to the NO group. Other workers investigated the mechanism of the Legal reaction[150,151], the conditions for its occurrence being studied in detail with aliphatic and cyclic aldehydes and ketones[152], acetone[153], acetaldehyde[7,151,153], 2-oxopropan-1,3-diol, methylglyoxal[154], and acetophenone[155]. Stanley[156] established the sensitivity of the reaction, and the absorption maxima of the coloured solutions, for many ketones. Rosenthaler[157] used the Legal reaction to detect citral, citronellol, vinyl acetate, and vinyl ether, and Tanabe and Kamiya[158] used it to detect benzimidazole, quinoxaline, quinazoline, adenine, methionine, and uric acid. It is used to verify the authenticity of pharmaceutical Chloretone [1,1,1-trichloro-2-methyl-2-propanol] and Lobeline [*N*-methyl-2-(β-hydroxy-β-phenylethyl)-6-phenaryl-piperidine] preparations, which are degraded to ketones by strong alkali[159]. Methods of macro- and spot-test analysis with sodium nitroprusside have been proposed for Novarsenol [Neosalvarsan; Neoarsphenamine; sodium 3,3′-diamino-4,4′-dihydroxyarsenobenzenemethanalsulphoxylate], differentiating this from organic arsenicals of similar structure[160]. The applicability of the Legal reaction to the analysis of compounds which are not aldehydes or ketones is therefore evident.

The sodium hydroxide used in the Legal reaction may be replaced by other bases; aldehydes give a colour reaction with sodium nitroprusside and trimethylamine[161], while the colour given by sodium nitroprusside, ethylamine or ethylenediamine, and acetone distinguishes the latter from formaldehyde and acetaldehyde[162]. Diethylamine and piperidine intensify or modify the colour produced in alkaline solution by sodium nitroprusside and 2-oxopropan-1,3-diol or methylglyoxal[154]. Sodium nitroprusside and piperidine are used to detect acrolein, acetaldehyde, and some other aldehydes[163,164]; compounds containing the CH_3CO-, C_2H_5CO-, and C_3H_7CO- groups give a red colour under these conditions, but the C_6H_5CO- group gives no colour[166]. A blue colour is given by a mixture of nitroprusside, piperazine, and piperidine and ethyl, propyl, or allyl aldehydes[167]. Some ketones may be detected with sodium nitroprusside and hydroxylamine[143]. Sodium nitroprusside is used to detect ketones mixed with alcohol[168] and in the chromatographic analysis of acetone[169], and has been examined in detail as a means of detecting acetone in pharmaceuticals containing volatile oil of mustard [allyl isothiocyanate (Ed. of Translation)][170-174].

The Legal reaction is used to identify organic compounds which may be oxidised or reduced to aldehydes. Acetaldehyde vapour, from the reduction of chloral with hydrogen, is identified with filter paper moistened with sodium nitroprusside and piperidine[175]. Feigl[176] modified this to a spot reaction by using filter paper moistened with sodium nitroprusside solution containing morpholine, and used this to detect the decomposition products of nitroethane[177], *N*-ethyl and propyl derivatives[178], traces of ethanol[179], and acetic acid impurity in formic acid[180]. Acrolein in air has been detected[181,182] by its well-investigated colour reaction with sodium nitroprusside in the presence of piperidine[163]. Isopropanol is detected, after oxidation to acetone with potassium dichromate solution, with sodium nitroprusside in the presence of ammonia and ammonium chloride[183]. The oxidation products of some alcohols are detected with sodium nitroprusside, piperazine, and piperidine[167]. Formic acid and sodium bisulphite react to give dithionous acid, which gives a green or dark blue colour with sodium nitroprusside[184]. The structure is described of the coloured reaction products from acetic acid and ethyl acetate and sodium nitroprusside in the presence of ammonia and aliphatic amines[185]. Butyric acid is detected by oxidation with hydrogen peroxide to acetoacetic acid, identified by the Legal reaction[186]; lactic acid may be detected with sodium nitroprusside after dehydration[167] or oxidation of silver lactate to acetaldehyde with iodine[187]. Viala and Grignon[188] identified lactic acid in pharmaceuticals by oxidation with bromine water to pyruvic acid, which gives a colour reaction with sodium nitroprusside[189]. Citric acid is identified after conversion to acetonedicarboxylic acid with acetaldehyde and concentrated sulphuric acid[190].

These colour reactions with aldehydes and ketones in the presence of aliphatic and heterocyclic amines are used to detect the latter. The colour reactions between sodium nitroprusside and methylamine, dimethylamine, ethylamine, and other aliphatic amines, in the presence of acetone, have been studied together with the structures of the coloured compounds[191]. A spot test for identifying secondary aliphatic amines with sodium nitroprusside in the presence of acetaldehyde[192] is used to detect secondary aliphatic and heterocyclic amine impurities in primary and tertiary amines[193] and to identify secondary amines and primary alkylamines[194]. Aqueous–alcoholic sodium nitroprusside and propionaldehyde or acetaldehyde are used for the systematic identification of amines[195].

A characteristic colour change occurs when a weakly alkaline solution of diethylamine, sodium nitroprusside, and potassium ferricyanide is heated and then cooled[196]. Sodium nitroprusside is used together with potassium ferricyanide and phenylhydrazine to identify 1-phenyl-2-methylaminopropane, and together with acetone to identify 1-phenyl-2-aminopropane[197]. The NO group is replaced when sodium nitroprusside reacts with alkaline solutions of hydrazine, phenylhydrazine, ethylamine, and diethylamine[198]. An alkaline or acetic acid solution of phenylhydrazine, glucose, and sodium nitroprusside acquires a characteristic colour[199].

Sodium nitroprusside gives colour reactions with some organic compounds containing sulphur. After hydrolysis with sodium hydroxide solution, carbon disulphide and mustard oil form coloured compounds with sodium nitroprusside similar to those of sulphides[200]. The method of detecting mercaptans with sodium nitroprusside[21] has been modified for the detection of small amounts[201], and the estimation[187], of sulphydryl derivatives, and is used for detecting organic sulphides in petroleum[202] and to test the authenticity of the sulphur-bearing pharmaceutical Unithiol [sodium propan-2,3-dithiol-1-sulphonate][203]. No colour reaction is given with aromatic sulphides[204].

Hofmann investigated and proposed a structure for the coloured compound formed by sodium nitroprusside and thiourea[27]; Cambi[205] reviewed this work critically and proposed a different structure. A solution of sodium nitroprusside, thiourea, and mercaptans assumes a characteristic colour in sunlight[206,207]. Okuma[208] used a colour spot test for thiourea and thiosemicarbazide with sodium nitroprusside and hydroxylamine. A more specific and sensitive test using sodium nitroprusside alone was developed for thiosemicarbazide later, whereby it may be distinguished from thiourea and thiosemicarbazones[209]; this test may be modified for application to the pharmaceutical thiosemicarbazones Thibone [Thiacetazone, or 4′-formylacetanilidethiosemicarbazone (Ed. of Translation)] and Cutisone [4-formylcumenylthiosemicarbazone][210]. Sodium nitroprusside is used in spot tests for thioethers and thioketones in pharmaceuticals and biological matter, which yield sulphides on fusion with sodium hydroxide[211]. The same test is used for onion and garlic phytoncidal preparations[210]. Organic compounds containing sulphur may be detected on filter paper, after reduction with sodium in liquid ammonia, with sodium nitroprusside[212].

A ruby red colour is given by alkaline creatinine solution and sodium nitroprusside[213], which disappears on acidification with acetic acid, and on subsequent heating becomes green[145] and then blue; a blue deposit is finally produced[214]. The reaction mechanism[215], the optimal conditions, and the effect of pH have been investigated[216]. Creatine, guanidine, and glycine give no colour reactions[213]. A solution of sodium nitroprusside, turned yellow-brown by sunlight, gives a red colour with creatine, guanidine, and their methyl derivatives[217].

Sodium nitroprusside has been examined as a reagent for phenols and primary aromatic amines. Aqueous or alcoholic phenol solutions, mixed with concentrated sulphuric acid and crystalline sodium nitroprusside, assume various colours according to the nature of the phenol, changed by addition of ammonia[218]. Colour reactions with phenols in the presence of caustic alkalis have been described[129]; ammoniacal pyrocatechol solution gives a cherry red colour[219]. Phenol derivatives and sodium nitroprusside give blue or green colours in the presence of caustic alkalis and hydroxylamine[220]. Aqueous sodium nitroprusside solution, illuminated with ultra-violet light, is used as a macro- and spot-reagent for aniline[221], whereby a simple method of analysis has been devised for antifebrin and phenacetin in medical preparations; the latter is detected in them by this means[222]. Sodium nitroprusside and potassium ferricyanide are used for the macro- and spot-detection of novocaine[223]. For the analysis of sulphanilamide preparations, mixtures of sodium nitroprusside, sodium hydroxide, and potassium permanganate[224] or diphenylamine, sodium nitroprusside, and concentrated sulphuric acid[225] are proposed. Reduction products of some sulphanilamide preparations may be detected with sodium nitroprusside paper[226]. A later colour reaction for sulphanilamide is used for the systematic qualitative analysis of such preparations[227].

Sodium nitroprusside is used as a reagent for heterocyclic compounds and some biologically active natural products; α-substituted pyrroles give characteristic colours[228], and alkaline indole solution assumes a muddy brown colour which acetic acid converts to blue[114]. Methyl indole gives a violet colour under these conditions only when the acetic acid solution is boiled[187]. The reaction of sodium nitroprusside with antipyrine[229], and its coloured products with antipyrine[230,231] and pyramidone[232] in the presence of iron salts, are described. Regitine [2-(*N'*-*p*-tolyl-*N'*-*m*-hydroxyphenylaminomethyl)-2-imidazoline] has been detected with sodium nitroprusside[233], and the method has been modified for the identification of imidazole derivatives[234] and their colorimetric estimation in pharmaceuticals[235]. Hydantoin reacts with alkaline sodium nitroprusside solution to give the coloured compound $\mathrm{Na_3[(CN)_5FeNO\underline{CH.NH.CO.NH.CO}]}$, which is hydrolysed to parabanic acid [oxalylurea] and hydroxylamine[236]. 2,3-Dimethylbenzothiazole gives an intense dark blue colour with alkaline sodium nitroprusside[237].

Wachsmuth[238] suggested that the colour reaction between sodium nitroprusside and isonicotylhydrazide be used to test the authenticity of pharmaceutical preparations of Tubazid [Isoniazid or isonicotinic acid hydrazide][239]. Sodium nitroprusside is used for the spectrophotometric estimation of isonicotinic nitrile[240], the colorimetric estimation of pyrazinamide[241], and the gravimetric estimation of pharmaceutical preparations of Chlorpromazine (Aminazine) [2-chloro-10-(3-dimethylaminopropyl)-phenothiazine][242]. The microchemical reaction of sodium nitroprusside with Demerol [ethyl-1-methyl-4-phenylpiperidine-4-carboxylate] has been described[243].

Dilute sodium nitroprusside solution is coloured pink by coniine[187]. The composition and properties have been studied of the compounds formed by sodium nitroprusside with strychnine, brucine, quinine, and quinidine[244]. Sodium nitroprusside is used in the microanalysis of strychnine[245] and brucine[246]. A colour reaction with sodium nitroprusside is used to detect methylnarceine impurity in narceine[247]. Feigl and Silva[248] used a micro-method of detecting ephedrine based on a reaction between its decomposition products and sodium nitroprusside solution containing morpholine. Solutions of vitamin B_1 and sodium nitroprusside give a greenish colour when alkaline, turning violet on acidification and then pale blue[249]. Sodium nitroprusside forms red compounds with cardiac glycosides, the aglycones of which contain an unsaturated five-membered lactone ring in the side chain (digitalis, strophanthus, and oleander glycosides); no colour reaction occurs with aglycones containing an unsaturated six-membered lactone ring (sea onion glycoside)[178]. This reaction is used also by the pharmacopeia[250] as a tentative test for the authenticity of crystalline cardiac glycosides and pharmaceutical preparations in which they are present. Dihydrostreptomycin is estimated colorimetrically with sodium nitroprusside and potassium ferrocyanide[251].

Division into three groups of the reactions between sodium nitroprusside and organic and inorganic compounds has been proposed: (1) those involving addition of inorganic ions or organic molecules to the NO group, giving complicated complex anions; (2) those involving replacement of the NO group by NH_3 or H_2O to give new pentacyano-complexes, which then form coloured compounds with organic substances; and (3) those involving replacement of the CN group, as with hydroxylamine[252]. The reactions considered above belong mainly to groups (1) and (3). The use in analysis of other iron pentacyano-complexes, first obtained by Hofmann[27] from sodium nitroprusside, has been considered. Sodium pentacyanoaquoferrate(II) and pentacyanoammineferrate(II) are used to analyse thioketones and thioaldehydes[253], aromatic nitroso- and nitro-compounds, hydrazine derivatives[254], aromatic and α- and β-unsaturated aldehydes[255], and derivatives of imidazole[256] and pyrazinamide[241]. Grote[206] showed that sodium pentacyanoaquoferrate(III) forms coloured compounds with sulphydryl derivatives; Grote's reagent is used for the colorimetric estimation of thiouracil[257], methylthiouracil[258], and other sulphur-bearing organic compounds[259]. Sodium pentacyanoaquoferrate(III) is used in the spot testing of primary aromatic amines[260]. Herington[261-263] studied the composition, properties, and mechanism of formation of the reaction products from sodium pentacyanoammineferrate(III) and aromatic amines. Iron pentacyano-complexes and hydrogen peroxide are used for the qualitative analysis of some sulphur-bearing organic compounds and primary aromatic amines[264] and, together with hydroxylamine, for detecting thiourea, thiosemicarbazide[208], and phenol derivatives[220].

It is clear from the above that sodium nitroprusside has been most thoroughly investigated as a reagent for aldehydes and ketones, and compounds which may be converted to them. It is also used in the analysis of hydrocarbons, phenols, amino-derivatives, sulphur compounds, heterocyclics, and other organic compounds. Irradiation of the solution with ultra-violet light may be used, or other reagents may be added — potassium ferro- or ferri-cyanide, hydrogen peroxide, phenylhydrazine, hydroxylamine, or ferric chloride. Other iron pentacyano-complexes may be used. Interaction of sodium nitroprusside and organic compounds involves either replacement of the NO group or the addition of the organic compound to the complex anion. Sodium nitroprusside cannot be regarded as a general reagent for defined groups of organic compounds since different conditions are needed for the analysis of each one, and varying colours are produced by the compounds in any group.

VII. BIOCHEMICAL ANALYSIS

Sodium nitroprusside is used to detect compounds bearing sulphydryl groups in tissues[265]. The influence of pH, and its optimal value, have been determined[216]; the reaction mechanism between sodium nitroprusside and cysteine has been studied[266]. This reaction has been studied spectrophotometrically[121] and used for the colorimetric estimation of cysteine in cystine[267]. Cysteine gives no colour with sodium nitroprusside in the presence of hydrogen peroxide[237]. Sodium nitroprusside solution (10%) is a reagent for the colorimetric estimation of methionine[268]. The optimum conditions for the colour reaction between glutathione and sodium nitroprusside have been investigated[216] and a structure suggested for the product[269]; the reaction is used to detect glutathione and its derivatives in the organs of white mice[270] and to estimate glutathione in normal tissues and tumours[271]. Arnold[272] showed that proteins containing cysteine are slowly coloured purple-red by sodium nitroprusside; the use of this reaction was developed later[273]. The sulphydryl group of keratin, treated with mild alkali, gives a pale red-violet colour with sodium nitroprusside, in contrast to other thiols[274]. Albumin gives a colour after prolonged boiling with sodium hydroxide solution[21]. A crystalline compound has been obtained from sodium nitroprusside and albumin from human blood serum[275]. Sodium nitroprusside is used, together with benzidine, fuchsine, and hydrogen peroxide in blood tests[276,277]. On account of its great capacity for adsorbing arsine, sodium nitroprusside is used to complex the latter in blood[60]. Paper soaked in alkaline sodium nitroprusside solution is recommended for detecting thioglycollic acid in hair[278]. Urine passed after muscular exertion gives a characteristic colour with sodium nitroprusside in alkaline or acetic acid solution[279]; the use of this reaction in biochemical analysis has been described in detail[280-282]. Sodium nitroprusside is used for the detection and differentiation of some bacteria[283-285]. Legal's reaction[144] was first used by him to detect acetone in urine; modifications of this test have been proposed[286-291]. A review, critical of some of these modifications, was based on interference by sulphides[292-294]. Methods of detecting acetone in biological liquids by means of sodium nitroprusside and ferric chloride have been comparatively assessed[295]. The Legal reaction is used to estimate acetone in urine and other biological liquids[296,297].

Sodium nitroprusside is therefore used to detect and estimate sulphydryl derivatives and amino-acids, polypeptides and proteins containing sulphur; it is used for microbiological tests, and for blood and urine analysis.

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STUDIES OF THE CHEMISTRY OF HYDROCARBONS AND THEIR CATALYTIC CONVERSIONS[†]

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CONTENTS

I. INTRODUCTION

In recent decades hydrocarbons have become more and more widely used in the chemical industry as most valuable raw materials and the petroleum industry has added the supply of such raw materials to its production of liquid fuels, the two developments giving rise to the petrochemical industry, based on much organic chemical research on various hydrocarbons and their reactions, as well as on an investigation of the composition of various types of petroleum. Russian scientists have played an enormous part in this research, so that petrochemistry has justifiably become traditional in Soviet chemical science. Soviet chemists and B.A.Kazanskii in particular, have contributed much new knowledge in this field.

The chief components of crude oil are paraffins, cyclopentanes, cyclohexanes, and aromatic hydrocarbons. Mutual transformations of cyclopentane hydrocarbons into paraffin ones and of paraffins into aromatic or cyclopentane hydrocarbons have been discovered in the past 25–30 years. A study has been made of the conditions favouring the conversion of paraffins into the industrially important unsaturated hydrocarbons as well as of the hydrogenation of diene and aromatic hydrocarbons under ordinary and high pressures. The laws governing the conversion of gem-substituted cyclohexanes in the presence of various catalysts have been elucidated and new ways found for the preparation of paraffins from carbon dioxide and hydrogen. Some of these reactions were discovered and studied in detail by Kazanskii and his school, who also made numerous new and original contributions to the study of the other reactions concerned. Recently much interest has been shown in the hydrocarbons with three- and four-membered rings as well as those with more than six-carbon atoms in the ring. Here the contribution of Kazanskii and his followers has also been very important. One of the analytical methods (the so-called combined

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[†] The article has been prepared with the help of M. G. Gonikberg, I. V. Gostunskaya, G. Ya. Kondrat'eva, M. Yu. Lukina, E. A. Mikhailova, A. F. Plate, M. I. Rozengart, O. D. Sterligov, G. A, Tarasova, S. I. Khromov, and Ya. T. Eidus.

method) developed for the determination of the composition of the petroleum part of crude oil was devised with the active participation of Kazanskii and his colleagues and was based on many years' work on the synthesis of some 200 individual hydrocarbons of high purity and the study of their Raman spectra. This method is widely used in Soviet laboratories and in some of the People's Democracies.

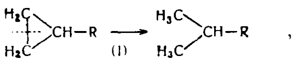
This article is a current review of some of the problems of the chemistry and catalytic reactions of hydrocarbons with particular reference to the work of Kazanskii and his school.

II. CATALYTIC HYDROGENATION OF CYCLIC HYDROCARBONS

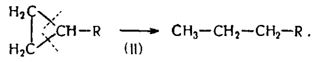
Reactions in which catalytic hydrogenation of cyclanes led to the formation of paraffins attracted attention many years ago. These reactions have been known for some time in the case of three- and four-membered rings: in an atmosphere of hydrogen cyclopropane is converted to propane at 180° in the presence of nickel on pumice[1], at 0° in the presence of nickel on kieselguhr[2], and at 25° in the presence of platinum[3]. The same reaction occurs with the homologues of cyclopropane[4,5,6]. Cyclobutane and its homologues also undergo hydrogenation in the presence of nickel and platinum, giving paraffin hydrocarbons[1,7,8]. These reactions were long thought to be associated with the considerable Bayer's strain in three- and four-membered rings and have even been regarded as proof of Bayer's hypotheses. However, it was subsequently shown that cyclopentanes, free of Bayer's strain, underwent hydrogenation relatively readily, and quite recently cyclanes with an even larger number of carbon atoms in the ring (from 8 to 10 at any rate) have been found to undergo this reaction.

Kazanskii first discovered hydrogenation of the five-membered ring as a student in N. D. Zelinskii's laboratory, where extensive work was carried out on the various catalytic reactions of hydrocarbons. He and his own students then studied this reaction in detail using cyclopentane and its homologues; they also discovered the hydrogenation of cyclanes with still larger numbers of carbon atoms in the rings. Kazanskii also reinvestigated the previously discovered analogous reactions of small rings, establishing new and important facts and finding explanations for some of the very contradictory data provided by earlier workers.

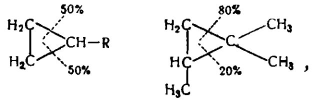
Cyclopropanes. Hydrogenation of cyclopropane shows a noteworthy feature in the wide variation of the requisite experimental conditions, depending on the catalyst used (complete conversion at 0° with kieselguhr and at 180° with nickel on pumice). Other data are equally contradictory. According to some authors hydrogenation of cyclopropane requires a higher temperature than that of its homologues[9], whereas other authors claim the exact reverse[4,5,6]. Some authors state that the hydrogen adds on to the ring carbon atoms carrying the most hydrogen atoms[4,6]:



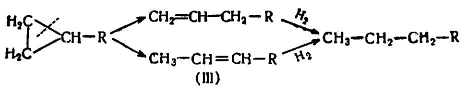
whereas others consider that the ring opens at the least hydrogenated carbon atoms[10]:



Kazanskii, Lukina, *et al.* have shown that these contradictions are only apparent, since two different reactions can take place under the conditions of hydrogenation. Hydrogenation itself occurs[11,12] with opening of the ring in accordance with scheme(I); this is especially clear-cut when platinised charcoal is used. With catalysts such as palladised charcoal or platinised kieselguhr some paraffins are always obtained which would appear to be formed in accordance with scheme (II)[13,14]. Kazanskii and his co-workers, however, showed that the process was more complex, the alkyl cyclopropanes undergoing isomerisation to open-chain olefines[15,16,17] when the following catalysts are employed: silica gel (~ 50°), aluminosilicates (~ 50°), kieselguhr (120°), pumice (170°–200°) and activated charcoal (~ 200°), the ring always opening at the bonds next to the least hydrogenated carbon atom in the ring:



the bond between the most hydrogenated carbon atoms remaining intact. If there is a double bond next to the ring the initial isomerisation is considerably more intense and is accompanied by immediate polymerisation of the resulting dienes[18]. The polymer which is deposited on the catalyst poisons it rapidly and completely, thus preventing further isomerisation. The list of catalysts above indicates that not all the carriers used for the catalysts are inert, and therefore they may induce isomerisation themselves. The olefines thus formed add on hydrogen to give the appropriate paraffins:

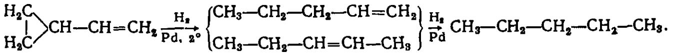


which are in fact the paraffins which are suggested by scheme (II). Thus the apparent contradictions mentioned above are resolved by competition between reactions (I) and (III). Platinised charcoal is so highly selective for cyclopropane hydrogenation because the rate of hydrogenation is particularly high in the presence of platinum, whereas the rate of isomerisation on activated charcoal is very low. In the case of platinised kieselguhr the carrier favours a relatively higher rate of isomerisation, and so the yield of scheme (III) products becomes appreciable. The ratio is shifted still further towards scheme (III) when the other catalysts mentioned are used.

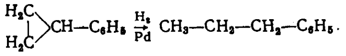
Particularly important in the work of Kazanskii's school are the studies of the hydrogenation of the cyclopropane hydrocarbons with a double bond or a benzene ring adjacent to the three-membered ring[19-22].

Modern theories claim that the structure of a three-membered ring allows some semblance of a π-electron cloud in the plane of the ring along its perimeter[23,24]; consequently the π-electron cloud of the adjacent double bond or benzene ring can interact with that of the three-membered ring. Spectroscopic investigation of such compounds has repeatedly confirmed the resemblance of these systems to conjugated ones, being close to π-π- than to σ-π-conjugation. For conjugation to occur, the axes of the π-clouds should be parallel or almost parallel.

One of the characteristic properties of such systems is the ease of their hydrogenation with ring opening under conditions which leave the three-membered ring of the alkyl cyclopropanes intact, the specific catalyst for this reaction being palladium black. This catalyst gives smooth hydrogenation of vinyl- and isopropenyl-cyclopropanes with the addition of two moles of hydrogen; experiments with incomplete hydrogenation have shown that the hydrogen adds initially not to the double bond but to the C–C bond in the ring adjacent to the substituent:



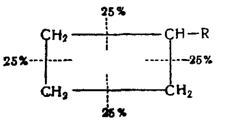
Such hydrogenation occurs when an unsaturated group, including the carbonyl group, is adjacent to the ring. In this case, as in that of the phenylcyclopropanes, the hydrogen adds on to the three-membered ring:



The properties of diphenylcyclopropanes indicate that the extent of conjugation of the phenyl and cyclopropyl rings depends on steric factors: conjugation is more marked in the case of *trans*-1,2-diphenylcyclopropane than in the *cis*-isomer, where steric hindrance displaces the phenyl substituent from the position most advantageous for conjugation. No conjugation can take place in 1,1-diphenylcyclopropane, where the axes of the π-electron clouds of the three-membered and the phenyl rings cannot be parallel. This has been substantiated by Raman spectra and by the fact that this substance does not add on hydrogen in the presence of palladium[25,26,27].

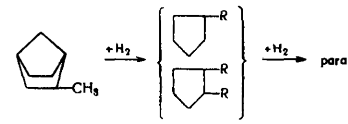
Cyclobutanes. Until recently little had appeared on the hydrogenolysis of the cyclobutane series of hydrocarbons, with total absence of comparative data on the hydrogenation of these compounds and cyclopropanes and cyclopentanes. This gap has been substantially filled by Kazanskii's school: it was shown[28] that under strictly comparable conditions, and using the same amount of catalyst, the three C_5H_{10} hydrocarbons with different rings — ethylcyclopropane, methylcyclobutane, and cyclopentane — undergo hydrogenation at different rates. Whereas at 260° cyclopentane only begins to undergo hydrogenation, methylcyclobutane is completely hydrogenated. The hydrogenation of ethylcyclopropane is complete even at 60°.

The orientation of hydrogenation was not as specific for alkylcyclobutanes as for alkylcyclopropanes, the former undergoing fission in all four ways with equal ease[28,29]:

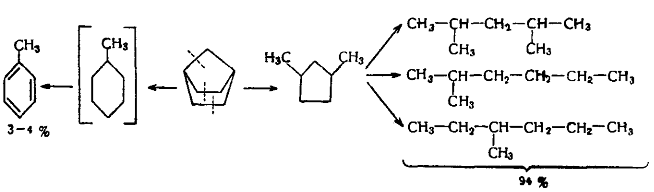


Alkylcyclobutanes are very stable to isomerisation catalysts, yielding only traces of cyclopentane hydrocarbons at ~250°, with aluminosilicates. This stability declines sharply, however, if there is a double bond adjacent to the ring. Kazanskii and his coworkers[30,31] showed that isopropenyl- and isopropylidene-cyclobutanes could isomerise in the presence of silica gel and kieselguhr with almost the same ease as alkylcyclopropanes. Despite this similarity, alkenylcyclobutanes give no evidence of conjugation, either during the specific hydrogenation reaction in the presence of palladium, or in their Raman spectra.

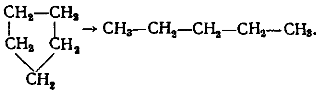
Cyclopentanes. Hydrogenation of cyclopentanes was first discovered in 1934 during an attempt to find out whether the six-membered ring of 2-methylbicyclo[2,2,1]-heptane could be dehydrogenated[32]. It was found that at 300°, with platinised charcoal, hydrogen was not split out, but added on. The authors suggested cleavage of the five-membered ring according to the scheme:



which was later confirmed by Kazanskii *et al.*[33] by fractional analysis of the hydrogenation products from bicyclo[2,2,1]heptane:

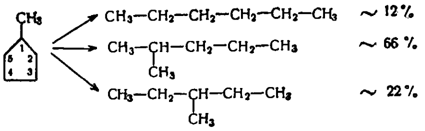


This scheme was subsequently confirmed with cyclopentane which was converted to n-pentane under the same conditions:

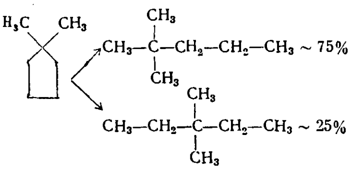


This led to a series of studies in which the hydrogenation of the five-membered ring was fully confirmed. At first only the fact of hydrogenation was established without detailed investigation of the reaction products and therefore without discovering which bonds underwent preferential cleavage. Hydrogenation of the five-membered ring was shown to occur in methyl-, ethyl-, and n-propyl-cyclopentanes[34], in n-butyl-, s-butyl-, and isoamyl-cyclopentanes[35,36], in n-hexylcyclopentane[36], and in n-nonylcyclopentane[38].

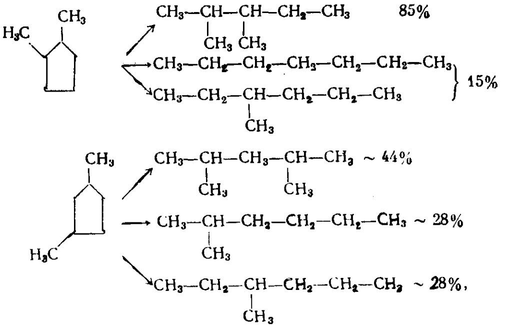
The orientation and kinetics of cyclopentane hydrogenation could be investigated more precisely with the help of Raman spectra and accurate fractionation. This enabled Kazanskii *et al.*[39] to show as early as 1941 that hydrogenation of ethyl- and n-propyl-cyclopentanes involved all the five bonds in the ring but with varying ease. The lowest yield was that of normal paraffins, indicating that the ring bond adjacent to the substituent is the most stable. Even more conclusive results were obtained with methylcyclopentane[40]:



Thus the 2–3 and 4–5 bonds rupture most easily, the 3–4 bond with rather more difficulty (it must be borne in mind that there is only one of these bonds in the molecule, so that the probability of finding products of its fission is half that expected in the case of the 2–3 and 4–5 bonds), the bonds adjacent to the methyl group being still more difficult to break. It is even more difficult to break bonds 1–2 or 1–5 in 1,1-dimethylcyclopentane[41], the other bonds behaving similarly to the previous case:

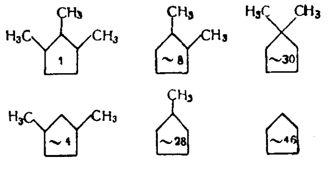


This was also confirmed for 1,2- and 1,3-dimethylcyclopentanes[42],



as well as for 1,2,3-trimethylcyclopentane[43], which yielded mainly 2,3,4-trimethylpentane.

These already fairly precise studies showed that the rates of hydrogenation of these hydrocarbons were closely related to their molecular structure, decreasing with an increase in the number of ring bonds screened by methyl groups. To verify this, Kazanskii *et al.* investigated the rates of hydrogenation of a number of hydrocarbons of the cyclopentane series under comparable conditions[42]. If the rate of hydrogenation of 1,2,3-trimethylcyclopentane is taken as unity, the rates for the other compounds are given by the values marked within their rings in the following figure:



Kinetic studies on the hydrogenation of cyclopentane on platinised charcoal[44] showed that the catalyst's activity at first declines fairly appreciably until a certain value is reached and then remains constant, suggesting that the most active centres of the catalyst are also the least stable. Once they become poisoned the catalyst surface becomes sufficiently constant to allow kinetic measurements. Kazanskii and Bulanova found that the energy of activation of cyclopentane hydrogenation was 35 kcal mole^{-1}.

Attempts made by Kazanskii and his coworkers to find other catalysts for the reaction at atmospheric pressure failed. Palladised charcoal was quite inactive[45,46]; nickel on alumina or kieselguhr did open the five-membered ring, but at the same time caused considerable destructive hydrogenation, both of the initial hydrocarbon and the reaction products, with the formation of methane and other low-molecular hydrocarbons[36,40,46], and so far platinum is the only known selective catalyst for cyclopentane hydrogenation.

Two hypotheses have been proposed for the reaction mechanism. The earlier one[47] was based on Balandin's multiplet theory, according to which cyclopentane is adsorbed on the surface of the catalyst and the interaction with hydrogen occurs as a typical doublet reaction. This, however, fails to explain the failure of n-pentane or cyclohexane to undergo hydrogenation, since they also can be adsorbed on the surface of the platinum catalyst and could then react by the same doublet mechanism. Kazanskii, Liberman, and Plate[48] suggested a different scheme, also based on the multiplet theory. It is feasible that the hydrocarbon molecules could become attached on the platinum surface by more than two carbon atoms, which in the case of n-pentane and cyclopentane could be all five. If it is assumed that the carbon atoms are adsorbed on the lattice sites preferred by platinum during crystal growth, then the distances between all the carbon atoms in the n-pentane molecule will remain unchanged when they are all involved in adsorption, and only the valency angles will increase to 120°. Distortion of the cyclopentane molecule in such an adsorption process would be much more marked and one of the five C–C bonds would necessarily be stretched. Rupture of this extended (and therefore weakened) bond and the addition of hydrogen follow the doublet scheme of the multiplet theory, but in order to achieve the ncessary molecular deformation, the latter must first be adsorbed at an active centre forming a complete sextet. For this reason the theory is called the sextet–doublet mechanism.

Further details of the studies of Kazanskii and his coworkers on the hydrogenation of the five-membered ring are given in a review article[49].

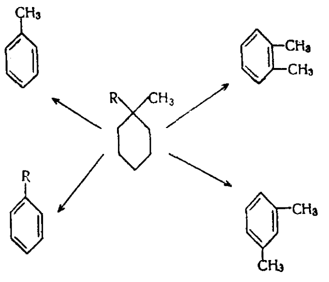
Cyclohexanes. The six-membered ring of the cyclohexane hydrocarbons cannot undergo hydrogenation in the presence of platinised charcoal. This had been supposed to be caused by purely kinetic factors, the rate of dehydrogenation of the cyclohexanes to aromatic hydrocarbons under the conditions employed being much higher than the rate of hydrogenation. However, Kazanskii and Liberman[50] refuted this suggestion. They placed 1,1-dimethylcyclohexane in contact with platinised charcoal in a large excess of hydrogen at 300°. This hydrocarbon is not as readily dehydrogenated as cyclohexanes without the geminal grouping, and under the conditions described it was converted into aromatic hydrocarbons with great difficulty. Nevertheless, although over 70% of the hydrocarbon remained unchanged, no signs of any products of hydrogenation were found in the product. The inability of cyclohexane hydrocarbons to undergo hydrogenation is thus connected with peculiarities of their structure.

Cycloheptanes, etc. Hydrogenation has not so far been observed in the case of cycloheptanes, nor in cyclanes with 8–10 carbon atoms in the ring until Kazanskii *et al.*[51] found that in the presence of nickel on kieselguhr at the relatively low temperature of 200° cyclo-octane gave a considerable yield of n-octane. They have also shown[52,53] that cyclononane and cyclodecane undergo hydrogenation to a greater or lesser degree in the presence of platinised charcoal at ~300°, yielding the corresponding normal paraffins.

III. CATALYTIC CONVERSIONS OF GEMINAL-DISUBSTITUTED CYCLOHEXANES USING PLATINUM AND ALUMINIUM SILICATE CATALYSTS

In 1947 Kazanskii and Liberman[50] showed that 1,1-dimethylcyclohexane, previously believed[54] to be chemically too stable to undergo aromatisation by catalytic dehydrogenation over platinum, could be converted to toluene and *o*- and *m*-xylenes using platinised charcoal at 300°. This reaction was then studied more widely[55,56,57] with a number of 1-methyl-1-alkyl- (or cycloalkyl-)cyclohexanes, using platinised charcoal at 320°, and the relative stability of the 1,1-dialkylcyclohexane series of compounds to catalytic action of platinum was confirmed, most of the hydrocarbons involved undergoing conversion to the extent of only 40–60%.

The catalytic reaction of these compounds occurs by splitting off of one alkyl group, usually the smaller one, to form monoalkylbenzenes, the tendency to split off diminishing with increasing length of the carbon chain in the radicals in the case of the longer straight chains. Small amounts of *o*- and *m*-xylenes are also formed, evidently as the result of toluene methylation:



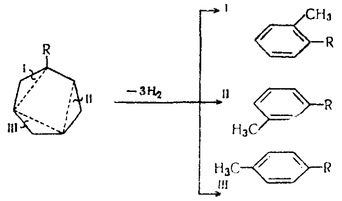
where R = C_2H_5; C_3H_7; C_4H_9.

The nature of the radical attached to the ring carbon atom also plays a considerable part in this catalytic aromatisation[58,59,60]. 1,1-Disubstituted cyclohexanes with two adjacent quaternary carbon atoms, of which one or both is in the six-membered ring (*e.g.* 1,1′-dimethyldicyclohexyl, 1-methyl-1-t-butylcyclohexane, 1,1′-diethyldicyclohexyl), undergo aromatisation readily and almost completely; the bond between the quaternary carbon atoms breaks with the greatest ease, giving toluene as the main reaction product in the case of the first two hydrocarbons, and ethylbenzene in the case of 1,1′-diethyldicyclohexyl.

The catalytic conversions of a series of 1-methyl-1-alkylcyclohexanes have been studied[61–65] using aluminosilicate catalyst at 500°. The reactions include hydrocracking, methylation, dehydrogenation, isomerisation of the six-membered ring to a five-membered one, and disproportionation of hydrogen. The main reaction products are aromatic hydrocarbons (benzene, toluene, xylenes, and trimethylbenzenes), together with smaller amounts of naphthenes with five- and six-membered rings. The catalytic conversion increases with increasing number of carbon atoms in the alkyl substituent, rising from 42% in the case of 1,1-dimethylcyclohexane to 84% in that of 1-methyl-1-butylcyclohexane. 1-Methyl-1-phenylcyclohexane undergoes this type of catalytic conversion very readily, giving a considerable amount of a mixture of aromatic hydrocarbons (benzene, toluene) and naphthenes (predominantly mono- and di-alkylcyclopentanes), even at 350°.

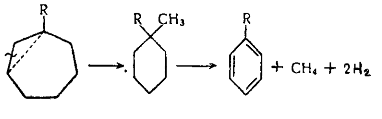
IV. CATALYTIC CONVERSIONS OF SEVEN- TO TEN-MEMBERED CYCLANES OVER PLATINISED CHARCOAL

Although the catalytic conversions of seven- to ten-membered cyclanes under hydrodehydrogenation catalysis conditions are of interest in connection with the special chemical properties of compounds with 8–12 carbon atoms in the ring (transannular reactions), until recently they have not been studied extensively. Prelog and Schenker investigated the behaviour of a series of such cyclanes in the presence of palladised charcoal and showed that transannular cyclisation gave aromatic hydrocarbons with condensed rings, *e.g.* cyclodecane yielded naphthalene and azulene[66]. However, they only examined the aromatic reaction products. Kazanskii and his school made much fuller studies on the contact conversions of cycloalkanes with larger than six-membered rings, using platinised charcoal and certain other catalysts. The hydrogenation of these rings has already been mentioned, but other reactions were found to occur in the course of these investigations[67–69] on a series of alkyl-, cycloalkyl-, and aryl-cycloheptanes. When methyl-, ethyl-, n-propyl-, or n-butyl-cycloheptanes are passed over platinised charcoal at 320° the seven-membered ring is isomerised to a six-membered one with the formation of isomeric methylalkylcyclohexanes and then a mixture of *o*-, *m*-, and *p*-methylalkylbenzenes (chiefly the *o*-isomer) as the result of dehydrogenation:



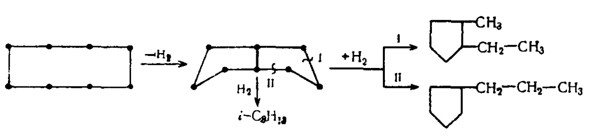
where R = CH_3; C_2H_5; C_3H_7; C_4H_9.

An interesting new observation is that under these conditions 1-methyl-1-alkylcyclohexanes are formed; they undergo partial conversion to alkylbenzenes, but the main bulk remains unchanged and they can be isolated from the products:



The yield of the corresponding 1-methyl-1-alkylcyclohexanes increases (from 21 to 29% of catalyst weight) as the radical becomes more complex (from C_1 to C_4) which is connected with the increasing stability of 1-methyl-1-alkylcyclohexanes to the catalytic action of platinum with increasing complexity of the alkyl substituents.

Kazanskii, Khromov, and Shokova studied the behaviour of cyclo-octane in the presence of such hydro- and dehydrogenation catalysts as platinised or palladised charcoal[70], nickel deposited on kieselguhr[51], and alumina-chromite catalyst[71]. The main reaction over platinised charcoal at 310° (without a carrier gas) is transannular C_5-dehydrocyclisation (*i.e.* dehydrocyclisation with the formation of a five-membered ring, *vide infra*, section on dehydrocyclisation) of cyclo-octane, with the formation of *cis*-bicyclo[3,3,0]octane (*cis*-pentalane), the yield of the products of hydrogenation of one and two five-membered rings in pentalane being smaller. The yield of the latter rises sharply when the reaction is carried out in a stream of hydrogen:

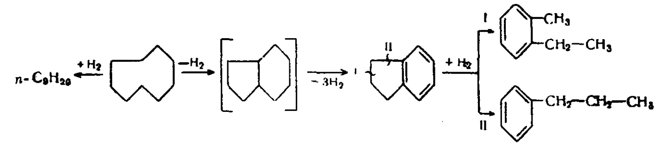


Hydrogenation of the pentalane formed was inhibited by using an iron-platinum catalyst increasing the pentalane yield to 75%, making it a practicable preparative method for this relatively inaccessible hydrocarbon.

When cyclo-octane is passed over 50% nickel on kieselguhr at 200° in a stream of hydrogen it reacts in three main directions: (1) hydrogenation to n-octane; (2) transannular C_5-dehydrocyclisation giving *cis*-pentalane; (3) stepwise isomerisation to hydrocarbons with seven-, six-, and five-membered rings. The quantitative ratio of the reaction products is affected substantially by the experimental temperature: at 200° reaction (1) predominates, whereas at 250° reaction (2) is most conspicuous.

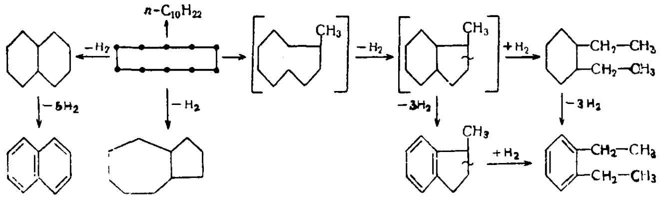
When cyclo-octane is passed over an alumina-chromite catalyst at 420° in a stream of hydrogen, the reaction products are *cis*-pentalane, ethyl benzene, and *o*-, *m*-, and *p*-xylenes, all of which are, in the authors' view, connected with transannular dehydrocyclisation of cyclo-octane.

Cyclononane undergoes transannular dehydrocyclisation over platinised charcoal at 300° to form perhydroindane[52], which is then dehydrogenated to indane, and the latter is partially converted by hydrogenation of the five-membered ring to *o*-methylethylbenzene and n-propylbenzene. Moreover, as already mentioned, the nine-membered ring undergoes direct hydrogenation to n-nonane (7% of catalyst weight).



Kazanskii *et al.*[53] found that under similar experimental conditions cyclodecane also shows dehydrogenation, hydrogenation, and ring isomerisation during its catalytic conversions. As a result of transannular C_6-dehydrocyclisation of cyclodecane, which passes through the initial stage of decalene formation, naphthalene is obtained as one of the main products of catalysis. Transannular C_5-dehydrocyclisation leads to *cis*-perhydroazulene — a bicyclic hydrocarbon with a five- and a seven-membered ring. n-Decane is formed by direct hydrogenation of cyclodecane. Part of the latter apparently isomerises to methylcyclononane, which is converted by transannular dehydrocyclisation first to 1-methylhydrindane and then to 1-methylindane. The five-membered ring in the greater part of the 1-methylhydrindane and 1-methylindane formed undergoes further hydrogenolysis, giving 1,2-diethylcyclohexane and *o*-diethylbenzene, which constitute a substantial part of the catalysate. No azulene is formed in the presence of platinised charcoal within this temperature range.

The above data on the conversions of cyclodecane can be represented by the following scheme:

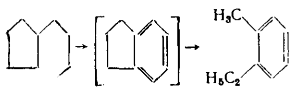


V. HYDROCARBON DEHYDROCYCLISATION REACTIONS

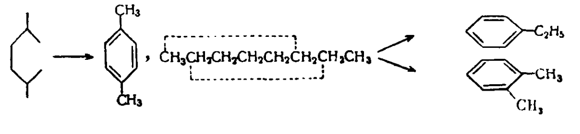
At present two types of dehydrocyclisation of hydrocarbons with catalytic closure of their open chain through dehydrogenation are known. The open chain may either belong to an aliphatic hydrocarbon or be a sufficiently long side chain of a cyclic hydrocarbon such as an alkylbenzene. Chronologically, the first type of dehydrocyclisation is the aromatisation of aliphatic hydrocarbons (or cyclic ones with a sufficiently long side chain) designated by Kazanskii and Liberman[72,73] as C_6-dehydrocyclisation from the number of carbon atoms constituting the newly-formed ring. The second type is C_5-dehydrocyclisation (using the same authors' terminology) giving rise to hydrocarbons with a five-membered ring, *e.g.* cyclopentane hydrocarbons from paraffins.

1. C_6-Dehydrocyclisation

Aromatisation of paraffin hydrocarbons on platinised charcoal discovered concurrently and independently a quarter of a century ago in three Soviet laboratories[74-76], immediately stirred the interest of chemists abroad, and was later the subject of numerous investigations both at home and abroad. This discovery stemmed from the studies of the hydrogenation of cyclopentane hydrocarbons, where aromatic hydrocarbons, which are not formed in similar reactions undergone by the lower homologues of cyclopentane, were found by Kazanskii and Plate[74] in the products of butylcyclopentane hydrogenolysis. Analysis of all the data suggested that under the experimental conditions used closure of a six-membered ring occurred to give a benzene ring:



The possibility of ring closure was verified by passing di-isobutyl and n-octane over platinised charcoal. The first gave *p*-xylene and the second ethylbenzene and *o*-xylene, two ways of ring closure being possible:



Later a series of other paraffins[77,78] of normal- and iso-structure was subjected to aromatisation over platinised charcoal at 260°–315°.

Aromatisation of paraffin hydrocarbons on chromic oxide at 450°–470° was discovered by Moldavskii and Kamusher[75] and on a chrome-copper-phosphate catalyst at 500°–550° by Karzhev *et al.*[76] Aromatisation with oxide catalysts is accompanied by side reactions, such as cracking and coking. Since no destruction occurs during reactions on platinum catalyst, it has become a useful means of investigating the mechanism of catalytic conversions of hydrocarbons, including their dehydrocyclisation, which was studied later by Kazanskii and Liberman. Work on di-isobutyl[79] showed that on platinised charcoal the energy of activation of C_6-dehydrocyclisation and dehydrogenation of cyclohexane was practically identical (16.3 and 16.1 kcal $mole^{-1}$ respectively). However, the rate of the second reaction is considerably higher than could have been explained by a larger number of active centres on which this reaction takes place. Further studies of the mechanism of dehydrocyclisation[80] showed that on platinised charcoal dehydrocyclisation occurs in two stages:

$$\begin{matrix}\text{paraffin}\\\text{hydrocarbon}\end{matrix} \rightarrow \begin{matrix}\text{cyclohexane}\\\text{hydrocarbon}\end{matrix} \rightarrow \begin{matrix}\text{aromatic}\\\text{hydrocarbon.}\end{matrix}$$

This is confirmed by the occurrence of 1,1-dimethylcyclohexane in the products of aromatisation of 3,3-dimethylhexane; this product undergoes further conversions, previously investigated[50].

The practical and industrial implications of the aromatisation of hydrocarbons became apparent at a very early stage, and during 1938–1939 Kazanskii and his collaborators undertook an extensive survey of over 30 oxide catalysts (chromium, vanadium, uranium, thorium, aluminium, and others). They obtained considerable yields of aromatic hydrocarbons[81-86] from the aliphatic hydrocarbon fractions of Synthol‡. This work laid the foundations for the selection of catalysts for aromatisation and clarified the action of individual oxides and the marked influence of the carriers (aluminium oxide, silica gel, activated charcoal, calcined chromic oxide) on the formation of a dehydrocyclising catalyst. In thorium catalysts (on aluminium oxide and activated charcoal) a product of catalytic conversion during coking was found to activate the heterogeneous catalyst. In all the other cases, both in this work and in later investigations, the more usual poisoning of dehydrocyclisation catalysts by surface coking was encountered. This phenomenon was studied in greater detail[87] during investigation of the effect of the pressure used in the preparation of aluminomolybdenum catalyst on its properties; when this pressure was increased from 2000 to 20 000 atm the efficiency of the catalyst (yield of aromatic products per unit volume of catalyst per hour) increased slightly, although the specific activity (yield of aromatic products per unit weight) dropped since the density of the dry catalyst had increased. The same was observed in dehydrogenation of cyclohexane. Coke poisoning of catalyst during dehydrocyclisation diminishes as the catalyst compacting pressure is increased.

Recently active aluminochromate catalysts have been reinvestigated in detail. It was found[88] that with an active catalyst giving up to 70% aromatic products from heptane at 515° and able to work without regeneration for up to 24 h, the dehydrocyclisation occurs outside the kinetic region. Introduction of various alkali and alkaline-earth elements into the catalyst revealed appreciable differences in the activity of different samples[89,90]. Most of these elements (excluding lithium, beryllium, and magnesium) activate the aluminochromite catalyst in dehydrogenation of cyclohexane and dehydrocyclisation of n-heptane. Maximum activating action in dehydrocyclisation is exhibited by rubidium among the alkali elements and by strontium among the alkaline-earth ones. Addition of potassium to pure chromic oxide catalyst had the opposite effect[91]: addition of 0.23 wt.% K_2O inhibited the dehydrocyclisation of n-heptane and dehydrogenation of cyclohexane, but only reduced the yield of aromatic products from hept-1-ene to two-fifths. The same effect occurred on addition of an equivalent amount of phosphoric acid. These findings suggest that the addition of these substances to the chromium catalyst affects the first stage of the catalytic process — the chemisorption of the saturated hydrocarbons on chromic oxide.

The growing requirements of the petrochemical industry for benzene and the presence of large deposits of n-hexane in the oil-bearing regions of the Soviet Union have made the preparation of benzene by dehydrocyclisation of petroleum hexane a project of practical interest, which has been studied by Kazanskii *et al.*[92] Like heptane, pure n-hexane at 550° gives a high yield of benzene during 24 h of continuous catalysis (without regeneration). The aromatisation of petroleum fractions was complicated by the presence of isohexanes and methylcyclopentane, which lowered the yield of benzene and increased coking. The role of the individual components in the process of aromatisation of narrow fractions isolated from petroleum was investigated, and revealed the practicability of obtaining benzene from hexane fractions of rectified petroleum using aluminochromite catalyst. Additional information was also gained about the dehydrocyclisation reaction; thus, for a given catalyst, a constant ratio was found to exist between the yields of benzene and of coke over a wide range of temperature and rates of passage of hexane.

2. C_5-Dehydrocyclisation

This reaction of paraffin hydrocarbons in the presence of platinised charcoal was discovered by Kazanskii, Liberman, and their coworkers in 1953 during investigations of a combined method of analysis of petroleum (to be mentioned in greater detail later), which required a catalyst which would dehydrogenate selectively cyclohexane hydrocarbons to aromatic ones. Platinised charcoal with certain additives to suppress the hydrogenation of cyclopentanes was proposed, but it was feared that this catalyst might be insufficiently selective, and in fact, as early as 1937 n-octane was found to be converted into a mixture of iso-octanes when it was passed in an atmosphere of hydrogen over platinised charcoal at 310°.[93] Kazanskii *et al.*[94] checked this and found that under combined method conditions n-heptane and n-octane remained unchanged but underwent conversion under more drastic conditions (310°, volume rate 0.2 h^{-1}), with homologues of cyclopentane among the conversion products. Before this work very little published material was available on the possibility of cyclising paraffins to cyclopentane. Cyclisation of n-pentane to cyclopentane on alumino-chromo-magnesium catalyst was suggested[95], but was confirmed experimentally only much later. Cyclopentane was found[96] in an extremely

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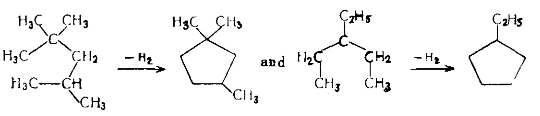
‡ In Russian: *sintin*. A colourless to dark yellow liquid produced by catalysed reaction of CO_2 and H_2 at medium pressures. It is available in two grades (nominal boiling ranges 100°–230° and 100°–300°) and is used in the automobile industry for case-hardening parts by a gas-phase process (Ed. of Translation).

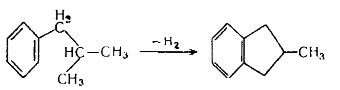
complex mixture obtained from n-heptane at pressure of up to 300 atm and at 450°–480°, but the complexity of the mixture made it impossible to assert that cyclopentane was a primary product. More reliable confirmation of Kazanskii's observation mentioned above was obtained by him with Liberman and others using 2,2,4-trimethylpentane[97,98] and 3-ethylpentane[99] which are particularly convenient, since each can give only one product of cyclisation:



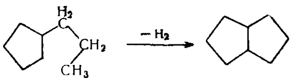
The reaction products could therefore be identified not only spectroscopically but also by actually isolating them.

These and subsequent studies on normal[100,101] and branched-chain paraffins[12] showed that n-pentane was the most difficult to cyclise, the other n-alkanes being rather less difficult and the extensively branched paraffins, especially 2,2,4-trimethylpentane, being the easiest. In all cases only those cyclopentanes were formed which would have been expected with no isomerisation of the carbon skeleton.

Later Kazanskii, Liberman, and Bragin showed that alkylbenzenes could also undergo C_5-dehydrocyclisation to yield indane and its homologues[102,103]:

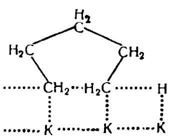


Alkylcyclopentanes were found to behave similarly[101,104]:



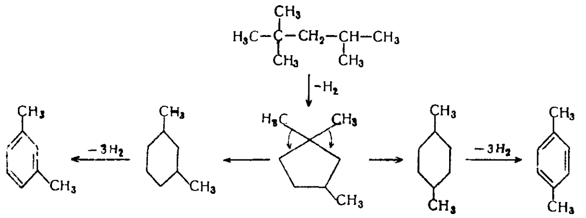
It was shown that C_5-dehydrocyclisation is a zero-order reaction[105] and its energy of activation for paraffins of any structure, whether normal or extensively branched, is the same and amounts to 20 kcal mole^{-1}. It is 7.5 kcal mole^{-1} higher for alkyl benzenes.

All these facts led Kazanskii and Liberman[73] to a number of speculations concerning the mechanism of the C_5-dehydrocyclisation reaction. Firstly, the reaction occurs most readily with hydrocarbons which need the least energy to undergo the transition from the more stable conformation to that most favourable for C_5-dehydrocyclisation, *i.e.* in practice those with the least number of energetically unfavourable rotations. Thus in 3-ethylpentane rotation through 120° at only one bond is necessary, and in 2,2,4-trimethylpentane it is only through 60°, whereas in n-alkanes two simultaneous rotations through 120° are needed, and the yields of cyclopentane (under identical conditions) rise on transition from n-alkanes (3–4%) to 3-ethylpentane (12%) and 2,2,4-trimethylpentane (40%). Secondly, these authors consider that C_5-dehydrocyclisation passes through a peculiar cyclic transitional state in which the catalyst atoms take part:

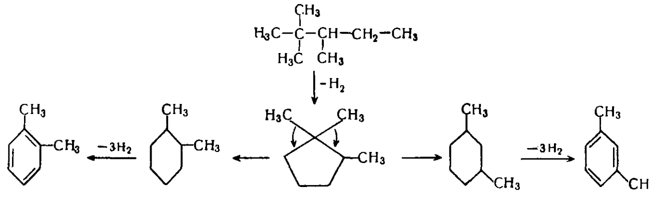


All the five carbon atoms of the ring arrange themselves on the sextet of the platinum catalyst. The reaction, as in hydrogenation of cyclopentane, thus follows a sextet–doublet scheme.

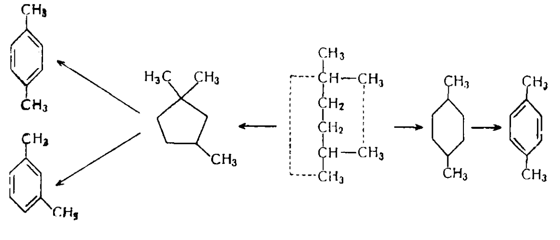
When paraffins containing five carbon atoms in the longest chain are cyclised in the presence of platinised charcoal, some aromatic hydrocarbons are always formed[72] by extension of the cyclopentane ring by means of geminal methyl groups and subsequent dehydrogenation. Thus, 2,2,4-trimethylpentane and 1,1,3-trimethylcyclopentane give approximately equal yields of *m*- and *p*-xylenes:



and 2,2,3-trimethylpentane gives *o*- and *m*-xylenes:



These findings indicate that with a six-carbon chain the aromatic products are formed by direct C_6-dehydrocyclisation and not through an intermediate formation of a five-membered ring: in the former case, di-isobutyl should yield *p*-xylene and in the latter approximately equal amounts of *m*- and *p*-xylenes:



In fact, the aromatic products given by di-isobutyl consisted of 96% *p*-xylene and 4% *m*-xylene. The C_5- and C_6-dehydrocyclisation reactions thus occur independently and in parallel.

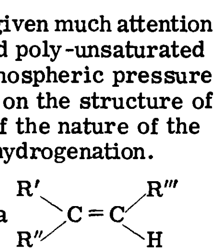
VI. SOME HYDROGENATION AND DEHYDROGENATION REACTIONS

The investigations in this field are too many for even a concise review to be included in this article, so that only some of the more important contributions of Kazanskii and his school will be mentioned here.

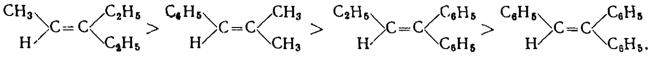
1. Catalytic Hydrogenation of Unsaturated Hydrocarbons

Over the last 20 years Kazanskii has given much attention to catalytic hydrogenation of mono- and poly-unsaturated hydrocarbons in the liquid phase at atmospheric pressure and room temperature, with emphasis on the structure of the initial hydrocarbon and the effect of the nature of the catalyst on the rate and selectivity of hydrogenation.

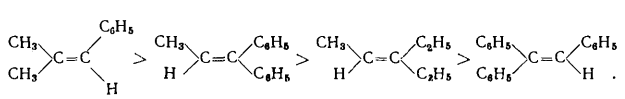
Four olefines of the general formula



were hydrogenated in the presence of platinum black and palladium black. In the presence of platinum[106] the rate of hydrogenation falls in the series:

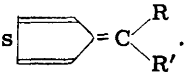


In the presence of palladium[107], on the other hand, the mono- and di-phenylated ethylenes are hydrogenated more rapidly than methyldiethylethylene; however, here an accumulation of phenyl groups also lowers the rate of hydrogenation:

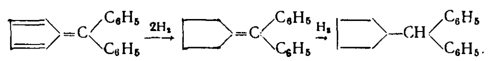


Nickel behaves similarly to palladium[108].

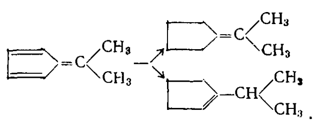
The effect of the nature of the substituents at the double bond and of the catalyst was also clearly seen in hydrogenation of fulvenes



. Thus, in the presence of platinum, and especially of palladium[109] and nickel[110], diphenylfulvene rapidly adds on two molecules of hydrogen to two double bonds of the five-membered ring, the third molecule being added on much more slowly, permitting the isolation of the intermediate reaction product:



With alkyl substituents hydrogenation occurs less selectively and when two molecules of hydrogen add on to dimethylfulvene, two reaction products are formed[111]:



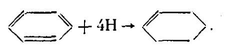
The mechanism of the addition of hydrogen to a conjugated system of double bonds has long been a controversial subject. Lebedev[112] suggested four types of addition of the first molecule of hydrogen depending on the structure of the dienes: (1) selective 1,4-addition; (2) non-selective 1,2-, 3,4-, or 1,4-addition; (3) non-selective addition to both double bonds at once; and (4) 1,2- or 3,4-addition, without 1,4-addition. All the compounds studied in detail by Lebedev belonged to type (2).

Kazanskii and Popova[113,114,115] showed by hydrogenation with platinum, palladium, and nickel that the dienes tentatively classified by Lebedev as belonging to type (1) (2,5-dimethylhexa-2,4-diene) or type (4) (hexa-2,4-diene and 2-methylhexa-2,4-diene) in fact belong to type (2). Moreover, two moles of hydrogen are also always added on. The structure of the dienes has a marked effect on the quantitative ratio of the different additions; it depends on the catalyst used[113-117], platinum being the least selective. In the presence of palladium the double bond in the intermediate mono-olefines can migrate, giving a mixture of mono-olefines with the addition of only one mole of hydrogen[118]. Such isomerisation is negligible with nickel[119] and totally absent with platinum[120]. All this indicates that the migration of the double bond in the presence of palladium undoubtedly affects the composition of the products and the kinetics of hydrogenation, so that any conclusions on the relation between the structure of the compound undergoing hydrogenation and the direction and rate of the reaction must take into account these possible complications.

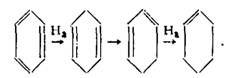
2. Reduction of Aromatic and Olefinic Hydrocarbons with Nascent Hydrogen

It had long been considered that nascent hydrogen only combined with polycyclic aromatic hydrocarbons but not with benzene and its homologues, and that it did not reduce the isolated double bond in unsaturated hydrocarbons. Kazanskii and his followers contributed a great deal to this subject. In 1916 it was noted[121] that when ammonia acts on metallic calcium in benzene, the latter adds on hydrogen to give "dihydrobenzene". Kazanskii and Smirnova found[122] that benzene and toluene readily added on two molecules of hydrogen evolved on decomposition of calcium ammine to give cyclenes:

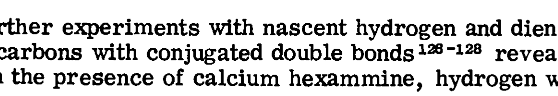
$$Ca + 6NH_3 \rightarrow Ca(NH_3)_6, \quad Ca(NH_3)_6 \rightarrow Ca(NH_2)_2 + 4NH_3 + 2H,$$



Later a detailed study was made of the reduction of ethylbenzene, *o*-, *m*-, and *p*-xylenes, tetralin, mesitylene, styrene, propylbenzene, and allylbenzene with calcium hexammine and strontium, barium, and lithium ammines[123-125]. The corresponding cyclenes were found to be the main reaction products in all cases. The mechanism of the reaction[124] involves the transposition of the even bonds in the diolefine hydrocarbons with the formation of a conjugated system which adds on the hydrogen in positions 1,4:



The migration of even bonds was investigated in many aliphatic and cyclic compounds with isolated double bonds which behaved as compounds with conjugated double bonds when reduced by calcium hexammine. An identical reaction product was obtained on reduction of propenyl- and allyl-benzenes, namely 1-propylcyclohex-1-ene:



Further experiments with nascent hydrogen and diene hydrocarbons with conjugated double bonds[126-128] revealed that in the presence of calcium hexammine, hydrogen was added on in positions 1,2 and 3,4 as well as 1,4, as in the case of other reducing systems[128-130]. The isomerising agent was found to be calcium amide, a product of calcium hexammine decomposition[131], which readily isomerises not only diene but also mono-olefinic hydrocarbons[131-135]. This reaction is catalytic in the vapour phase and the mechanism suggested for it[12,133,134] envisaged acid–base character with intermediate carbanion formation:

$$\underset{\text{acid.}}{CH_3{-}CH_2{-}CH{=}CH_2} + \underset{\text{base}}{MNH_2} \rightarrow [CH_3{-}\overset{-}{C}H{-}CH{=}CH_2]\,M\overset{+}{N}H_3 \rightarrow$$

$$\rightarrow [CH_3{-}CH{=}CH{-}CH_2]\,M\overset{+}{N}H_3 \rightarrow CH_3{-}CH{=}CH{-}CH_3 + MNH_2 .$$

Later[136-139] repeated reduction of mono-olefines with calcium hexammine was found to result in partial formation of paraffin hydrocarbons and a multi-stage ionic mechanism was proposed for the reduction of unsaturated compounds with nascent hydrogen. In an alkaline medium the first stage consists of the addition of electrons to the carbon–carbon bond and the second one of proton addition; formation of free hydrogen is a parallel reaction which competes with the reduction:

$$\begin{array}{l} >C{=}C< + 2\bar{e} \rightarrow\ >C\bar{e}{-}C\bar{e}< \\ >C\bar{e}{-}C\bar{e}< + 2H^+ \rightarrow\ >CH{-}CH< \end{array}, \quad H^+ + \bar{e} \rightarrow H,\ 2H \rightarrow H_2.$$

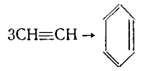
Mono-olefines with various molecular weights and positions of the double bond were reduced with alkali metals (K, Na, and Li) in the presence of methyl, ethyl, and t-butyl alcohols in liquid ammonia, and it was shown that the activity of these metals with respect to the evolution of nascent hydrogen decreased in the order K > Li > Na, whereas their reducing capacity followed the reverse order. The acidity of the alcohol also affects the rate of the competing reactions, the amount of free hydrogen being directly related to the acidity of the alcohol: $(CH_3)_3COH < C_2H_5OH < CH_3OH$, the rate of reduction increasing in the reverse order. These results substantiate the proposed scheme for reduction with nascent hydrogen.

3. Dehydrogenation of Paraffins to Olefines

This line of research, directly connected with the requirements of the Soviet chemical industry, was prompted by the need for a reliable, active, and stable catalyst for the conversion of isopentane into amylenes, intermediates in the production of isoprene. Such an alumino-chromo-potassium catalyst was developed in 1957.[140] Under fixed conditions the process is carried out at 550° with a wide range of volume rates, and the liquid dehydrogenated product contains up to 58% of unsaturated compounds, chiefly isoamylenes. The olefine yield is 45–59% of the isopentane throughput; the selectivity of the catalyst reaching 70–90%. Since side reactions, such as isomerisation and cracking, are inevitable at such high temperatures, it was essential to develop accurate analytical methods for the complex polycomponent catalysts. This was achieved by means of vapour-phase chromatography[141].

VII. CATALYTIC POLYMERISATION REACTIONS

As in the previous section only some of Kazanskii's work in this field will be reviewed. It is interesting that his first research project was related to this subject, when, under the direction of N. D. Zelinskii, he found[142] that acetylene was converted into aromatic hydrocarbons in the presence of activated charcoal at 650°, with benzene as the main reaction product (approximately 70% of the initial acetylene):



He also worked on the polymerisation of olefinic hydrocarbons such as isobutylene, butylene, and ethylene, showing[143] that in the presence of hydroaluminosilicate catalysts isobutylene is polymerised to dimers and higher polymers, the maximum yield of the former being obtained at 200° and of the latter at room temperature. A rise in temperature also favours isomerisation, so that not only 2,4,4-trimethylpentene but also its structural isomers are formed. When but-1-ene is polymerised it is isomerised to isobutylene and but-2-ene, which then combines to 2,3,4-trimethylpentene.

Polymerisation of ethylene with a series of catalysts (nickelous oxide on aluminosilicates)[144] showed that it could be dimerised to but-2-ene at atmospheric pressure and temperatures of 275°–300°. In the studies of the catalytic synthesis of hydrocarbons from carbon dioxide and hydrogen[145], particular attention was paid to the selection of active catalysts and effective carriers from Soviet raw materials. Additives were found which lowered very considerably the temperature of catalyst regeneration.

VIII. HIGH-PRESSURE REACTIONS

In the last decade the investigation of the effect of pressure on the rate and nature of a reaction has often served to elucidate its mechanism. Kazanskii and his coworkers[146] examined the effect of pressure on the rate of thermal cracking of n-hexane and n-heptane. At pressures of 300–3000 atm the rate diminished with increasing pressure; published data, however, stated that at lower pressures (up to 10–20 atm) the opposite was true. This discrepancy was reconciled on the basis of a chain mechanism for the decomposition of paraffin hydrocarbons[147]; at low pressures the reaction chains are terminated predominantly by interaction of shorter (compared to the initial hydrocarbon) radicals; at high pressure this occurs predominantly with "long" radicals; hence the observed reversal of the effect of pressure.

Isomerisation of n-hexane[148] and methylcyclopentane[149] in the presence of aluminium chloride under pressure showed that the rate of isomerisation diminished with increasing hydrostatic pressure (or pressure of nitrogen). This suggested that the isomerisation included a stage involving a considerable increase in volume, and that the equilibrium at this stage of the reaction determined the rate of the overall process. As suggested[150] in 1932, such a stage could be dehydrogenation of the initial hydrocarbon. If this were so, the reaction would be inhibited most when the pressure was created by hydrogen with the dehydrogenation equilibrium particularly strongly displaced towards the initial hydrocarbon. This was fully confirmed experimentally, and subsequent studies[151,152] showed that such a mechanism also very probably operates in the presence of heterogeneous catalysts.

Studies in destructive dehydrogenation are of great theoretical and practical interest. Kazanskii and his co-workers[153] investigated the thermal conversions of various classes of hydrocarbons under high hydrogen pressure and put forward a radical-chain reaction mechanism for homogeneous destructive hydrogenation of alkylarenes, which includes the reaction of a hydrogen atom with the hydrocarbon molecule and splitting off the whole alkyl radical from the aromatic ring. The presumed mechanism of this substitution reaction is the addition of the hydrogen atom to the carbon atom in the aromatic ring which bears the alkyl group and subsequent stabilisation of the radical formed by splitting off the alkyl group. This is substantiated by the fact that increasing the hydrogen pressure markedly accelerated the splitting off of the alkyl group from the alkyl aromatic hydrocarbon, and is further supported by the fact that in methylcyclopentane, where it is impossible to add a hydrogen atom to the molecule, the splitting off of the methyl group is not accelerated by increasing the hydrogen pressure[154].

IX. SYNTHESIS OF HYDROCARBONS

Kazanskii and his school have, in the course of their general work on catalytic conversions of hydrocarbons and the composition of natural petroleums, synthesised many hydrocarbons of various classes, either to study their behaviour, as mentioned in previous sections, or to discover their physical properties (molecular constants, their relation to structure, spectral characteristics). These problems were often tackled in parallel. In the case of spectroscopic studies, the synthesis of hydrocarbons had a dual purpose: first, in collaboration with Landsberg and his school, the accumulation of a large collection of Raman spectra of pure hydrocarbons (some not previously described and many well-known ones) provided a means of their identification and quantitative estimation even in relatively complex mixtures, such as petroleum fractions; second, correlation of spectroscopic properties with a particular structural feature.

The synthetic work begun in 1939 (producing ~ 200 hydrocarbons of high purity) is still continuing. They form the foundation of a spectroscopic atlas of almost 160 spectra[155], the remaining ones appearing in later publications[101,156-158]. A combined method of determination of individual hydrocarbon constituents of petroleum was developed on the basis of this enormous work[155]. The search for spectroscopic correlation with chemical structure was also in some cases successful, as, for instance, in the case of differentiating *cis*-1,2- and *cis*-1,4-dialkylcyclohexanes from their *trans*-isomers[156].

The high purity requirements for hydrocarbon standards initiated a number of methodological studies on the separation and purification of hydrocarbons[159-162], which also entailed elaboration of known methods of preparation or devising of new ones.

In this article it is impossible to list even the most important of the hydrocarbons synthesised and the methods used. The preparation of individual *cis*- and *trans*-isomers of di- and tri-alkylcyclanes is very important. Among the substances prepared were diphenyl- and phenyl-cyclopropylcyclopropanes[25-27]; 1,2-dimethyl-, 1,3-dimethyl-, methyl-ethyl-, and methyl-n-propyl-cyclobutanes[163] (the first dialkylcyclobutanes to be separated into their isomers); 1,2,3-trimethyl- and 1,4-dimethyl-2-ethylcyclopentanes[164-166] (the first trialkylcyclopentanes to be separated into their stereoisomers) and a series of 1,2- and 1,4-dialkylcyclohexanes[167] among which 1,4-di-isopropylcyclohexanes are particularly noteworthy as the first representatives of 1,4-disubstituted cyclohexanes in which the boiling points do not obey the Auwers–Skita rule.

Kazanskii and his school can be confidently credited with having prepared for the first time about half the individual stereoisomeric hydrocarbons known in world literature.

X. INVESTIGATION OF THE COMPOSITION OF PETROLEUM

Among the various methods available in the Soviet Union the one that has gained great importance is the combined one[155] based on chromatographic separation of aromatic from naphthene and paraffin hydrocarbons, subsequent analytical dehydrogenation of the de-aromatised part and chromatographing of the catalysate followed finally by accurate fractionation. Highly efficient fractionating columns separate narrow fractions of primary and secondary aromatic and paraffincyclopentane components of petroleum. The individual fractions usually contain from two to four hydrocarbons which can be easily identified by Raman spectra.

This method was developed through the collaboration of Kazanskii and Landsberg and their schools, combining the synthetic and spectroscopic research mentioned above. The first investigation which showed the possibility of combining successfully accurate fractionation, dehydrogenation catalysis, and optic measurements was the analysis of Kalinskii petroleum[168]. The same but somewhat more refined method was used during the Second World War for the analysis of a number of German and American aviation fuels and high-octane additives[169]. In 1948 the method was supplemented by silica-gel chromatography for the isolation of aromatic hydrocarbons and the use of a new dehydrogenation catalyst which acted selectively for cyclohexanes without opening the ring in the cyclopentane hydrocarbons. This combined method permits identification of up to 90 wt.% of the hydrocarbon constituents of petroleum, while in the case of Karami petroleum (KNR) the figure is even higher (93%)[170].

The method is used in various institutes and the individual hydrocarbon composition of 36 petroleums[170-188] from the directly refined crude oils from the Azerbaidzhan, Bashkir, Kazakh, Tartar, Turkmen, Uzbek, and Chinese People's Republics, Maikop, and Sakhalin has been determined. In addition, a simplified version of the method has been applied to 15 petroleums from Azerbaidzhan[189].

The combined method also proved applicable to the analysis of petroleum obtained by thermal and catalytic cracking[190-193] and of other oil fractions of secondary origin[194,195], containing unsaturated hydrocarbons, which were separated and identified. When suitably modified, the method can also be used for analysis of the higher boiling fractions (ligroins and kerosenes)[177,196-198], but the identification of the individual constituents of the isolated ligroin fractions from their Raman spectra is difficult in the absence of standard hydrocarbons; their synthesis would require an enormous expenditure of time and effort. An attempt was therefore made to limit this to group-identification within the narrow fractions of ligroin from Koschagyl oil[196] (b.p. 150°–250°) from lines in the molecular spectra characteristic for certain structural features *e.g.* characteristic of rings, number and position of side-chains, or the presence of individual structural groups (tertiary, quaternary carbon atoms, etc.). Thus for mono-, di-, tri-, and tetra-alkylbenzenes there are lines characteristic of a certain type of substitution in the benzene ring, regardless of the structure of the alkyl group. Since such lines proved to be more reliable and precise for aromatic hydrocarbons, 70% of the aromatic part of the ligroin was identified and 50% of the hexahydroaromatic part.

Work on the Raman spectra of hydrocarbons with boiling points of the ligroin and kerosene fractions is still going on.

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On 25th April, 1961 Academician Boris Aleksandrovich Kazanskii, full of creative energy and projects, celebrated the 70th anniversary of his birth.

Kazanskii graduated from the Moscow State University in 1918 and was retained by N. D. Zelinskii in the Department of Organic and Analytical Chemistry. In 1930 he was appointed Reader; in 1935 he obtained his doctorate in Chemical Sciences and was appointed Professor. From 1945 until 1960 Kazanskii was first Deputy and then Head of the Department of Petrochemistry at Moscow State University.

Kazanskii has worked at the Institute of Organic Chemistry of the Academy of Sciences of the USSR practically since its inception — since 1935; he heads the Laboratory of Catalytic Synthesis, created by him. In 1943 Kazanskii was elected Corresponding Member and in 1946 an Academician of the Academy of Sciences of the USSR. He has been Director of the N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR since 1954.

Kazanskii took part as Editor-in-Chief in the publication of the classical works of such Soviet chemists as A. M. Butlerov, N. D. Zelinskii, and A. E. Arbuzov. He has edited a number of books and monographs.

Kazanskii has been an active organiser and participant of many chemical meetings, conferences, and congresses. He is a member of the Bureau of the International Union of Pure and Applied Chemistry.

Always very exacting towards his own experimental work and conclusions, Kazanskii inculcated this attitude into his followers; much of his attention is devoted to the training of highly qualified scientific workers, including those from the Socialist countries.

Kazanskii has been awarded the Order of the Red Banner of Labour and the Order of Lenin, as well as the Stalin Prize of the First Class.

Kazanskii's profound knowledge and understanding of the most important problems in organic chemistry and his immense organisational ability and creative energy make it certain that he will, at the head of his school, make still greater contributions to Soviet science and the building of Communism.

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ADVANCES IN INTERFACIAL POLYCONDENSATION

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CONTENTS

I. INTRODUCTION

Polycondensation is an important method for obtaining various high-molecular compounds. It can be used to prepare both heterochain compounds (polyamides, polyesters, polypeptides, polyanhydrides, polysulphides, polysiloxanes, etc.) and carbon-chain compounds (polymethylenes, polyarylenealkyls, phenol–formaldehyde resins, etc.).

Until recently, polycondensation was carried out mainly as an equilibrium process, *i.e.* under conditions of the reversible interaction of the resulting polymer with the starting materials and with reaction products of low molecular weight[2]. Such equilibrium polycondensation was usually undertaken in a homogeneous medium, *i.e.* in a solvent boiling at a sufficiently high temperature or in a melt of the polymer and the monomers.

The laws of equilibrium polycondensation have been examined in detail and elucidated in various reviews and monographs[1-6]. Considerably less research has been done on the process of polycondensation under conditions which exclude reversible reactions, such that the whole process has the character of an irreversible, non-equilibrium change. It has been suggested[7] that such a case of polycondensation should be termed "non-equilibrium polycondensation". Not very many cases of non-equilibrium polycondensation are yet known. Among them are the formation of polyaminotriazoles by the polycondensation of dicarboxylic acids with hydrazine[8], and also the formation of polyamides and polyesters by the interfacial polycondensation of dichlorides of dicarboxylic acids with diamines and diphenols[9,10]. Several polyamides and polyesters have been obtained in this way.

The polycondensation of acid dichlorides with diamines or diphenols is carried out at the boundary between two immiscible liquids, *e.g.* water and a hydrocarbon or halogenated hydrocarbon. This has been termed interfacial polycondensation or polycondensation at the phase boundary[9,10].

Interfacial polycondensation opened up new opportunities for the synthesis of polymers and therefore immediately attracted the attention of investigators. After a short interval of time a large number of papers appeared dealing with the laws of interfacial polycondensation and its application to the synthesis of various high polymers.

The method of polycondensation at the phase boundary is based on the well-known Schotten–Baumann benzoylation reaction[11]. The production of polymers from the dihalide of a dicarboxylic acid together with another bifunctional compound (a diamine, diamide, dihydric phenol, etc.) was known long ago. Thus Michler and Zimmermann[12] first found in 1881 that a polyamide is formed by the reaction of *m*-phenylenediamine with carbonyl chloride in chloroform solution. Somewhat later Einhorn[13] described a method for obtaining polyesters by stirring a 20% solution of carbonyl chloride in toluene with an alkaline aqueous solution of a dihydric phenol (quinol, resorcinol, catechol). This method for obtaining polymers represents essentially what is now termed the method of interfacial polycondensation. However, Einhorn's work was forgotten, and only recently has this method again attracted the attention of scientists. It became clear that interfacial polycondensation opens up new possibilities for the synthesis of high polymers, by greatly extending the range of suitable monomers and making it possible to utilise monomers of high melting point as well as those which are unstable, and represents a great new advance in the development of a science of polymeric reactions. We therefore considered it useful to review and summarise published data on this question, and this is the purpose of the present survey.

II. MECHANISM OF INTERFACIAL POLYCONDENSATION

As in other cases, a polymer macromolecule formed by interfacial polycondensation passes through three different stages in the course of its formation[3]: (1) the start of the growth of the macromolecule chain; (2) the growth of the macromolecule chain; (3) the cessation of the growth of the macromolecule chain or its termination.

Each of these stages has a characteristic feature distinguishing it from the corresponding stages both of polymerisation and of equilibrium polycondensation.

1. Start of Macromolecular Chain Growth

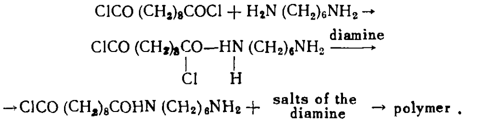
A macromolecular chain is initiated by the reaction of an acid dichloride with a diamine or a dihydric phenol:

$$ClCORCOCl + H_2NR'NH_2 \rightarrow ClCORCONHR'NH_2 + HCl.$$

In this stage of the reaction, if it occurs at the beginning of the process, when no film of polymer is yet present at the interface, polymer formation either occurs at the surface of separation or is displaced deeper into the phase which is the better solvent for the starting materials. This is usually the hydrocarbon phase.

Acylation in homogeneous medium[14-17] of both aliphatic and aromatic amines, as well as the acylation of alcohols and phenols, occurs by a nucleophilic substitution mechanism and is a well studied reaction.

Morgan and Kwolek[10,18] consider that interfacial polycondensation, *e.g.* polyamide formation, occurs according to the following equation[18]:

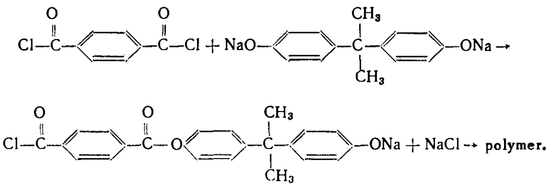


$$ClCO(CH_2)_8COCl + H_2N(CH_2)_6NH_2 \rightarrow$$
$$ClCO(CH_2)_8\underset{\displaystyle Cl}{\underset{|}{C}}O{-}H\underset{\displaystyle H}{\underset{|}{N}}(CH_2)_6NH_2 \xrightarrow{\text{diamine}}$$
$$\rightarrow ClCO(CH_2)_8COHN(CH_2)_6NH_2 + \begin{matrix}\text{salts of the}\\ \text{diamine}\end{matrix} \rightarrow \text{polymer}.$$

Here a protonated amide is formed, from which the proton is easily removed by the action of a base. An amino-group in the diamine molecule or at the end of the oligomeric chain can also serve as acceptor for the proton. Water also can act as a proton carrier. The protonated amino-group can be easily reconverted into a free amino-group by contact with an inorganic base in the aqueous phase:

$$\cdots{-}NH_2{\cdot}HCl + NaOH \rightarrow \cdots{-}NH_2 + NaCl + H_2O.$$

The formation of polyesters[10,18,19] by interfacial polycondensation differs in several features from the production of polyamides. Thus reaction between dihydric phenols and halides of dibasic acids takes place very slowly at room temperature if the phenol is not present in the form of the phenoxide ion. Morgan[10] assumes that the production of polyesters from acid dihalides and dihydric phenols occurs *via* a nucleophilic attack of the phenoxide on the chloride of the dibasic acid, as represented by the following equation:



The characteristic feature of interfacial polycondensation is its heterogeneous nature;—the presence in the reaction zone of two immiscible solutions of reactants. When solutions of the two starting materials come into contact, the reactants as well as the solvents tend to move in opposite directions. Thus the diamine tends to pass from the aqueous phase into the organic phase, while the chloride of the dicarboxylic acid tends to pass into the aqueous phase. The diamine is readily soluble in nearly all the organic solvents employed (the partition coefficient $C_{H_2O}/C_{solvent}$ of the diamine in the solvent systems employed varied from 400 to 1)[18], but the acid chloride is in most cases almost insoluble in the aqueous phase. Polymer formation obviously takes place in the organic phase close to the boundary between the mutually immiscible solvents. This conclusion follows from several indirect observations, *e.g.* the reactions of unifunctional compounds in water–organic solvent systems, and also from direct observations on the formation of a polymer film by interfacial polycondensation[10,18].

Morgan[10,18] considers that polycondensation is initiated by the diamine coming into contact with the acid halide in the organic phase. The halide concentration considerably exceeds that of the diamine, which is apparently acylated at both ends, forming oligomers.

2. Growth of Macromolecular Chain

Chain growth takes place by reaction between the oligomers formed and the starting materials:

$$ClCORCONHR'NH_2 + ClCORCOCl \rightarrow ClCORCONHR'NHCORCOCl + HCl$$
$$ClCORCONHR'NHCORCOCl + H_2NR'NH_2 \rightarrow ClCORCONHR'NHCORCONHR'NH_2 + HCl$$
$$ClCORCONHR'NHCORCONHR'NH_2 + ClCORCOCl \rightarrow$$
$$\rightarrow ClCORCO[NHR'NHCORCO]_2Cl + HCl.$$

Here, depending on the phase in which reaction takes place, the end-groups of the polymer will be those of the starting material initially in the phase in which the reaction occurs. Since it apparently takes place more often in the hydrocarbon phase, the terminal groups will be acid chlorides in this case: *i.e.* the polymer will have the structure

$$ClCORCO[NHR'NHCORCO]_x Cl.$$

Subsequent quantities of diamine, which diffuse into the organic phase, collide with the layer of oligomers having acid chloride end-groups and with the chloride of the dicarboxylic acid (Fig. 1). Reaction takes place by irreversible combination of the oligomers with the diamine. The concentration and the size of the oligomers increase until a high-polymer film is formed. Thus the polymer is obviously formed by reaction of the diamine with an oligomer and not with a fresh molecule of acid chloride.

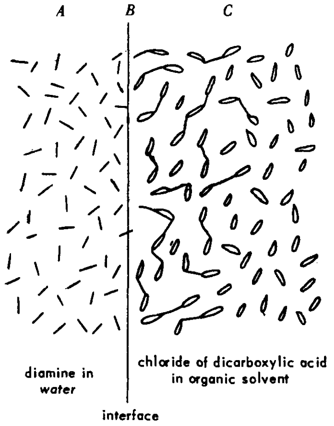


Fig. 1. Diagram of the initial relationship between reactants in the interfacial formation of a polyamide.[10, 18]

It is probable that, during this period of rapid reaction, oligomers having protonated amino-groups can also diffuse from the organic into the aqueous phase, where the free amino-groups are regenerated by removal of the proton by an inorganic base; in addition, oligomers having free amino-groups can diffuse into the organic phase together with the diamines. The diffusion of the polymeric chains, however, is comparatively slow. The diffusion of reactants through the film does not cease, but merely slows down, after formation of the high-polymer film, as can be seen from a diagram of film growth with time (see Fig. 2).

Other views also exist as to the location of interfacial polycondensation. Thus Sokolov and Kruglova[20] consider that the reaction occurs neither in the aqueous nor in the organic phase, but in the polymer film itself.

In the case of polyesterification the interfacial polycondensation occurs somewhat differently, since the starting materials used in this case have rather different properties from those employed for the production of polyamides. The poor solubility of diphenoxides in the organic phase[10,18] and of the dicarboxylic acid chloride in the aqueous phase, produces a different mechanism for interfacial polyesterification compared with that of polyamide formation.

Several workers[10,18] assume that in the preparation of polyesters by interfacial polycondensation the film is formed initially in the organic phase, but subsequent film growth occurs from the aqueous phase side (Fig. 2). This mechanism is consistent with the investigations of Eareckson[19], who found that polyphenylene esters are best prepared in a rapidly stirred system of solvents containing detergents, which produces a large reaction surface. In this way the maximum possible quantity of polymer is kept in contact with the interface, and the acid chloride encounters the smallest obstacles to passing into the reaction zone[10,18]. Since the acid chlorides must react at the phase surface and be in a region of high ionic concentration, the less readily hydrolysed chlorides of aromatic acids give polymers of higher molecular weight than do readily hydrolysable aliphatic acid chlorides[10,18,19]. The reaction of polyesterification at the interface between two immiscible phases is considerably accelerated in the presence of catalysts such as quaternary ammonium salts and bases, which is apparently due to the formation of phenoxides soluble in the organic phase[21,22].

During interfacial polyesterification the inorganic base in the aqueous phase not only combines with the acid produced in the course of the reaction but also takes part in the formation of the phenoxides which react with the halides of dicarboxylic acids to form the polyesters.

3. Cessation of Growth of Macromolecules or Chain Termination

The stopping of chain growth for one reason or another determines the molecular weight of the resulting polymer, and this stage is therefore very important. In the case of interfacial polycondenstion, chain growth may cease for the following reasons:

(1) As a result of hydrolysis of terminal acid chloride groups:

$$\ldots-\mathrm{RCOCl}+\mathrm{H_2O}\rightarrow\ldots-\mathrm{RCOOH}+\mathrm{HCl}.$$

(2) As a result of the combination of acid with terminal amino-groups:

$$\ldots-\mathrm{RNH_2}+\mathrm{HCl}\rightarrow\ldots-\mathrm{RNH_2\cdot HCl}.$$

(3) As a result of the conversion of phenoxides into phenols:

$$\ldots-\mathrm{RC_6H_4ONa}+\mathrm{HCl}\rightarrow\ldots-\mathrm{RC_6H_4OH}+\mathrm{NaCl}.$$

(4) As a result of the reaction of a terminal group with a unifunctional compound:

$$\ldots-\mathrm{RCOCl}+\mathrm{H_2NR'}\rightarrow\ldots-\mathrm{RCONHR'}+\mathrm{HCl}$$
$$\ldots-\mathrm{RNH_2}+\mathrm{ClCOR'}\rightarrow\ldots-\mathrm{RNHCOR'}+\mathrm{HCl}$$
$$\ldots-\mathrm{RC_6H_4ONa}+\mathrm{ClCOR'}\rightarrow\ldots-\mathrm{RC_6H_4OCOR'}+\mathrm{NaCl}$$
$$\ldots-\mathrm{RCOCl}+\mathrm{NaOC_6H_5}\rightarrow\ldots-\mathrm{RCOOC_6H_5}+\mathrm{NaCl}.$$

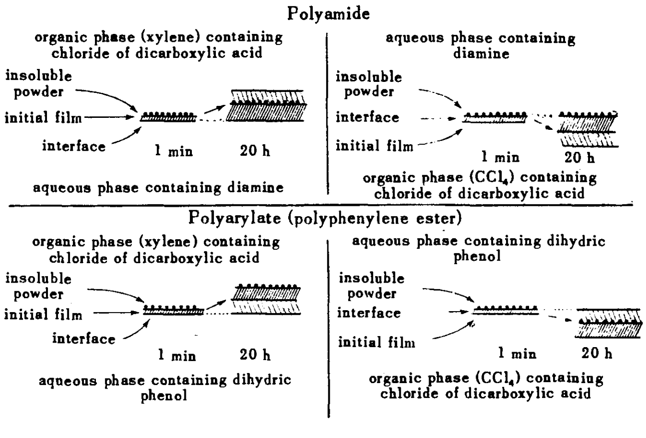


Fig. 2. Diagrams of growth of polymeric film (polyamide and polyester) at the interface between two liquids.[18]

Such unifunctional compounds can probably include also the partly saponified acid chloride:

$$\ldots - RNH_2 + ClCOR'COOH \rightarrow \ldots - RNHCOR'COOH + HCl,$$

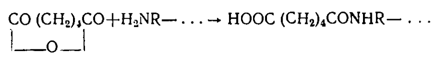
and also the basic salt of the diamine:

$$\ldots - RCOCl + H_2NR'NH_2 \cdot HCl \rightarrow \ldots - RCONHR'NH_2 \cdot HCl + HCl,$$

or the monophenoxide of a dihydric phenol:

$$\ldots - RCOCl + NaOC_6H_4OH \rightarrow \ldots - RCOOC_6H_4OH + NaCl.$$

(5) The impurities in the chloride of adipic acid can include its anhydride, which will terminate the chain by the reaction:



$$\underbrace{CO(CH_2)_4CO}_{O} + H_2NR - \ldots \rightarrow HOOC(CH_2)_4CONHR - \ldots$$

(6) Apart from the above chain-terminating reactions, chain growth may stop owing to inhibition of the entry of one of the original monomers through the polymer film which is being formed, as a result of which the polymer molecules terminate in the same groups:

$$ClCORCO[NHR'NHCORCO]_x Cl \quad \text{or} \quad H_2NRNH[COR'CONHRNH]_x H$$

or

$$HOC_6H_4O[CORCOOC_6H_4O]_x H.$$

These macromolecules are unable to react with the starting materials of similar chemical nature to their end-groups, *i.e.* with those among which they find themselves. Similarly, they cannot react with one another.

III. KINETICS AND FUNDAMENTAL LAWS

Special difficulties occur in the study of the kinetics of interfacial polycondensation, since the process occurs with high reaction velocities. The quantity of diamine or diphenoxide which can be transferred to the organic phase determines the reaction velocity at any concentration of the reactants, so that the rate of reaction is ultimately governed by the rate of diffusion of monomers from one phase to the other[10,18]. The rate constants of the reactions of aliphatic acid chlorides with primary diamines are very high, their order of magnitude in homogeneous solution being 10^2–10^4 litre × × mole^{-1} sec^{-1}, *i.e.* similar to the rate of chain propagation in the radical polymerisation of vinyl compounds[18]. The reaction velocity of interfacial polycondensation is considerably higher than the rate of mixing of the reactants. Morgan and Kwolek[18] found the rate constant for the formation of polyamides in the water–chloroform system to be 570 litre mole^{-1} sec^{-1}.

Fainberg and Mikhailov[23] worked out a technique for studying the kinetics of interfacial polycondensation based on measurement of the electrical conductivity of the aqueous phase (the diamine solution). Entelis *et al.*[24] think it possible to investigate the kinetics of this reaction by utilising the chemiluminescence which they observed to accompany condensation between a toluene solution of adipoyl chloride and an aqueous solution of hexamethylenediamine.

Interfacial polycondensation makes it possible to obtain polymers of higher molecular weight than have been obtained by other methods of polycondensation. Conix[21] prepared polyphenyl esters with a mean molecular weight of 250 000. Schnell[22] reported having prepared polycarbonates with molecular weights up to 200 000, and Wittbecker and Morgan[10] have described polyurethanes having molecular weights up to 1 000 000.

The yield and the molecular weight of polymers obtained by interfacial polycondensation are greatly affected by the temperature and the duration of the reaction, the presence of excess of the starting materials, the concentration of the latter, the presence of emulsifiers, and other factors.

1. Effect of Temperature

A characteristic feature of interfacial polycondensation is that it occurs at relatively low temperatures. The molecular weight and the yield of polyamides and polyesters are affected in a similar way by the reaction temperature[25,26] (see Figs. 3 and 4), an increase in temperature leading to a decrease in the molecular weight of the polymers. This phenomenon is obviously associated with the increased rate of hydrolysis of the chlorides of dicarboxylic acids at higher temperatures[27] (Fig. 5), which leads to chain termination.

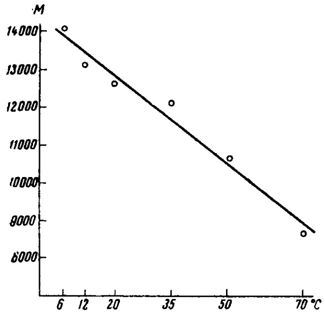


Fig. 3. Variation of the molecular weight of polyhexamethyleneadipamide with the temperature of interfacial polycondensation.[25]

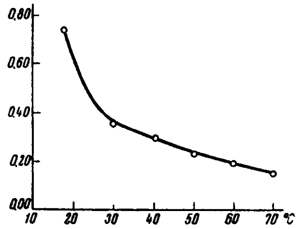


Fig. 4. Variation of the reduced viscosity of polyester with the temperature of interfacial polycondensation of isophthaloyl chloride and bisphenol A.[26]

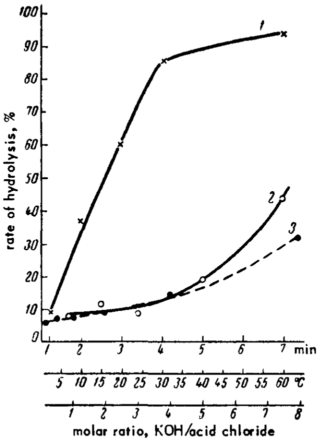


Fig.5. Variation of the rate of hydrolysis of adipoyl chloride in benzene solution (0.15M) with: 1) time of hydrolysis at 25°; 2) temperature of reaction (reaction time 1 min); 3) quantity of caustic potash (reaction time 1 min at 25°).

The rate of hydrolysis of the carbonyl chloride end-groups on the growing macromolecule should be similarly increased, resulting in the formation of carboxyl groups at the ends of the chain, which are inactive in this reaction:

$$\mathrm{ClCORCO[NHR'NHCORCO]_x\,Cl + 2H_2O \rightarrow HOOCRCO[NHR'NHCORCO]_xOH + 2HCl.}$$

In addition, it is possible that chain termination may result from the formation of the monochloride of the dicarboxylic acid:

$$\mathrm{H_2NR'NH\,[CORCONHR'NH]_x\,H + 2ClCORCOOH \rightarrow}$$
$$\mathrm{\rightarrow\ 2HCl + HOOCRCO\,[NHR'NHCORCO]_{x+1}\,OH}$$

The yield of polymer, however, is only slightly affected by a rise in reaction temperature at the phase boundary from 20° to 70°.[26] Similar results were obtained by Sundet *et al.*[28] for the formation of polysulphonamides. At -40° high-molecular-weight polymers can be obtained[29].

2. Effect of Reaction Time

Since polycondensation at a phase boundary takes place rapidly, polymer formation occurs within very short intervals of time (2–10 min). Increasing the reaction time above ~10 min does not produce any increase in the yield or molecular weight of the polymers[25,26].

Table 1 [25] shows that the bulk of the polymer is formed within the first few minutes of the reaction. Nor does the molecular weight change when the duration of the process is increased. An increase in the rate of stirring of the reaction system substantially increases both the yield and the molecular weight of the polymer[25,26,29]. This effect has been studied also by Akutin and Rodivilova[31].

TABLE 1. Effects of time and rate of stirring on the molecular weight and yield of polyamide[25] (concentration of reactants 0.15M).

Time of stirring, min	Yield, %	Viscosity of 0.5% solution in cresol	Molecular weight
Rapid stirring (~7 500 rev/min)			
0.5	34	0.71	19 000
1.0	45	0.69	18 500
1.5	42	0.71	19 000
3.0	49	0.68	18 700
6.0	46	0.72	19 200
12.0	43	0.73	19 700
Slow stirring (~1 000 rev/min)			
3.0	25	0.46	12 500
10.0	32	0.53	14 300
12.0	33	0.46	12 500
90.0	33	0.49	13 200

3. Effect of an Excess of One Reactant

If polymers of high molecular weight are to be formed by carrying out the reaction in a melt, equimolecular proportions of the starting materials must be present. If excess of one of the reactants is present, the molecular weight of the polymer falls sharply[32-35].

When, however, polycondensation is carried out at the interface between two phases, several workers[7,25,29,36] have shown that the relative proportions of the starting materials has no effect on the molecular weight of the resulting polymers in nearly all cases other than polyesters[26,38]. Thus in the preparation of polyamides[7,25,29] polysulphonamides[36], and polyureas[37], for example, an excess of any of the reactants up to 100–300 mole% does not lead to any lowering of the molecular weight of the resulting polymers. Fig.6 shows the results obtained by Korshak *et al.*[7]

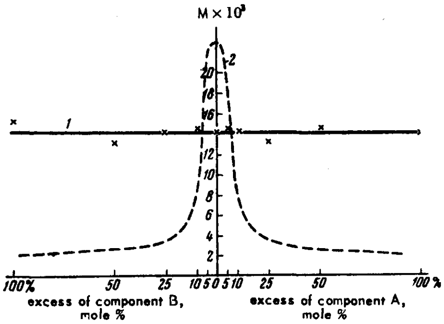


Fig.6. Dependence of the molecular weight of polyhexamethyleneadipamide on the excess of starting materials:
1) in interfacial polycondensation (non-equilibrium);
2) in equilibrium polycondensation (in the melt); A — hexamethylenediamine; B — adipic acid.[7]

In contrast to this, with polyesters[26,38] an excess of one of the reactants lowers the molecular weight (Fig. 7 [38]). This difference in the effect of excess of the reactants on the molecular weight with the different types of polycondensation polymers is obviously associated with the nature of the reactants and with the mechanism of the formation of these high polymers.

The absence of any effect of excess of the starting materials on the molecular weight of a polyamide is due to the fact that, thanks to the high reaction velocity of the starting materials, the molecular weight is governed by kinetic factors, and in particular the rate of diffusion of monomers through the polymer film which is formed. Therefore the chain-terminating reactions constitute the main factor determining the molecular weight of the polyamide. In the preparation of polyesters, film formation does not occur, and therefore the presence of excess of one of the starting materials does have an effect on the molecular weight of the polyester, since in this case the process takes place with high degrees of conversion, so that an existing excess can block the end-groups of the polymer and terminate its growth.

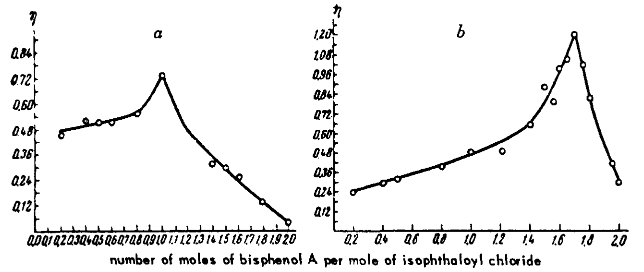


Fig. 7. Variation in the reduced viscosity of the polyester obtained by interfacial polycondensation from isophthaloyl chloride and bisphenol A: *a*) with a bisphenol A: caustic soda ratio of 0.5; *b*) with an isophthaloyl chloride: caustic soda ratio of 0.25.[38]

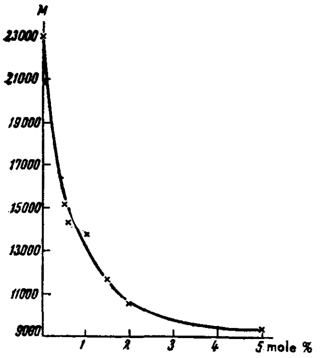


Fig. 8. Change in the molecular weight of polyhexamethyleneadipamide on addition of different amounts of butyryl chloride (abscissae). Polymer obtained by drawing out of solution.[7]

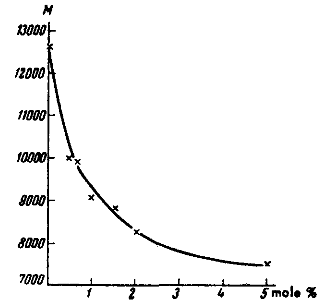


Fig. 9. Change in the molecular weight of polyhexamethyleneadipamide on addition of different amounts of butylamine (abscissae). Polymer obtained by stirring solutions of the reactants.[7]

4. Effect of Unifunctional Additives

Equilibrium polycondensation in the presence of unifunctional additives is known to yield polymers of lower molecular weight than in the absence of such additives[39-42]. This is due to degradation of the polymer under the influence of such additives, as well as to the cessation of chain growth owing to blocking of the functional end-groups of the polymer. Unifunctional compounds also cause a diminution in the molecular weight of polymers obtained by interfacial polycondensation[7,38].

Korshak *et al.*[7] showed that, in the preparation of polyamides, the molecular weight of the resulting polymer is lower if unifunctional substances of similar chemical nature to the starting materials are added to the reaction mixture. Fig. 8 shows the effect of different quantities of butyryl chloride on the molecular weight of the polyamide, and Fig. 9 shows the effect of adding various quantities of butylamine.

Addition of benzoyl chloride or phenol in the preparation of polyesters by interfacial polycondensation also leads to polyesters of lower molecular weight (Fig. 10)[38]. This effect of unifunctional additives is explained by their reacting with the end-groups of the growing macromolecule and forming end-groups which are incapable of reaction, thus causing chain termination:

$$\cdots -\mathrm{CORCOCl} + \mathrm{H_2NR'} \rightarrow -\mathrm{CORCONHR'} + \mathrm{HCl}$$

$$\cdots -\mathrm{C_6H_4ONa} + \mathrm{ClCOR} \rightarrow \cdots -\mathrm{C_6H_4OCOR} + \mathrm{NaCl}.$$

A similar state of affairs is observed in the preparation of polysulphonamides, polyureas, polyurethanes, and other polymers. It follows from this that, in order to obtain polymers of high molecular weight by interfacial polycondensation, the reactants must not contain as impurities unifunctional compounds which can react with one of the reactants. Therefore statements in the patent literature that the purity of the starting materials does not affect the properties of the resulting polymer must be regarded as incorrect.

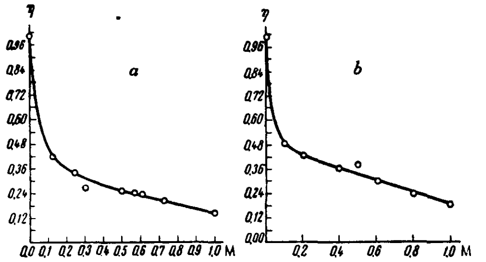
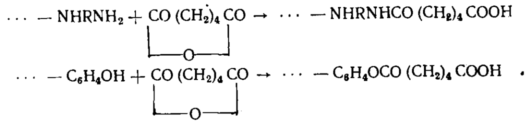


Fig. 10. Change in the reduced viscosity of the polyester obtained by interfacial polycondensation from isophthaloyl chloride and bisphenol A on addition of various amounts of: *a*) benzoyl chloride; *b*) phenol.[38]

Mikhailov *et al.*[43] have shown (see Fig. 11) that the molecular weight of polyhexamethylenesebacamide is greatly dependent on the purity of the initial sebacoyl chloride. As can be seen from Fig. 11, even 2% of impurities in the acid chloride lower the molecular weight of the polymer almost to one-third. In the preparation of polysulphonamides, too, the purity of the original disulphonyl chloride has an effect on the yield and the molecular weight of the polymer[28]. Among the impurities which diminish the molecular weight of polymers obtained from acid chlorides must be included the anhydrides of dicarboxylic acids. These are quite difficult to separate from the chlorides owing to the similarity in their boiling points. Anhydrides are harmful because, by reacting with the growing chain, they terminate it, forming unreactive end-groups:



$$\cdots-\text{NHRNH}_2+\underbrace{\text{CO}(\text{CH}_2)_4\text{CO}}_{\text{O}}\rightarrow\cdots-\text{NHRNHCO}(\text{CH}_2)_4\text{COOH}$$

$$\cdots-\text{C}_6\text{H}_4\text{OH}+\underbrace{\text{CO}(\text{CH}_2)_4\text{CO}}_{\text{O}}\rightarrow\cdots-\text{C}_6\text{H}_4\text{OCO}(\text{CH}_2)_4\text{COOH}\;.$$

Other reactive impurities are possible in the starting materials. Hence it follows that the requirement that the reactants used in equilibrium polycondensation must have maximum purity applies equally to interfacial polycondensation.

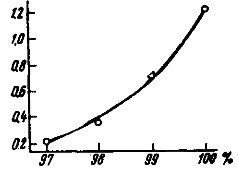


Fig. 11. Variation of the specific viscosity of polyhexamethylenesebacamide with the purity of sebacoyl chloride (abscissae).[43]

5. Effect of Reactant Concentration

The concentration of the reactants is of considerable importance.

Interfacial polycondensation can be effected even when one of the solvents is completely eliminated: *i.e.* the concentration of one of the reactants, if liquid, can be 100%[29,30,36,37]. But it is evident from several papers (see Figs. 12–15) that the preparation of each polymer has its own strictly defined relationship between molecular weight, yield of polymer, and concentration of reactants[10,18,25,26]. The accompanying diagrams show that in all cases the maximum molecular weight corresponds to a strictly defined concentration of the reactants. It is interesting that the yield of polymer depends on this concentration in the same way as the molecular weight[25]. The effect of reactant concentration on the course of the reaction was studied by Akutin and Rodivilova[31,44] and other workers[45].

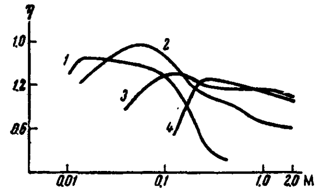


Fig. 12. Variation of the intrinsic viscosity of polyhexamethylenesebacamide with reactant concentration. Molarity of diamine solution: 1) 0.1; 2) 0.4; 3) 0.8; 4) 1.4.[18] The abscissae give the concentrations of sebacoyl chloride in carbon tetrachloride.

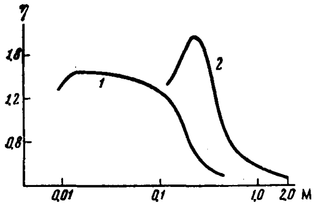


Fig. 13. Variation of the intrinsic viscosity of polyhexamethylenesebacamide with reactant concentration: 1) in the absence, 2) in the presence of an emulsifier. Concentration of diamine 0.1M. Abscissae as in Fig. 12.

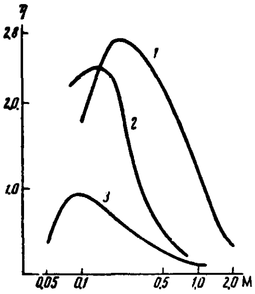


Fig. 14. Variation of the intrinsic viscosity of polyamides obtained by interfacial polycondensation with the concentration of dicarboxylic acid chlorides: 1) polyhexamethylenesebacamide; 2) polypiperazineterephthalamide; 3) polyhexamethyleneterephthalamide. Concentration of diamines 0.4M.[18] The abscissae represent concentrations of acid halide in chloroform.

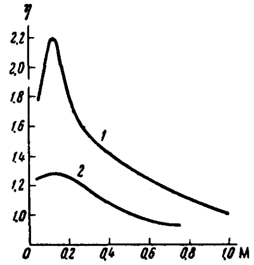


Fig. 15. Variation of the intrinsic viscosity of polyhexamethylene-*m*-benzenedisulphonamide with the concentration of the disulphonyl chloride. Effect of acid acceptor in: 1) 0.25M Na_2CO_3 + 0.13M diamine; 2) 0.25M NaOH + 1.13M diamine.[18, 28] The abscissae represent concentrations of the disulphonyl chloride in dichloromethane.

6. Effect of Acid Acceptor

In order to achieve high molecular weights in ordinary equilibrium polycondensation, it is necessary to bond or to remove the products of low molecular weight (water, alcohol, ammonia, hydrogen chloride, etc.) formed during the reaction[1,4]. With polycondensation at the boundary between two phases, the reaction between the chloride of the dicarboxylic acid and the diamine or dihydric phenol leads to the evolution of hydrogen chloride, which also can cause chain termination. In most cases, therefore, a necessary condition for obtaining polymers at the interface is the presence of an acid acceptor in the aqueous phase. Several papers have shown[10,25,29,46] that we can use for this purpose various bases, oxides, hydroxides, and carbonates of the alkali and alkaline-earth metals which are particularly soluble in water, such as KOH, NaOH, $Ba(OH)_2$, or Na_2CO_3, as well as various organic bases (pyridine, triethylamine, etc.). When one of the monomers is a diamine, it itself can serve this purpose.

The quantity of the acid acceptor may vary within wide limits, from zero to a fivefold excess[30,36]. However, it is preferable not to use more than a threefold excess. Korshak *et al.*[38] have shown that the highest yields and molecular weights are obtained with polyesters by using acid acceptors in amounts approximately equivalent to the bifunctional compound. Fig. 16 shows the effect of the quantity of alkali on the molecular weight and the yield of a polyester.

Organic bases (pyridine)[25] do not give nearly such good results as do inorganic bases. Clearly, this can be explained by the fact that pyridine hydrochloride is appreciably soluble in the organic phase, causing the following equilibrium to be established:

$$C_5H_5NHCl + H_2N(CH_2)_6NH_2 \rightleftarrows C_5H_5N + H_2N(CH_2)_6NH_2\cdot HCl$$

Sokolov and Kudim[47] point out that, in the preparation of polyamides from chlorides of aromatic dicarboxylic acids and aromatic diamines, better results are obtained in acid medium. Not only the nature and amount of the acid acceptor but also its concentration are important in determining the course of reaction, and therefore the pH of the aqueous phase has a substantial effect.

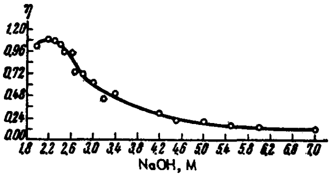


Fig. 16. Variation of the reduced viscosity of polyester from isophthaloyl chloride and bisphenol A with the quantity of caustic soda added.[38]

7. Effect of Emulsifiers

As shown above, vigorous stirring at the interface between two phases increases the reaction surface and leads to an increase in the yield and the molecular weight of the polymers[25] (see p. 256). A similar effect is exerted by emulsifiers[10,19,29,30,36,37,48], which may be either cationic, anionic, or neutral in character and can be soluble in either water or the organic solvent. The most widely used emulsifier in interfacial polycondensation is sodium lauryl sulphate.

It is evident from the results of Korshak *et al.*[48] summarised in Table 2 that the best emulsifiers with respect to the yield and molecular weight of polyesters are sodium Mersolate and Nekal.

The data in Table 3 show the effect of varying the amount of emulsifier.

The optimum concentration is ~1%. Excess of the emulsifier lowers the molecular weight of the polyester. In this case the use of an emulsifier, apart from increasing the molecular weight and the yield of polymers, makes it possible to extend the range of organic solvents which can be employed in interfacial polyesterification.

TABLE 2. Effect of the nature of emulsifier on the reduced viscosity and yield of polyester.

(Concentration of emulsifier in aqueous layer 1 wt. %)*

Emulsifier	Reduced viscosity of polyester in cresol	Yield of polyester, %
Na stearate	0.78	76
Na Mersolate	1.54	79
New product	1.06	75
OP-20	0.94	82
Trilon B [EDTA]	0.22	50
Nekal	1.44	75

* Concentration of reactant solutions: 0.125M alkaline solution of dihydric phenol, 0.5 g of emulsifier in 10 ml of water, and 0.1M solution of isophthaloyl dichloride in *p*-xylene. Stirring continued for 20 min.

TABLE 3. Effect of emulsifier concentration (Na Mersolate) on the reduced viscosity and yield of polyester.

Concn. of emulsifier in aqueous layer, wt.%	Reduced viscosity of polyester in cresol	Yield, %
0.25	1.10	78
0.50	1.24	75
0.88	1.14	77
1.00	1.54	79
1.35	1.24	83
1.75	1.10	75
2.00	1.02	82
2.50	0.76	84

8. Effect of Solvent

Interfacial polycondensation is carried out in a solvent system consisting of water and an organic solvent. The latter may belong to various classes of organic compounds which are immiscible or not very miscible with water and which do not react with the reactants. The most widely used are such solvents as benzene and its homologues, aliphatic hydrocarbons, halogenated hydrocarbons, and several other substances[25,29,30,49]. The organic solvent affects such variables in interfacial polycondensation as the distribution of the reactants between the two phases, the diffusion of the reactants, and the swelling and permeability of the polymer which is formed[50]. Wittbecker and Morgan[50], as well as Sokolov and Turetskii[51], consider that to obtain a high-molecular-weight polymer, it is necessary that the solvent should merely cause the resulting polymer to swell, whereas Eareckson[19] considers that the polymer must be dissolved. The influence of these factors has at present no theoretical explanation, and in most cases the solvents which promote the synthesis of polymers of sufficiently high molecular weight and in sufficiently high yield are selected empirically. Thus the best solvents for the preparation of polyesters, for example, prove to be chloroform, 1,1,2-trichloroethane, trichloroethylene[19], and *p*-xylene[26]. Solvents which may be successfully used for the preparation of polyamides are benzene, methylene chloride, chloroform, and carbon tetrachloride[18,25,49].

Emulsifiers can play a large part in extending the range of organic solvents which can be utilised[52]. In the preparation of polyesters, for example, Nekal increases the molecular weight of the polyester with nearly all the organic solvents used (see Table 4).

Organic solvents are used to prepare solutions of the acid halides, whereas solutions of the second reactant are usually made up with water. In the preparation of polyamides by interfacial polycondensation, water can be replaced by ethylene glycol[29]. Polycondensation can then be carried out at low temperatures (around -40°).

Inorganic salts, especially neutral salts such as sodium chloride, when added to an alkaline aqueous solution of a diamine, increase the proportion of the latter in the organic phase[18]. Furthermore, the presence of salts in the aqueous phase lowers the solubility of acid chlorides in water, and hence diminishes their hydrolysis. This considerably improves the preparation of polymers from the lower aliphatic acid dichlorides, which are more soluble in water than are the higher dichlorides. Addition of salts to the aqueous phase is especially important in the preparation of polymers of the A-B type[9,52] (see p. 263).

TABLE 4. Effect of the nature of solvent on the reduced viscosity and yield of polyester.

Solvent of isophthaloyl chloride	With emulsifier*		Without emulsifier	
	reduced viscosity of polyester in cresol	yield, %	reduced viscosity of polyester in cresol	yield, %
Xylene	1.46	80	1.02	88
Tetralin	0.64	80	0.28	86
n-Heptane	0.94	84	0.30	quantitative
Carbon tetrachloride	1.12	83	0.40	»
Chloroform	0.44	77	0.12	»
Dichloroethane	0.72	80	0.16	80
Tetrachloroethylene	1.02	82	-	-
Trichloroethylene	0.96	80	-	-
Chlorobenzene	0.72	80	0.20	83
Ethyl ether	0.58	87	0.33	77

* Concentration of emulsifier 1.5% in water.

IV. COMPARISON OF EQUILIBRIUM AND INTERFACIAL POLYCONDENSATION

The formation of polyamides and polyesterification, like other forms of equilibrium polycondensation taking place in solution or in a melt at high temperatures, are reversible reactions:

$$x\,\mathrm{H_2NR'NH_2} + x\,\mathrm{HOOCRCOOH} \rightleftarrows [\mathrm{-NHR'NHCORCO-}]_x + 2x\,\mathrm{H_2O}$$

$$x\,\mathrm{HOR'OH} + x\,\mathrm{HOOCRCOOH} \rightleftarrows [\mathrm{-OR'OOCRCO-}]_x + 2x\,\mathrm{H_2O}$$

Therefore the extent of conversion and the molecular weight of the resulting polymers are determined by the completeness of removal of reaction products of low molecular weight, *i.e.* of water in this case[2,32,53]. The molecular weight of the polymers then depends on the relative proportions of the starting materials, or more generally of the initial functional groups[2,3,32–35]. Polymers of high molecular weight are formed only when the starting materials are present in equivalent proportions. The presence of excess of any of the starting materials or of a product which is chemically similar leads to a diminution in the molecular weight of the polymer. Since an inverse relationship exists between the amount of this excess and the molecular weight of the polymer, the maximum value of the latter can be predetermined by adding the calculated quantity of the acid, diamine, or other compound as molecular-weight regulator[34]. Exchange reactions between the polymer molecules[4,54,55] and also between the polymer molecules and the starting materials[4,56–67] play an important role in polycondensation. These exchange reactions result in a degradation of the polymer molecules[4,57–67], which takes place more readily and more rapidly the higher the molecular weight of the polymer[68,69]. As a result, the longer molecules are first broken down under the influence of the degradative exchange reactions during polycondensation, and the polymer formed has comparatively small polydispersity, in contrast to the polymers obtained by polymerisation[69–75], as investigations of the molecular-weight distribution of the polymers have shown[1,71,75].

Unlike high-temperature equilibrium polycondensation in a melt, polycondensation at the boundary between two immiscible phases is an irreversible process[7,10,18,25,26]:

$$x\,\mathrm{ClCORCOCl} + x\,\mathrm{NH_2R'NH_2} \rightarrow [\mathrm{-NHR'NHCORCO-}]_x + 2x\,\mathrm{HCl}$$
$$x\,\mathrm{ClCORCOCl} + x\,\mathrm{HOR'OH} \rightarrow [\mathrm{-OR'OOCRCO-}]_x + 2x\,\mathrm{HCl}.$$

Since the reaction takes place at low temperatures, the products of low molecular weight which are formed do not react with the polymer, and hence do not affect its molecular weight or the extent of conversion. In the formation of polyamides by interfacial polycondensation, the molecular weight of the resulting polymer is independent of the relative proportions of the starting materials[7,10,18,36]; in polyesterification[38] the proportions of the starting materials do to some extent affect the molecular weight of the polyester (see p. 256). A peculiarity of interfacial polycondensation is the heterogeneity of the process. Another important feature which affects the preparation of polymers of high molecular weight is the occurrence of side-reactions which terminate the chains by forming end-groups which do not react under the given conditions. With equilibrium polycondensation, on the other hand, most of the terminal functional groups are retained as such, and hence the macromolecules do not lose their capacity for further chain growth.

The molecular-weight distribution[18] of polymers obtained by interfacial polycondensation may vary depending on the reaction conditions. In some cases[18] the distribution was narrower than in the case of polycondensation in a melt, and in other cases it was broader or similar.

A comparison of the properties of polymers obtained by interfacial polycondensation with those obtained at high temperatures has led several workers[10,18,76,77] to conclude that the polymers are identical in melting point, crystallinity, and also solubility. Schnell[22] points out, however, that polymers obtained by interfacial polycondensation have good mechanical properties only at relatively high molecular weights.

Table 5 gives a comparison of the two methods of polycondensation with respect to the requirements to be met by the starting materials, the conditions of polycondensation, and the properties of the resulting polymers[10,18].

Examination of these data shows that interfacial polycondensation has several advantages over polycondensation in a melt, the main advantages being as follows:

(a) The reaction is carried out at low temperatures, which permits an extension of the range of monomers which can be used, since it becomes possible to utilise thermally unstable monomers, and thus to obtain polymers which it had previously been impossible to prepare by high-temperature equilibrium polycondensation[78,79].

(b) The method of interfacial polycondensation makes it possible to obtain polymers having a high melting point, often lying above the temperature at which they decompose. It is impossible to obtain such polymers by equilibrium polycondensation in the melt, since they are decomposed.

TABLE 5. Comparison of interfacial polycondensation and polycondensation in the melt.

	Interfacial	In the melt
Starting materials		
Purity	moderate to high	high
Thermal stability	not essential	essential
Equilibrium	not essential	essential
Conditions of polycondensation		
Time	a few minutes	a few hours
Temperature	0°–40°	> 200°
Pressure	atmospheric	high or low
Equipment	simple, open	special, sealed
Products		
Yield	low to high	high
Structure	unrestricted	restricted by thermal stability and fusibility

(c) The reaction can be carried out within a very short period of time, it requires very simple apparatus, and is therefore very convenient for the laboratory preparation of polymers.

(d) Polymers of high molecular weight can often be obtained without requiring equimolecular proportions of the starting materials.

(e) The method provides an opportunity for obtaining, at the boundary between the two phases, polymer films which can be removed from the reaction zone in the form of a continuous film[80]. This enables goods made of high polymers (films, fibres) to be obtained by a continuous method directly from the reaction zone[43,46].

In this connection the production of articles from materials which are difficult or even altogether impossible to work in industry (*e.g.* cross-linked, infusible, insoluble polymers) is of particular interest. In spite of the series of favourable aspects indicated above, interfacial polycondensation has specific disadvantages: (*a*) the process requires the presence of chlorides of dicarboxylic acids, which are less readily available than the acids themselves and require an additional stage in the synthesis of the monomers; (*b*) the yield of polymers may vary within wide limits depending on the nature of the starting materials; (*c*) the polymers contain such impurities as sodium chloride and other substances. Washing out the impurities is often a quite lengthy stage in the preparation of the polymers.

It is still too early to arrive at final conclusions concerning the future of interfacial polycondensation. The study of the process has only just begun, but it is already clear that this method has its place in the series of synthetic reactions which can be used to prepare polymers.

V. METHOD OF CARRYING OUT INTERFACIAL POLYCONDENSATION

Two procedures can be employed for polycondensation at an interface[10,30,80].

1. Preparation of Polymers with Stirring

Various macromolecular compounds can be prepared by stirring solutions of the reactants at the interface between two phases. The polymers are then obtained in the form of a powder, and can be further processed into various goods (films, fibres, etc.) in the usual way. Stirring enables the formation of the polymer to be accelerated, and the molecular weight and the yield to be increased. The preparation is carried out in an apparatus fitted with a mechanical stirrer rotating at high speed. A solution of the acid dihalide in an organic solvent immiscible with water (benzene, chloroform, hexane, etc.) is run into an alkaline aqueous solution of the multifunctional compound (diamine, dihydric phenol, etc.) with stirring, and the polymer is immediately formed as a film, a powder, or granules. The hydrogen chloride evolved during the reaction is absorbed by the alkali. The reaction is carried out at moderate temperatures, usually room temperature, in short periods of time, and is practically complete within 2–15 min.

If the multifunctional compound is insoluble in water but soluble in some organic solvent, it can be suspended in the water–organic solvent system for the purpose of polycondensation[10,29,37]. The organic solvent must not react, or may react only slightly, with the acid dihalide[29,30,37]. A water-insoluble multifunctional compound can also be introduced in the form of its water-soluble derivatives (*e.g.* the hydrochlorides of aromatic diamines)[28,30]. The calculated quantity of alkali required to liberate the free diamine and also to combine with the hydrogen chloride eliminated during the process is gradually added to a stirred solution of the reactants. The resulting polymer is most frequently obtained in solid form, and is easily separated from the reaction mixture by simple filtration. When, however, the polymer is soluble in the solvent system employed, it is isolated by distilling off the solvent or by precipitating the polymer with a suitable precipitant[49,78]. The precipitated polymer is washed successively with an aqueous solution of acetone or alcohol and warm water until chloride has been completely removed. The yield of polymer may vary within wide limits depending on the nature of the starting materials and the reaction conditions, and it is often quantitative.

The molecular weights and yields of polymers depend, as already mentioned, on several factors — intensity of stirring, concentration, temperature, presence of emulsifiers, etc.

2. Preparation of Polymers without Stirring

Polymers can also be obtained without stirring the solutions of the reactants[10,80]. When a solution of the acid dihalide is run into an alkaline aqueous solution of the diamine, a film of polymer is instantly formed at the interface, and it is often so strong that it can be removed from the reaction zone in the form of a continuous filament (Fig. 17).

The polymer obtained in this way is subjected to further treatment as described above; the yield of polymer is rather lower (25–50%) because the polymer carries a proportion of the reactants away from the zone of reaction.

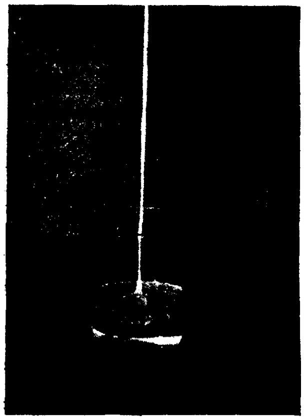


Fig. 17. Continuous preparation of polymer filament by interfacial polycondensation: first layer — alkaline aqueous solution of diamine; second layer — solution of dicarboxylic acid halide in organic solvent; third layer — polymer film formed at interface.

The molecular weights of polymers obtained without stirring are not lower than those of polymers obtained with stirring, and depend on the experimental conditions.

Interfacial polycondensation without stirring will probably find application in the direct manufacture of polymeric goods (films, fibres) from the reaction zone, using both linear and three-dimensional macromolecular compounds[10,43,46,81].

3. Design of Apparatus for Interfacial Polycondensation

Interfacial polycondensation takes place at room temperature and atmospheric pressure; therefore it can be carried out in very simple apparatus and can easily be arranged as a continuous process[36,82]. Fig. 18 illustrates

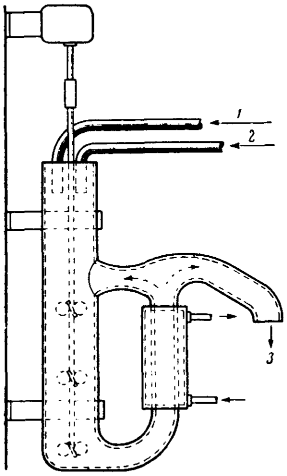


Fig. 18. Apparatus for continuous preparation of polymers by interfacial polycondensation:[10, 36]
1) acid dichloride; 2) diamine; 3) polymer.

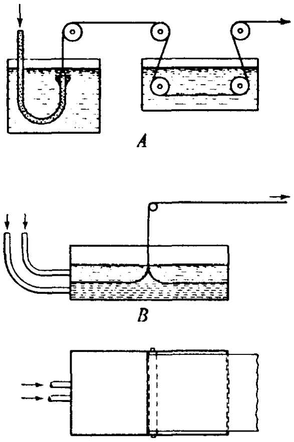


Fig. 20. Arrangement for continuous production of polyamide filament (*A*) and film (*B*) by interfacial polycondensation.[46]

an apparatus for carrying out such a process with stirring of the initial reactants and partial recirculation of the reaction mixture.

By utilising the ability of certain polymers to form a sufficiently strong film at the phase boundary, this process can be used to produce ready-made polymeric materials (films, fibres)[43,46]. Figs. 19 and 20 show arrangements for obtaining polymeric goods directly from the reaction zone.

The continuous preparation of polymers directly from the reaction zone opens up prospects for the development of a new technology for the production of polymeric materials. As a result, it becomes possible to process into fibres and films polymers which are practically insoluble and which possess melting points close to the temperatures at which they decompose.

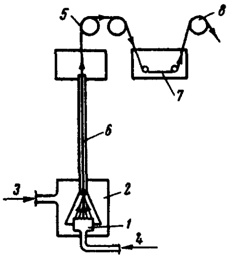


Fig. 19. Scheme for fibre production by interfacial polycondensation:
1) spinneret; 2) spinning head; 3) supply of diamine solution; 4) supply of dicarbonyl chloride solution; 5) guide roll; 6) filament after formation; 7) washing bath; 8) take-up device.[41]

VI. MACROMOLECULAR COMPOUNDS OBTAINED BY INTERFACIAL POLYCONDENSATION

1. Polyamides

Polyamides represent the class of polymers which is most readily obtained by interfacial polycondensation and is able to form films at the boundary between the immiscible phases. From the preparative viewpoint, polyamides are least sensitive to the effect of the solvents, the proportions of the reactants, and similar factors[7,10,18,25,83].

Polyamides can be prepared from substances of differing structure — aliphatic and aromatic diamines and chlorides of aliphatic and aromatic dicarboxylic acids, as well as chlorides of unsaturated acids (see Table 6).

2. Polymers of Type A-B [9,52]

Polymers of type A-B are macromolecular compounds obtained from monomers containing both interacting functional groups in a single molecule. The amino-acids form an example of such monomers. Polymers of this type are produced according to the scheme:

$$x\,ClCO(CH_2)_5NH_2\cdot HCl + 2x\,NaOH \rightarrow [-OC(CH_2)_5NH-]_x + 2x\,NaCl + 2x\,H_2O\,.$$

The mechanism of the interfacial polycondensation of such monomers differs somewhat from that for two different bifunctional compounds (*e.g.* a diamine or a dihydric phenol with the dichloride of a dicarboxylic acid, etc.). The main difference is that the monomers must be used in the form of salts (to block the amino-groups).

The formation of polymers of type A-B by interfacial polycondensation takes place in the following way[52]. Since the monomer is a salt, which is only sparingly soluble in the organic solvent, it diffuses into the alkaline-aqueous phase, where the amino-group is set free. The monomer free from the salt group is readily soluble in the organic phase, where reaction takes place between the free amino-group and the acid chloride group of another molecule.

TABLE 6. Polyamides obtained by interfacial polycondensation from diamines and dichlorides of dicarboxylic acids.

Diamine	Dichloride of dicarboxylic acid	Literature references
Ethylenediamine	sebacoyl	84
	terephthaloyl	84, 85
	phthaloyl	86
N,*N'*-Dimethylethylenediamine	terephthaloyl	85
N,*N'*-Diethylethylenediamine	terephthaloyl	85
N,*N'*-Dibutylethylenediamine	terephthaloyl	85
Trimethylenediamine		85
1, 2-Diaminopropane		83
N,*N'*-Dimethyltrimethylenediamine		85
N,*N'*-Diethyltrimethylenediamine		85
2-Hydroxytrimethylenediamine	sebacoyl	83
Tetramethylenediamine	biphenyl-*p*, *p'*-dicarbonyl	83
	terephthaloyl	85
	sebacoyl	30
N,*N'*-Dimethyltetramethylenediamine	terephthaloyl	85
Pentamethylenediamine		85
Hexamethylenediamine	oxalyl	29
	fumaroyl	87, 88
	β-hydromuconoyl	83
	adipoyl	29, 30, 43, 76, 81, 83, 89, 90
	azelaoyl	76
	sebacoyl	29, 43, 76, 80, 81, 83, 89, 90
	terephthaloyl	84
	isophthaloyl	76, 83
	phthaloyl	86
	cyclohexane-1, 4-dicarbonyl	83
	oxotriphenylphosphorane-*p*, *p'*-dicarbonyl	91
	methylphosphonyl	78
	phenylphosphonyl	78, 79
	phosphoryl	78
2, 5-Diaminohexane	terephthaloyl	29
Bis-3-amino-octyl ether	sebacoyl	29
Nonamethylenediamine	sebacoyl	90
Piperazine	adipoyl	29, 90
	azelaoyl	90
	sebacoyl	18, 90
	cyclopentane-1, 3-dicarbonyl	31
	terephthaloyl	18, 89, 90
	isophthaloyl	49, 90
	phthaloyl	86, 90
	trans-hexahydroterephthaloyl	49
	cis-hexahydroterephthaloyl	49
Piperazine	biphenyl-*p*, *p'*-dicarbonyl	49, 83
	bibenzyl-*p*, *p'*-dicarbonyl	49
	2, 2-diphenylpropane-*p*, *p'*-dicarbonyl	49
2-Methylpiperazine	terephthaloyl	49
	isophthaloyl	49
	trans-hexahydroterephthaloyl	49
	bibenzyl-*p*,*p'*-dicarbonyl	49
2-Phenylpiperazine	phthaloyl	86
	terephthaloyl	49
2, 5-Dimethylpiperazine	terephthaloyl	49
	isophthaloyl	49
	phthaloyl	86
	trans-hexahydroterephthaloyl	49
	cis-hexahydroterephthaloyl	49
	cyclopentane-1, 3-dicarbonyl	49
	cis-hexahydroisophthaloyl	49
	1, 4-dihydroterephthaloyl	49
	biphenyl-*p*, *p'*-dicarbonyl	49
	2, 3, 5, 6-tetrachloroterephthaloyl	49
	2, 2-diphenylpropane-*p*, *p'*-dicarbonyl	49
2, 5-Diethylpiperazine	terephthaloyl	49
2, 6-Dimethylpiperazine	terephthaloyl	49
2, 3, 6-Trimethylpiperazine	*trans*-hexahydroterephthaloyl	49
2, 3, 5, 6-Tetramethylpiperazine	terephthaloyl	49
	trans-hexahydroterephthaloyl	49
p-Phenylenediamine	fumaroyl	88
	sebacoyl	92
	terephthaloyl	84, 92
m-Phenylenediamine	fumaroyl	88
	sebacoyl	83
m-Tolylenediamine	sebacoyl	92, 93
p-Xylylenediamine	sebacoyl	92
	terephthaloyl	92
1, 4-Hexahydroxylylenediamine	adipoyl	29, 83
Bis-(4-aminocyclohexyl) methane	terephthaloyl	83
	phthaloyl	86
Benzidine	fumaroyl	88
	sebacoyl	92
	terephthaloyl	92
4, 4'-Diamino-3, 3'-dimethylbiphenyl (tolidine)	sebacoyl	92
	terephthaloyl	92
Dianisidine	fumaroyl	88
1, 5-Naphthylenediamine	fumaroyl	88
Bis(4-aminophenyl) methane	sebacoyl	92
	terephthaloyl	92
Bis(4-aminophenyl) ethane	sebacoyl	92
	terephthaloyl	92
Bis(4-amino-3-methylphenyl)methane	sebacoyl	92
	phthaloyl	89
	terephthaloyl	92
Bis(*N*-methyl-4-aminophenyl)methane	sebacoyl	92
	terephthaloyl	92
Bis(*N*-ethyl-4-aminophenyl)methane	sebacoyl	92
	terephthaloyl	92
Bis(*N*-ethyl-4-amino-3-methyldiphenyl)-methane	sebacoyl	92
	terephthaloyl	92

Repetition of this reaction many times over leads to the production of a macromolecular compound. The molecular weight and the yield of polymers of type A – B depend to a considerable extent on the hydrolysability of the acid chloride groups of the monomers, since hydrolysis of these groups becomes possible when they are released in the alkaline-aqueous layer. In order to suppress this reaction, which would lead to termination of the polymer chain, high concentrations of neutral salts are introduced into the alkaline-aqueous phase, as these salt-out the "unblocked" monomer into the organic phase, thereby reducing the amount of hydrolysis.

Schaefgen *et al.*[52] used a series of salts of aminoalkyl esters of chloroformic acid for the preparation of polyurethanes and polyamides — for example, the hydrochlorides of 5-aminopentyl chloroformate and *p*-aminomethylbenzoic acid, toluenesulphonates of 4-aminobutyl chloroformate and 3(γ-piperidyl)propyl chloroformate, and similar compounds.

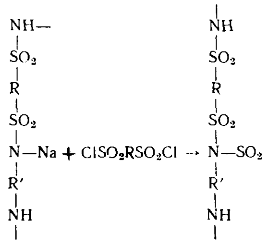
3. Polysulphonamides

Polymers of this class obtained by interfacial polycondensation are of practical interest, since they possess a molecular weight which is sufficient for the production of oriented films and fibres[28,36,94,95]. Attempts to obtain polysulphonamides by other methods of polycondensation yielded polymers having predominantly low molecular weights[96-99].

The most important factors in the preparation of polysulphonamides are strict concentration ratios of the reactants in both phases, a high degree of purity of the disulphonyl chlorides, a definite pH of the aqueous medium (9–10), and several other factors[28,36,94,95].

Polysulphonamides, apart from being soluble in the solvents ordinarily used for polyamides, dissolve in 10% aqueous caustic soda solution[10,28,96].

A high concentration of alkali in the aqueous phase may, apart from favouring hydrolysis of the disulphonyl chloride, promote the formation of branched chains in the polysulphonamide, as well as leading to cross-linking of the polymer chains by reaction with the hydrogen atom of the amide group[10]:



$$-NH-SO_2-R-SO_2-N(Na)-R'-NH- + ClSO_2RSO_2Cl \rightarrow -NH-SO_2-R-SO_2-N(SO_2-)-R'-NH-$$

Table 7 lists a series of polysulphonamides synthesised by interfacial polycondensation.

TABLE 7. Polysulphonamides obtained by interfacial polycondensation from aliphatic and aromatic disulphonyl chlorides.

Diamine	Disulphonyl dichloride	Literature references
Ethylenediamine	*m*-benzene-	28, 36
	p-benzene-	28
	biphenyl-4, 4′-	28, 94
	naphthalene-1, 5-	28
	phenoxybenzene-4, 4′-	28
N,N′-Dimethylethylenediamine	*m*-benzene-	28
	cyclohexane-1, 4-	28
Propylenediamine	biphenyl-4, 4′-	94
2-Hydroxytrimethylenediamine	*m*-benzene-	28
Trimethylenediamine	biphenyl-4, 4′-	94
1-Methyltrimethylenediamine	biphenyl-4, 4′-	94
2, 2-Dimethyltrimethylenediamine	biphenyl-4, 4′-	94
Tetramethylenediamine	biphenyl-4, 4′-	94
	pentane-1, 5-	95
Hexamethylenediamine	pentane-1, 5-	94
	m-benzene-	28, 36
	p-benzene-	28
	ethane-1, 2-	28
	hexane-1, 6-	28, 36
	cyclohexane-1, 4-	28
	naphthalene-1, 5-	28
	naphthalene-2, 7-	28
	biphenyl-4, 4′-	28, 36
	diphenylemthane-4, 4′-	35
Bis(3-aminopropyl) ether	*m*-benzene-	28
p-Xylenediamine	*m*-benzene-	28
4, 4-Dimethylheptamethylenediamine	biphenyl-4, 4′-	94
Piperazine	biphenyl-4, 4′-	94
2-Methylpiperazine	biphenyl-4, 4′-	94
trans-2, 5-Dimethylpiperazine	biphenyl-4, 4′-	94

4. Polyurethanes

Polyurethanes belong to a class of fibre-forming polymers somewhat resembling polyamides in structure. Two methods of practical interest have been worked out for preparing polyurethanes: (1) reaction between a di-isocyanate and a glycol, and (2) reaction between a bischloroformate and a diamine. Both methods have been known since 1939[96,100,101].

The preparation of polyurethanes by interfacial polycondensation is a variant of the second of the above methods; the reaction is carried out using two immiscible solvents (water and an organic solvent).

The first information on the preparation of polymers of this class by the interfacial polycondensation method dates back to 1941[102], but the very broad investigation of this method began only relatively recently[103-112]. Its application allows us to obtain polyurethanes of a great variety of structures, including those containing aliphatic and aromatic groupings, as well as various copolymers[104-106].

Table 8 lists polyurethanes which have been obtained by interfacial polycondensation.

5. Polyureas

The polyureas, which are widely known representatives of polycondensation polymers, also can be obtained by interfacial polycondensation using as starting materials carbonyl chloride or thiocarbonyl chloride and a diamine,

TABLE 8. Polyurethanes obtained by interfacial polycondensation.

Diamine or diol	Bischloroformate of diol	Literature references
Ethylenediamine	butane-1, 4-diol	104, 108, 111, 112
	ethane-1, 2-diol	112
	2, 2-dimethylpropane-1, 3-diol	112
	cyclohexane-1, 4-diol	112
	diglycol	112
Tetramethylenediamine	butane-1, 4-diol	103–108, 111
1, 3-Diaminobutane	ethane-1, 2-diol	112
hexamethylenediamine	ethane-1, 2-diol	112
	diglycol	112
	2, 2-dimethylpropane-1, 3-diol	112
	cyclohexane-1, 4-diol	112
3-Methoxyhexamethylenediamine	2, 2-dimethylpropane-1, 3-diol	112
Bis(3-aminopropyl)ether	2, 2-dimethylpropane-1, 3-diol	112
Piperazine	butane-1, 4-diol	112
	hexane-1, 6-diol	112
	quinol	112
	ethane-1, 2-diol	110, 112
	cyclohexane-*trans*-1, 4-diol	112
	cyclohexane-*cis*-1, 4-diol	112
	pentane-1, 5-diol	110
	diphenylpropane-*p*, *p*′-diol	109, 110
	cyclohexane-1, 4-diol	105, 110
trans-2,5-Dimethylpiperazine	ethane-1, 2-diol	112
	quinol	112
1, 4-Diaminocyclohexane	ethane-1, 2-diol	112
1, 3-Diaminocyclohexane	ethane-1, 2-diol	112
p-Phenylenediamine	2, 2-dimethylpropanediol	112
m-Tolylenediamine	2, 2-dimethylpropanediol	112
Bis(4-aminophenyl)methane	2, 2-dimethylpropanediol	112
Bis(4-amino-3-methylphenyl)methane	2, 2-dimethylpropanediol	112
2, 2-(*p*-Hydrophenyl) propane	*N,N*′-diphenoxycarbonylpiperazine	109
Quinol	*N,N*′-diphenoxycarbonylpiperazine	109
4, 4′-Dihydroxybiphenyl	*N,N*′-diphenoxycarbonylpiperazine	109
Bis(hydroxyphenyl)propane	piperazine-1, 4-dicarbonyl chloride	109

TABLE 9. Polyureas obtained by interfacial polycondensation.

Diamine	Second component	Literature references
Tetramethylenediamine	carbonyl chloride	84
Hexamethylenediamine	carbonyl chloride	84, 113
Bis(3-aminopropyl)ether	carbonyl chloride	84
Hexamethylenediamine	thiocarbonyl chloride	84
Bis(3-aminopropyl)ether	hexamethylene di-isocyanate	114
Bis(3-aminopropyl)methylamine	hexamethylene di-isocyanate	114

or a di-isocyanate and a diamine[84,113,114]. Carbonyl chloride and di-isocyanates are dissolved in an organic solvent, and diamines in an alkaline-aqueous solution. Polyureas are obtained in higher yields from a di-isocyanate and a diamine, since di-isocyanates are more resistant to the action of water than is carbonyl chloride.

6. Polyesters

Interfacial polycondensation provides one of the best methods for synthesising polyarylates, *i.e.* polyesters of dihydric phenols and dicarboxylic acids. Various polyesters obtained by this method have been described in several papers[19,21,26,38,48,88], and Table 10 lists the monomers from which these polyesters were prepared.

Polyphenyl esters are products of high molecular weight, melting at high temperatures, possessing good dielectric properties, and capable of being fabricated.

Korshak *et al.*[115] suggested using interfacial polycondensation to obtain graft and block copolymers of polyester type.

Polyesters containing carbonic acid radicals and dihydric phenols, the so-called polycarbonates, are of great practical interest. They possess good dielectric properties and high melting points. They can be obtained both by polyesterification and by "phosgenisation". The preparation of polycarbonates by the latter method represents an interfacial polycondensation reaction. Schnell[22] has described a series of polycarbonates, but his paper gives no clear indication of exactly which polymers he obtained at the phase boundary.

7. Mixed Polyamides

Korshak *et al.*[76,90,116] showed that the use of mixtures of chlorides of different dicarboxylic acids in an interfacial polycondensation reaction leads to the formation of a mixed polyamide. This is similar in composition and properties to copolymers obtained from the corresponding starting materials by the high-temperature polycondensation method, as can be seen from Figs. 21 and 22.

A limited difference in reactivity between the acid chlorides or the diamines has no material effect on the composition or properties of the copolymer[76]. The production of mixed polymers having an ordered structure requires that the reactant should differ sharply in reactivity. Otherwise it is necessary to carry out the reaction with the initial reactants introduced alternately into the zone of polycondensation. In this way Lyman and Jung[117] have synthesised mixed polyurethanes of regular and irregular structure.

Mixed polyamides have been described, obtained[2,40,86,87,90,116] by the interfacial polycondensation of the following substances: hexamethylenediamine with the following pairs of acid chlorides: adipoyl and azelaoyl, adipoyl and sebacoyl, azelaoyl and sebacoyl, adipoyl and isophthaloyl, sebacoyl and terephthaloyl, and adipoyl and fumaroyl; piperazine with adipoyl and isophthaloyl, azelaoyl and phthaloyl, chlorides; etc.

TABLE 10. Polyesters obtained by interfacial polycondensation from aromatic diols and chlorides of various dicarboxylic acids.

Diol or dithiol	Chloride of dicarboxylic acid	Literature references
Quinol	succinyl	19•
	adipoyl	19, 45
	sebacoyl	19
	terephthaloyl	19, 45
	isophthaloyl	19
Resorcinol	fumaroyl	19
	terephthaloyl	19
	isophthaloyl	19
2, 2-Bis(*p*-hydroxyphenyl)propane	oxalyl	19
	fumaroyl	19, 21, 88
	adipoyl	
	sebacoyl	
	terephthaloyl	19, 21
	isophthaloyl	21, 26, 38, 48
	quinoldiglycolloyl	
	diphenylmethane-*p*, *p*′-dicarbonyl	21
	2, 2-diphenylpropane-*p*, *p*′-dicarbonyl	
	benzophenone-*p*, *p*′-dicarbonyl	21
	phenoxybenzene-*p*, *p*′-dicarbonyl	21
	diphenyldichloromethane-*p*, *p*′-dicarbonyl	21
	sulphonyl-*p*, *p*′-dibenzoyl	19, 21
p, *p*′-Dihydroxybenzophenone	sebacoyl	19
	2, 2-diphenylpropane-*p*, *p*′-dicarbonyl	21
p, *p*′-Dihydroxydiphenyl sulphone	isophthaloyl	19
	sulphonyl-*p*, *p*′-dibenzoyl	19, 21
2, 2-Bis(*p*-hydroxyphenyl)butane	isophthaloyl	21
2, 2-Bis(*p*-hydroxyphenyl)butane	phenoxybenzene-*p*, *p*′-dicarbonyl	21
	fumaroyl	21
3, 3-Bis(*p*-hydroxyphenyl)pentane	isophthaloyl	21
	terephthaloyl	21
	diphenylmethane-*p*, *p*′-dicarbonyl	21
	phenoxybenzene-*p*, *p*′-dicarbonyl	21
1, 1-Bis(*p*-hydroxyphenyl)ethane	phenoxybenzene-*p*, *p*′-dicarbonyl	21
Phenylbis(*p*-hydroxyphenyl)methane	terephthaloyl	21
	isophthaloyl	21
	phenoxybenzene-*p*, *p*′-dicarbonyl	21
1, 1-Bis(*p*-hydroxyphenyl)-1-phenylethane	isophthaloyl	21
	phenoxybenzene-*p*, *p*′-dicarbonyl	21
Bis(*p*-hydroxyphenyl) diphenylmethane	isophthaloyl	21
1, 1, 1-Tris(chloromethyl)-2, 2-bis(*p*-hydroxyphenyl)ethane	terephthaloyl	21
	isophthaloyl	21
2, 2-Bis(*p*-hydroxyphenyl)-3-methylbutane	isophthaloyl	21
Ethane-1, 2-dithiol	adipoyl	82
	sebacoyl	82
	terephthaloyl	82
	isophthaloyl	
Butane-1, 4-dithiol	adipoyl	82
Pentane-1, 5-dithiol	isophthaloyl	82

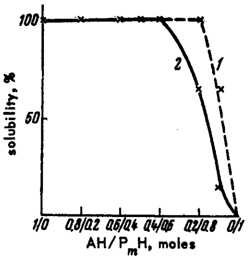


Fig. 21. Dependence of the solubility of mixed polyamides prepared from adipoyl (A) and isophthaloyl (P) chlorides and hexamethylenediamine (H) on the reactant ratio: 1) for polyamides obtained by interfacial polycondensation 2) for polyamides obtained by polycondensation in the melt.^{76}

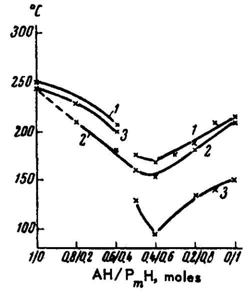


Fig. 22. Dependence of the softening temperature of mixed polyamides on the reactant ratio: 1) for polyamides obtained by polycondensation in the melt; 2) for polyamides obtained by interfacial polycondensation; 3) for polyamides obtained by polycondensation in the melt (without washing out products of low molecular weight).^{76}

8. Mixed Polyesters

Eareckson^{19} prepared a series of mixed polyphenyl esters whose molecular weights were greater than those of the corresponding homopolymers; this is explained by the greater solubility of the mixed polyesters in the organic phase. Examples are provided by the polyesters obtained$^{19,118-120}$ from the following substances: resorcinol plus isophthaloyl and terephthaloyl chlorides; 2,2-bis-(*p*-hydroxyphenyl)propane plus isophthaloyl and fumaroyl, isophthaloyl and oxaloyl, or isophthaloyl and terephthaloyl chlorides; 4-chlororesorcinol plus isophthaloyl and terephthaloyl chlorides; 1,5-dihydroxynaphthalene plus isophthaloyl and terephthaloyl chlorides; 4,4′-dohydroxybenzophenone plus isophthaloyl and terephthaloyl chlorides; etc.

9. Mixed Poly(amide-esters)

The interfacial polycondensation method has also been applied to the preparation of poly(amide-esters).[49] However, no detailed investigation of this class of high polymers was undertaken. The following parent compounds were used[49,121]: hexamethylenediamine + bis(hydroxyphenyl)propane + terephthaloyl chloride; hexamethylenediamine + bis(hydroxyphenyl)propane + sebacoyl chloride; piperazine + bis(hydroxyphenyl)propane + sebacoyl chloride; 2,5-dimethylpiperazine + resorcinol + terephthaloyl chloride; etc.

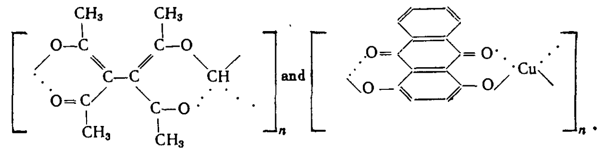
10. Mixed Poly(amide-urethanes)

Mixed poly(amide-urethanes) also can be prepared by interfacial polycondensation. Several polymers of this class have been obtained[49,86,117] by this method from the following starting compounds: piperazine + 1,2-diphenylethane-*p,p'*-dicarbonyl chloride + ethylene bischloroformate; methyl piperazine + terephthaloyl chloride + ethylene bischloroformate; 2,5-dimethylpiperazine + terephthaloyl chloride + ethylene bischloroformate; *trans*-2,5-dimethylpiperazine + terephthaloyl chloride + ethylene bischloroformate; etc.

11. Co-ordination Polymers

Recently the attention of chemists has been attracted to the preparation of co-ordination polymers[121].

Knobloch and Rauscher[123] have shown that interfacial polycondensation can be used to obtain co-ordination polymers from salts of copper and tetraketones of the type:

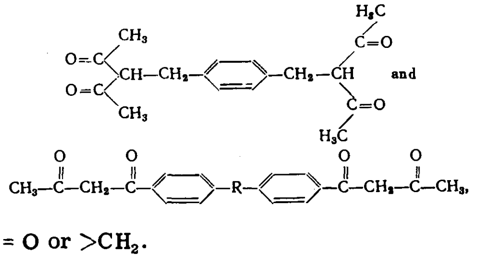


Such polymers have been obtained by mixing an aqueous solution of copper salts and a solution of the ligand in an organic solvent.

The successful preparation of co-ordination polymers requires that the copper should be present in the aqueous phase in the form of unstable ions, *e.g.* $[Cu(NH_3)_4^+]Cl^-$.

Solutions of tetra-acetylethane in methylene chloride and of 1,4-dihydroxyanthraquinone in benzene were taken as the initial ligands. The structure of such polymers was confirmed by chemical analysis and by their infra-red spectra.

Glukhov *et al.*[124] prepared a series of complex polymers containing Be, Mg, Ca, Cu^{II}, Fe^{II}, and Co^{II} from tetraketones having the structure:



where R = O or $>CH_2$.

VII. CONCLUSION

The distinctive feature of interfacial polycondensation is that highly reactive starting materials can be used, and hence the process can be carried out at a low temperature. Polycondensation then takes place as an irreversible process and in this respect differs fundamentally from polycondensations in solution or in a melt (*i.e.* in a homogeneous system) which have been thoroughly investigated.

This feature of interfacial polycondensation brings it close to the processes by which polymers are synthesised in the living cell, where it is possible that this type of synthesis is used. Furthermore, interfacial polycondensation has already opened up several new prospects in polymer synthesis, the most important of which is the possibility of preparing polymers having high melting points, which lie above the temperatures at which the polymers decompose. In addition, this method of synthesis enables the polymer to be obtained in the form of ready-made goods (films, fibres) and thus gives rise to the possibility of "moulding" goods from polymers at the instant they are prepared, in contrast to most known methods, which are based on the manufacture of goods from already finished polymers.

The above features explain the great interest which interfacial polycondensation has aroused among investigators in different countries, who are vigorously developing this process.

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RESERVE GALACTOMANNANS AND GLUCOMANNANS IN SEEDS, BULBS, AND RHIZOMES†

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CONTENTS

I. INTRODUCTION

The great majority of plants contain starch reserves, although *Compositae* and *Gramineae* contain fructose polysaccharides as their main reserve carbohydrate. Other plant reserve polysaccharides have attracted little attention[1-3], but recently heteropolysaccharides, particularly galactomannans and glucomannans, have been studied successfully. The structure of known galactomannans and glucomannans has been further elucidated, and new compounds of this type have been discovered. These polysaccharides are of interest to industry as well as in terms of organic chemistry (in relation to their structure and properties) and comparative, or evolutionary, biochemistry. Some of them are foodstuffs, especially in oriental countries; on account of their high viscosity,

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others are used in the foodstuffs, pharmaceutical, paper, and tobacco industries, etc. Although such use is extensive abroad, especially in the USA, little attention has been paid in the Soviet Union to the extraction and use of these valuable compounds; the rich Soviet flora might well provide the excellent emulsifiers and gums, etc., needed by many industries.

This review considers work done on reserve galactomannans and glucomannans after 1952, earlier work being described in Whistler and Smart's monograph[4]. Industrially important galactomannans, recently reviewed[5-8], are described only shortly here.

II. NATURAL DISTRIBUTION OF GALACTOMANNANS AND GLUCOMANNANS

Appreciable quantities of galactomannans occur in the endosperm of bean seeds (*Leguminosae*), and smaller quantities in the seeds of palms (*Palmaceae*) and madder (*Rubiaceae*)[4]. Glucomannans have long been known as reserve polysaccharides in the tubers of different species of *Amorphophallus* (*Araceae*)[1], and in some orchids (*Orchidaceae*)[9,10]; they have recently been extracted from the bulbs of some lilies (*Liliaceae*) and from iris seeds (*Iridaceae*) (Tables 1 and 2, pp. 273 and 275). The heteropolysaccharides sometimes occur together with starch, as in lily bulbs, or they may appear as the sole reserve polysaccharide (*e.g.*, eremuran). They occur to varying extents, but some plants are very rich in them; about 35% of the seeds is composed of the galactomannans guaran and caroban, and the content of the glucomannan eremuran may be 30% of the dry weight of the rhizomes.

On account of insufficient study, the distribution of galactomannans and glucomannans is probably much wider than is now apparent. Some older data based on the separation of these heteropolysaccharides[9,10] should be checked, however, since inadequate procedures leave open the possibility that mixtures of homopolysaccharides, separable only with difficulty, were in fact obtained.

III. EXTRACTION AND PURIFICATION

Extraction with cold water or alkali, and precipitation with ethanol of varying concentration, is used to separate galacto- and gluco-mannans in dependence on solubilities. Monosaccharides and amino-acids are sometimes extracted first with methanol, the raw material then being dried. Galactomannans and glucomannans have for many years been purified through precipitation of their sparingly soluble copper complexes, formed when Fehling's solution is added to the polysaccharide solution, on account of the *cis*-hydroxyl group in the mannose residues. Special investigation showed that galactans, accompanying galactomannans in *Nux vomica*, remain in solution on such treatment[11]; it is hard to say whether such separation is generally complete. Fractionation of the polysaccharides of hemicellulose by means of barium hydroxide was recently proposed[12]; this forms complexes with galactomannans and glucomannans, apparently on account of the *cis*-hydroxyl groups therein. These complexes are soluble in dilute acids and water, but not in organic solvents or the cupric ethylenediamine complex. The separation of polysaccharides by means of Cetavlon‡ (cetyltrimethylammonium bromide) seems to be of great promise[13]; Barker and coworkers suggest that precipitation is due to interaction between Cetavlon and the borate complexes formed by the *cis*-hydroxyl groups of the mannose residues in mannans and galactomannans.

Although electrophoresis of neutral polysaccharides§ is described in the literature[14], this method has been used only recently for purifying and fractionating galactomannans and glucomannans; the electrophoresis of polysaccharides on fibreglass paper in an alkaline medium is of great interest[15]. The authors consider fibreglass paper to have an advantage over cellulose paper in that no complexes are formed between glass fibres and polysaccharides, so that the localisation of all types of the latter is facilitated. The great majority of the polysaccharides examined were heterogeneous; two components were found in the galactomannans in particular (guaran and another), while glucomannans such as konjac mannan and Iles mannan also appeared to be heterogeneous. Electrophoresis was conducted in a borate buffer (pH 9–10) or in 2 *N* NaOH or KOH solution, so that association of polysaccharide molecules was minimised. The movement of polymeric carbohydrates on glass paper apparently depends on the ionisation of hydroxyl groups under the influence of the alkaline electrolyte. It is difficult to evaluate such a separation briefly; unless some sort of artefact arises, such as an alkali-induced transformation, the indications produced of the heterogeneity of a series of polysaccharides will compel us to modify our concepts of their structure.

IV. PROPERTIES

Individual properties appear in Tables 1 and 2 and in the descriptions below of particular galactomannans and glucomannans; the following is only a general survey.

Solubility. Most galactomannans and glucomannans are soluble in cold or hot water or alkaline solutions, but a few have to be dissolved in concentrated sodium xylenesulphonate solution. Alkali, as in Fehling's solution used for purification, often induces loss of solubility. Solutions yield gels, or coagulate, on the addition of boric acid or salts of heavy metals[4]; a solution of konjac mannan coagulates on the addition of Congo red, and cools to a gel after being heated on the water-bath with this dye[16].

Viscosity. The high viscosity of solutions of some of these polysaccharides has been much studied recently, being the basis of their industrial use. Thus, the viscosity of guar sols is more than doubled on reaction with formaldehyde[17]; the viscosity of the gum from guar and acacia beans has been compared with that of other gums[18,19]; and

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‡ On treatment of a mixture of 250 mg mannan and 250 mg glycogen with equal volumes of 10% Cetavlon solution and 1% borate buffer (pH 8.5), 204 mg of mannan separated, yielding only mannose on hydrolysis.

§ In 0.05 M borate buffer in Tiselius' apparatus, one of two components of yeast mannan had an electrophoretic mobility of 8.8×10^{-5} cm^2 V sec^{-1}, and the mannan A of stone walnut, 5.6×10^{-5} cm^2 V sec^{-1}. Electrophoresis of the glucomannan eremuran was carried out in Tiselius' apparatus under the same conditions, in our laboratory (p. 277).

the viscosity and elasticity of konjac mannan gels after thermal treatment has been studied[20-22]. The viscosity of gums of the mannan type is lowered more than six times by boiling with aqueous hydrogen peroxide containing 50–90% of a lower aliphatic alcohol such as butanol or methanol, and a small quantity of sodium carbonate[23].

Infra-red absorption. Galactomannans and glucomannans have been studied little in this respect. Of the infra-red spectra of water-soluble gums, only those of acacia bean and guar flour gums have been obtained[24]. The infra-red spectrum of a glucomannan, of unspecified source, was described by Barker[25]. The author of the present article used infra-red spectroscopy in the study of the glucomannan eremuran, whereby fractions were identified and the presence of mannose and β-glycoside links was established (p.277).

Reaction with iodine. Indications appear in the literature that most galactomannans and glucomannans give no colour with iodine, but they are sometimes less positive, *e.g.* "the polysaccharide does not give a blue colour with iodine" (p.275). A glucomannan isolated by us, eremuran, gave a red-brown colour with iodine, showing beyond doubt that it was a heteropolysaccharide (p.277). Recently, the mechanism of the reaction between polysaccharides of the amylose type and iodine, involving a spiral structure, has become much clearer, but little is known yet with regard to branched polysaccharides, especially those having other than α-1,4-links. Earlier we established successfully a dependence of the iodine reaction on molecular weight, for a given degree of branching, for synthetic glycogens[26] and amylopectins[27]. Detailed study of the structures of some of the polysaccharides mentioned below may be a new basis for elucidation of the iodine reaction.

V. STRUCTURE

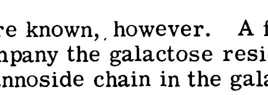
To elucidate the structures of galactomannans and glucomannans the usual polysaccharide methods are used; these give unusual results in only a few cases, where the configurational similarity of glucose and mannose epimers is involved.

Hydrolysis to the structural components is usually effected with sulphuric acid, or sometimes with formic acid; the resulting formic esters are then hydrolysed. The components are identified by paper chromatography (using as solvents butanol–ethanol–water, ethyl acetate–acetic acid–water, butanol–pyridine–water; etc.) or by means of crystalline derivatives such as mucic acid, mannose phenylhydrazone, and the glucoside of *p*-nitroaniline. Cellulose is normally used as adsorbent for the column chromatography of hydrolysates. The possible epimerisation of mannose and glucose must be borne in mind during analysis, especially if the latter is quantitative[28,29]. Polysaccharides methylated, as a rule, by repeated treatment with dimethyl sulphate and alkali, and then with methyl iodide, have recently been more uniformly fractionated by means of chloroform and hexane. Cleavage of the methylated polysaccharides is usually effected by methanolysis (2–5% HCl) and subsequent hydrolysis of the glycosides, or, less often, by hydrolysis with formic acid and subsequent hydrolysis of the esters. The methylated sugars are separated by paper chromatography in solvents such as butanol–ethanol–water or benzene–ethanol–water, or by chromatography on columns of cellulose and/or hydrocellulose in benzene–ethanol or butanol–ethanol–water. Corresponding methyl derivatives of glucose and mannose cannot usually be separated by chromatography; they are usually demethylated with hydrobromic acid, the free glucose and mannose being separated by chromatography or by paper electrophoresis[30,31], or as crystalline derivatives directly from their mixture. Thus, 2,3,6-tri-*O*-methylglucose crystallised from a trimethylhexose fraction after seeding, and after oxidation the mother-liquor yielded the phenylhydrazide of tri-*O*-methylmannonolactone. Estimations in such cases are based on optical activity. Alternatively, the whole of the mixture might be oxidised and the lactones separated by chromatography and converted to crystalline derivatives such as 2,3,6-tri-*O*-methylmannonamide[32]. Rebers and Smith[33] proposed a most interesting method involving the treatment of 2,3,6-tri-*O*-methylated mannose and glucose with cold methanolic hydrogen chloride; methyl 2,3,6-tri-*O*-methylglucofuranoside readily forms, and moves rapidly on the chromatogram. The planarity of the furanoside ring makes the conditions very unfavourable for formation of methyl 2,3,6-tri-*O*-methylmannofuranoside, with *cis*-methoxy groups at $C_{(2)}$ and $C_{(3)}$. According to Wickberg[34], methylated mannoses and glucoses may be separated by chromatography after acetylation of the free hydroxyl groups. Methylated sugars are usually estimated with hypoiodite. Data obtained by means of methylation are often verified by means of periodate oxidation, but continuous formation of formic acid is sometimes observed, and this method becomes invalid. Recently more study has been made of polyaldehydes, formed on the periodate oxidation of polysaccharides, and also of the polyalcohols which they yield on sodium borohydride reduction.

Optical activity and its modification by hydrolysis indicates the nature of α- and β-glycosidic links; infra-red spectra and enzymatic methods have found little application as yet in the study of glycosidic links in galactomannans and glucomannans.

Partial hydrolysis of polysaccharides, for the separation and identification of oligosaccharides, is usually effected by acetolysis after conditions have been established which give the maximum yield. Oligosaccharides are usually separated on carbon–Celite and cellulose columns. Control experiments are conducted to ensure that oligosaccharides have not formed by a partial reversion process during the hydrolysis of the polysaccharides.

Despite the widely differing galactose : mannose ratios, nearly all the galactomannans studied hitherto have much in common structurally; to a chain of mannopyranoside residues, with mainly glycosidic β-1,4-linkages, galactose residues are joined as end-groups, apparently mainly by α-glycosidic linkages[¶]:



$$-\Big[-4\ \overset{\substack{\text{Gal}p\\1\\|\\6}}{\text{Man}p}\ 1\Big]_x-[4\ \ \text{Man}p\ \ 1]_y-\tag{1}$$

Some exceptions are known, however. A few glucose end-groups may accompany the galactose residues as branches of the main polymannoside chain in the galactomannan of Kentucky coffee beans (p.274).

Glucomannans have been studied much less than galactomannans; oligosaccharides from particularly few polysaccharides have been separated and examined. The best

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[¶] p = pyranoside residue.

studied glucomannan from *Amorphophallus oncophillus* contains an unbranched chain of glucopyranoside and mannopyranoside residues, bonded mainly by β-1,4-glycoside linkages; the glucose residues are in groups of two or more (p.275), as apparently are the mannose residues. All the other glucomannans studied appear to be branched to varying extents; many β-1,4-glycoside linkages are found in most of them. The end-groups are mainly glucose residues in some glucomannans (lily bulbs, p.276), mainly mannose residues in others (*Licoris radiata* bulbs, p.276), and a combination of these in others (*Amorphophallus konjac*, p.275).

VI. INDIVIDUAL COMPOUNDS

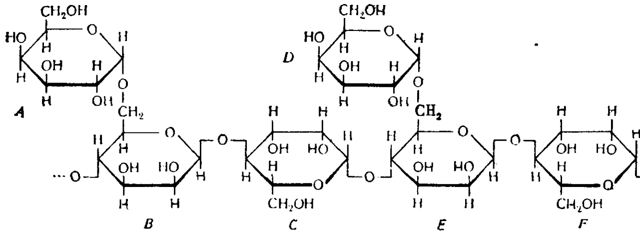
A. Galactomannans (Table 1)

1. **Guaran**; this, one of the best studied galactomannans, constitutes about 35% of the endosperm of seeds of *Cyamopsis tetragonolobus* (*Leguminosae*), and is one of the most important industrial gums on account of its high viscosity[4]. It contains galactose and mannose in the ratio 1 : 2, the extent of branching in the molecule is indicated by the large quantity of formic acid formed on periodate oxidation. Tosylation confirms this result and indicates the presence of 1,6-branches. Investigation of the strength of guaran triacetate films, and X-ray examination of films of dry guaran, show the side-chains to be very short. The hydrolysis of trimethylguaran yielded equimolecular quantities of 2,3,4,6-tetra-*O*-methylgalactose, 2,3,6-tri-*O*-methylmannose, and 2,3-di-*O*-methylmannose. Soon after 1950 it was concluded from these data that guaran contained a polymannoside backbone with 1,4-linkages, a galactose residue being connected by a 1,6-linkage to every other mannose residue, on the average:

TABLE 1. Galactomannans.*

Source			Name	$[\alpha]_D$	Galactose: mannose ratio	$[\alpha]_D$ of methylated derivative	References
family	species	part of plant					
1 *Leguminosae*	*Cyamopsis tetragonolobus* (guar)	seeds	guaran	+53° (NaOH solution)	1 : 2	+42° (chloroform)	36,37,38
2 »	*Ceratonia silique*	»	caroban		1 : 3—4 (impure)		4
3 »	*Trigonella foenum graecum* (fenugreek)	»		+70°±10° (water)	5 : 6		11,39,40
4 »	Lucerne (var. *provensa*)	»		+118°±11° (water)	4 : 5	+ 66° ± 3° (chloroform)	41,40
5 »	*Trifolium pratense*	»		+78°±11° (water)	7 : 9	+ 76° ± 2° (chloroform)	41
6 »	*Gymnocladus dioica* (Kentucky coffee bean)	»		+ 29° (water)	1 : 4	0° (acetone)	43
7 »	*Glicina hispida*	bean husks		+63° (water)	2 : 3	+58°	44
8 *Palmaceae*	*Borassus flabillijer L.*	seeds of fruit		—	1 : 2.83		45

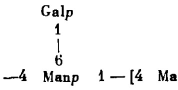
* All the galactomannans were purified by means of copper complexes except 6, which was purified by means of the acetyl derivative.



(II)

This structure was confirmed by partial acid and enzymatic hydrolyses, with subsequent separation of oligosaccharides and determination of their structure. Firstly, disaccharides were isolated: 4-*O*-β-D-mannosyl-D-mannose, apparently from the units *BC*(*EF*) or *CE*[35], and 6-*O*-α-D-galactopyranosyl-D-mannopyranose, apparently from *AB* and *DE*[36]. Trisaccharides were later also isolated; enzymatic hydrolysis of guaran† gave 65% of monosaccharide product and 7.5% of a crystalline mannotriose, *O*-β-D-mannopyranosyl-(1 → 4)-*O*-β-D-mannopyranosyl-(1 → 4)-*O*-β-D-mannopyranose[37], probably from units *BCE* or *CEF*. The structure of the triose was established by means of periodate oxidation, by partial hydrolysis to mannose and mannobiose, and by reduction to glycitol and acetylation. Finally, partial acid hydrolysis of guaran gave a 13.1% yield of a new crystalline trisaccharide, *O*-α-D-galactopyranosyl-(1 → 6)-*O*-β-D-mannopyranosyl-(1 → 4)-D-mannopyranose, from *ABC* and *DEF*; the structure of this has been demonstrated[38]. The fragment *CED*, while theoretically possible, has not yet been isolated, but the data given adequately confirm the above formula (I). As with the structure of other carbohydrate polymers, it must be asked to what extent the proposed formula, based on mean results for many molecules, represents the structure of the single molecule with respect to the regularity of branching. Study of the mechanism of this polysaccharide's biosynthesis may clarify this problem. The molecular weight of guaran triacetate is 220 000 (osmometer)[4].

2. **Caroban**; this, the galactomannan of acacia beans, *Ceratonia siliqua* (*Leguminosae*), constitutes about 88% of commercial gum, of which the beans contain about 35%. Commercial locust bean gum, known also as pigs' bread, etc., is of wide industrial application in countries such as the USA. Reports of the galactose : mannose ratio differ from 27 : 73 to 14 : 86.[4] Hydrolysis of fully methylated caroban yielded 2,3,4,6-tetra-*O*-methylgalactose (1 mole), 2,3,6-tri-*O*-methylmannose (between 2 and 4 moles reported), and 2,3-di-*O*-methylmannose (1 mole)[4]. These data, and those from periodate oxidation, indicate that caroban is a polymannoside, like guaran, but with few galactose residue side-chains:



$$\begin{array}{l}\qquad\ \ \text{Gal}p\\ \qquad\quad\ 1\\ \qquad\quad\ |\\ \qquad\quad\ 6\\ -4\ \ \text{Man}p\ \ 1-[4\ \ \text{Man}p\ \ 1]_{3\ \text{or}\ 4}\end{array}$$

The molecular weight of caroban is 310 000.[4]

3. **The galactomannan from fenugreek seeds** (*Trigonella foenum graecum*), extracted in 1932 by Daoud[39], was recently examined carefully by Andrews and co-workers[11]. The galactomannan, comprising 13.6—15% of

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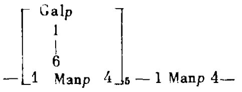
† The fraction of the enzyme from germinating guar seeds was used which was precipitated by 20—30% ammonium sulphate solution.

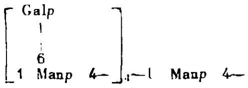
these seeds, was extracted with cold water and purified by means of the copper complex. Crystalline galactose and mannose were obtained in the ratio 5 : 6. Hydrolysis after complete methylation yielded 2, 3, 4, 6-tetra-*O*-methylgalactose, 2, 3-di-*O*-methylmannose, and 2, 3, 6-tri-*O*-methylmannose in the ratio 5 : 5 : 1. The tetra-*O*-methylgalactose was identified chromatographically and also characterised as the anilide; the methylmannoses were characterised, after oxidation with bromine water, as the crystalline lactones and as the hydrazides of the corresponding acids. Periodate oxidation confirmed these results, the yield of formic acid indicating 43.6% of end-residues (methylation gave 43.3%). This galactomannan is therefore similar in general structure to guaran and caroban, having a polymannoside chain with 1, 4-links, to the $C_{(6)}$ atoms of which galactose residues are connected through $C_{(1)}$, forming short side-chains or end-groups. The difference from guaran lies in the greater degree of branching and the greater content of galactose end-groups. A possible structure is:



$$-\left[\begin{array}{c}\text{Gal}p\\ 1\\ |\\ 6\\ 1\ \ \text{Man}p\ \ 4\end{array}\right]_5-1\ \text{Man}p\ 4-$$

supported[40] by the partial acid hydrolysis of the compound to the following oligosaccharides. (*a*) 4-*O*-β-D-mannopyranosyl-D-mannose, (*b*) 6-*O*-α-D-galactopyranosyl-D-mannose, and (*c*) the mannotriose *O*-β-D-mannopyranosyl-(1 → 4)-*O*-β-D-mannopyranosyl-(1 → 4)-D-mannose.

4. The galactomannan from lucerne seeds (*Provensa*) was obtained in a yield of about 5.5% by extraction with hot water[41], and purified by means of the copper complex. Its aqueous solution gives no colour with iodine. Galactose and mannose are contained in the ratio 4 : 5. Methylation and hydrolysis yielded 2, 3, 4, 6-tetra-*O*-methylgalactose, 2, 3, 6-tri-*O*-methylmannose, and 2, 3-di-*O*-methylmannose in the ratio 4 : 1 : 4, the methylated sugars being separated on a hydrocellulose column and identified as crystalline derivatives. The extent of branching is very large, almost every residue in the polymannoside chain having a gelactose residue as a branch from $C_{(6)}$. Periodate oxidation indicated 43.7% galactose end-residues (methylation gave 44.2%). About 10% of unchanged mannose was found in the hydrolysate of the galactomannan after "complete" periodate oxidation, indicating that in a highly branched structure periodate has less easy access to the mannose residues, and oxidation of these at $C_{(2)}$ and $C_{(3)}$ is slower. More prolonged attack of an excess of $NaIO_4$ at pH 7 oxidised the mannose fully, the resultant data then agreeing exactly with those obtained by methylation. A possible structure for this compound is:



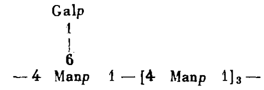
$$\left[\begin{array}{c}\text{Gal}p\\ 1\\ |\\ 6\\ 1\ \ \text{Man}p\ \ 4-\end{array}\right]_4-1\ \ \text{Man}p\ \ 4-$$

Recent partial acid hydrolysis of this compound yielded the crystalline oligosaccharides: 4-*O*-β-D-mannopyranosyl-D-mannose, 6-*O*-α-galactopyranosyl-D-mannose, and *O*-β-D-mannopyranosyl-(1 → 4)-*O*-β-D-mannopyranosyl-(1 → 4)-D-mannose. This supports the above structure and refines our conception of the character of glycosidic bonds[40].

In 1947 extraction of another lucerne (*Medicago sativa*) with hot 10% NaOH solution yielded a galactomannan with a unique high galactose content, twice as large as its mannose content[42]. Data from methylation implied that half the galactose constitutes all the end-residues and the rest enters with the mannose into the backbone. However, the compound was later shown to be a polysaccharide mixture, largely composed of a galactomannan similar in structure to guaran[42a].

5. The galactomannan from clover seeds (*Trifolium pratense*), extracted with hot water and purified by means of the copper complex, is very similar to that from lucerne (*Provensa*)[41]. The galactose : mannose ratio is 7 : 9. Methylation and hydrolysis yields 2, 3, 4, 6-tetra-*O*-methyl-D-galactose, 2, 3, 6-tri-*O*-methyl-D-mannose, and 2, 3-di-*O*-methyl-D-mannose in the ratio 7 : 2 : 7. Thus, as with the *Provensa* galactomannan, almost every residue in the polymannoside chain bears a galactose residue branch, bonded by a 1, 6-link. No oligosaccharides were obtained from this compound.

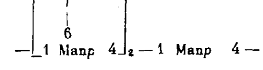
6. The galactomannan from Kentucky coffee bean seeds (*Gymnocladus dioica*) was extracted with alkali and purified as the acetate[43]. Viscous solutions of the compound give precipitates with Fehling's solution, and gels with small amounts of borax. Galactose and mannose, identified as the methylphenylhydrazone and the phenylhydrazone respectively, are contained in the ratio 1 : 4. Methylation and hydrolysis yields 2, 3, 4, 6-tetra-*O*-methyl-D-galactose (1 mole), 2, 3, 6-tri-*O*-methyl-D-mannose (3 moles), 2, 3-di-*O*-methylmannose (1 mole), and 3.3% 2, 3, 4, 6-tetra-*O*-methylmannose. A possible unit for the main part of this compound is:



$$\begin{array}{l}\qquad\ \ \text{Gal}p\\ \qquad\quad\ 1\\ \qquad\quad\ |\\ \qquad\quad\ 6\\ -4\ \ \text{Man}p\ \ 1-[4\ \ \text{Man}p\ \ 1]_3-\end{array}$$

The 2, 3, 4, 6-tetra-*O*-methylmannose may arise from the end-residue of the polymannoside chain, but its percentage would then imply a chain of about 30 residues, and therefore reducing properties, which are not in fact observed. It is therefore more likely that on the average one mannose end-group per thirty hexose residues accompanies the galactose end-groups. Periodate oxidation supports this, one molecule of formic acid appearing per five hexose residues with the adsorption of 6 moles of periodate.

7. The galactomannan from soya-bean husks; the husks, after extraction with acetone, are then extracted with water at 40°. The product obtained in 2% yield is purified as the copper complex[44]. Crystalline galactose and mannose are obtained in the ratio 2 : 3, (compare 1 : 2 in purified guaran, 2 : 3 in impure guaran). 2, 3, 4, 6-tetra-*O*-methylgalactose, 2, 3, 6-tri-*O*-methylmannose, and 2, 3, -di-*O*-methylmannose are obtained from the methylated compound in the ratio 2 : 1 : 2. These data imply a polymannoside backbone as in guaran and other galactomannans, with two 1, 6-linked galactose branches to every three 1, 4-linked mannose residues, on the average:



$$-\left[\begin{array}{c}\text{Gal}p\\ 1\\ |\\ 6\\ 1\ \ \text{Man}p\ \ 4\end{array}\right]_2-1\ \ \text{Man}p\ \ 4-$$

Such a structure should need 1.4 moles periodate per anhydrohexose unit, to give 0.4 mole formic acid; the actual quantities are 1.2 moles and 0.37 mole. The authors suggest the presence of β-links in the polymannoside chain, and the α-configuration of the galactose residues. The polysaccharide has a molecular weight of 32 000, much lower than that of guaran.

8. **The galactomannan from palm-fruit kernels** (*Borassus flabellijer* L.) was obtained[45] by extraction with hot 10% NaOH solution after the raw material had been dehydrated, treated with 80% alcohol to remove free sugars, and dried. The polysaccharide, purified by means of its copper complex, was hydrolysed; the galactose and mannose, produced in the ratio 1 : 2.83, were identified chromatographically and by conversion into mucic acid and a phenylhydrazone respectively. The structure of the polysaccharide was not investigated.

Glucomannans from *Amorphophallus* species of the *Araceae* family are the best known, but there is not yet sufficient proof that they are not mixtures of homopolysaccharides.

B. Glucomannans (Table 2)

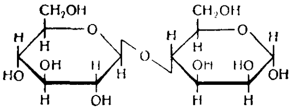
1. **The glucomannan from tubers of** ***Amorphophallus oncophillus***, plants growing in Indonesia, etc.; flour containing about 40% by dry weight of polysaccharides is prepared from these tubers. It was shown in 1954 that Iles mannan, extracted from these tubers, is a mixture of a glucomannan and a polyglucosan, resembling amylose, in a ratio of about 6 : 1.[33] On account of the low solubility of the glucomannan in water and NaOH solution, it was dissolved in 50% sodium xylenesulphonate solution; the resultant gel dissolved in 30% aqueous NaOH to give a solution stable to dilution and to neutralisation with acetic acid. The glucomannan may be fractionally precipitated from the diluted alkaline solution with Fehling's solution, the polyglucosan remaining dissolved. The glucomannan thus obtained is stable in aqueous solution, but polysaccharide is deposited on boiling; it gives no blue colour with iodine. A more complete separation of the polysaccharides was effected by methylation and subsequent repeated recrystallisation from ethanol or acetone; as the solvent cooled, the solid separating was richer than the solution in the methylated glucomannan. Hydrolysis of the latter was slow, indicating the pyranoside nature of the hexose residues, and gave a mixture of 2,3,6-tri-*O*-methylglucose and 2,3,6-tri-*O*-methylmannose, inseparable by chromatography. The ready conversion of the glucose derivative to the methyl glucofuranoside afforded a separation, since the non-reducing methyl 2,3,6-tri-*O*-methylglucofuranoside moved faster on a hydrocellulose–cellulose column than did the 2,3,6-tri-*O*-methylmannose mixed with it. Both trimethylhexoses were identified by means of their rotatory power and the formation of crystalline di-*p*-nitrobenzoates. The 2,3,6-tri-*O*-methylglucose : 2,3,6-tri-*O*-methylmannose ratio, and hence the ratio of the free sugars in the hydrolysate, was 1 : 2. The absence of di- and tetra-methylhexoses shows this glucomannan to be an unbranched chain with 1,4-glycoside links; the increased rotation on hydrolysis indicates the predominance of β-glycoside links. The following structures are therefore possible:

$$-[1\beta\text{D}\ \ \text{Man}p\ \ 4-1\beta\text{D}\ \ \text{Man}p\ \ 4-1\beta\text{D}\ \ \text{G}p\ \ 4]_n- \qquad \text{(A)}$$

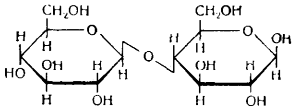
$$-[1\beta\text{D}\ \ \text{G}p\ \ 4-]_2-[1\beta\text{D}\ \ \text{Man}p\ \ 4]_4 \qquad \text{(B)}$$

$$-[1\beta\text{D}\ \ \text{G}p\ \ 4-1\beta\text{D}\ \ \text{Man}p\ \ 4]_2-[1\beta\text{D}\ \ \text{Man}p\ \ 4]_2 \qquad \text{(C)}$$

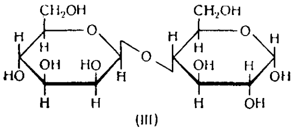
Recently, acetolysis of the glucomannan under special conditions‡ gave a mixture from which three crystalline disaccharides were separated[46]: (1) 4-*O*-β-D-glucopyranosyl-*O*-α-D-mannopyranose (I, below), identified by means of its physical constants, by oxidation with bromine water and hydrolysis to glucose and mannonic acid, and by conversion to an octa-acetate; (2) cellobiose (II, below), identified by means of its physical constants, by conversion to an octa-acetate, and by the action of β-glucosidase to give glucose alone; and (3) 4-*O*-β-D-mannopyranosyl-*O*-α-D-glucopyranose (III, below). The structure of the last new disaccharide was partly established by oxidation with bromine and hydrolysis, to give mannose and gluconic acid, and by methylation and hydrolysis to give 2,3,4,6-tetra-*O*-methylmannose and 2,3,6-tri-*O*-methylglucose:



(I)



(II)



(III)

If the units represented by (I)–(III) above are repeated regularly, then these results force us to reject (A) and (C) (since cellobiose was obtained) in favour of (B), replication of which makes production of all three disaccharides possible. (B) should, however, give rise to mannobiose and mannotriose, which have not yet been found. The authors assume the links between mannose units to be broken more readily than the others on acetolysis. (B) may be accepted, or other structures sought, on the results of searches for other oligosaccharides in acetolysis and hydrolysis products.

2. **The glucomannan from tubers of** ***Amorphophallus konjac*** (or *Conophallus konjac* **Schott**), known for

TABLE 2. Glucomannans.*

Source			Name	$[\alpha]_D$	Glucose: mannose ratio	$[\alpha]_D$ of methylated derivative	References
family	species	part of plant					
Araceae	*Amorphophallus oncophillus*	tubers		—21.3° (water)	1 : 2	—41° (chloroform)	33,46
»	*Amorphophallus konjac*	»	konjac mannan	—38° (water)	2 : 3	—19° (chloroform)	4,49,50
Liliaceae	*Lilium candidum*	bulbs	—	—26°	1 : 1.83	—	32
»	*L. henrii*	»	—	—21°	1 : 1.93	—23°	32
»	*L. umbellatum*	»	—	—25°	1 : 2.00	—20°	32
Amarillidaceae	*Licoris radiata*	»	khiganbana mannau	—	1 : 4	–30.46° (chloroform)	52,53
Liliaceae	*Eremurus regelii*	rhizomes	eremuran	–30°±2° (0.1 *N* NaOH)	1 : 2	–37°±6° (water)	54–57
Iridaceae	*Iris ochroleuca*	seeds	—	–25°±2° (2 *N* NaOH)	1 : 1**	—9° (chloroform)	58
»	*I. sibirica*	»	—	–26°±3° (2 *N* NaOH)	1 : 1**	—11.1° (chloroform)	58

* All the glucomannans were purified by means of copper complexes.

** These polysaccharides contained 97% and 98% of (glucose + + mannose) and 1–2% of galactose (p. 277).

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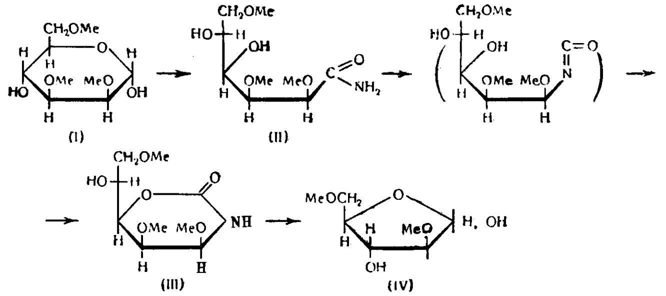
‡ Under these conditions a 30% yield of oligosaccharides was obtained.

many years as "konjac mannan"; this is the main polysaccharide in "konjac flour", prepared from the macerated, dried, and ground tubers[4] and widely used for food in Japan and other countries. The polysaccharide may be extracted with water[4] at 1.5 atm. Preliminary study, mainly by Japanese workers, showed the glucose : mannose ratio in konjac mannan to be 1 : 2, although it may vary. The action of spore-bearing bacteria from "konjac flour" on the mannan yielded the polysaccharide levidulin, consisting of one glucose to two mannose residues[47]. A similar or identical trisaccharide, named levidulinose, was obtained by the action of Taka-diastase[48], and the acetolysis of konjac mannan yielded a similar trisaccharide[49]. For none of these trisaccharides was a structure established. Hydrolysis of methylated konjac mannan yielded 2,3,4-tri-*O*-methylglucose, 2,3,4-tri-*O*-methylmannose, and 2,3,6-tri-*O*-methylmannose; on this basis a structure was suggested involving an unbranched chain with a predominance of 1,6-links[49].

Recent studies[50] have utilised hitherto inaccessible techniques. Hydrolysis of the polysaccharide, purified by means of the copper complex, gave glucose and mannose in the ratio 2 : 3[§]. Methanolysis and hydrolysis of the fully methylated glucomannan yielded 2,3,4,6-tetra-*O*-methylglucose, 2,3,4,6-tetra-*O*-methylmannose, 2,3,6-tri-*O*-methylglucose, 2,3,6-tri-*O*-methylmannose, 2,6-di-*O*-methylglucose, and, apparently, 2,6-di-*O*-methylmannose. The ratio, tetra- : tri- : di-methylhexose was 1 : 11 : 1, indicating a mean chain length of approximately 13; the ratio tetramethylglucose : tetramethylmannose was 2 : 3, in agreement with the ratio of the free sugars in the hydrolysate of the initial polysaccharide. The tetramethylhexoses were not separable, but after demethylation with hydrobromic acid the free sugars were easily separated by chromatography and electrophoresis on paper. The trimethylhexoses and dimethylglucose were identified by means of the di-*p*-nitrobenzoates and the trinitrobenzoate respectively.

These data are not in accordance with the structure based on earlier work by Nishida[49]; the polysaccaride is branched, not linear, with mannose as well as glucose residues as end-residues; 1,4-glycoside links, not 1,6-links, predominate in the backbone; the low rotatory power of konjac mannan and its methylated derivative imply that they are β-links. This new structure, based on methylation studies, is supported by: (1) data from periodate oxidation; the chain length was found to be 11, some hexose residues at the branching point being unoxidised; and (2) study of hydrolysis products from the polyalcohol, obtained by sodium borohydride reduction of the polyaldehyde to which konjac mannan is oxidised by periodate. The ratio of glycerol, formed from end-residues, to erythritol, formed from hexose residues between branching points, was 1 : 15.

3. The glucomannan from lily bulbs, comes from three types[32]: *Lilium candidum*, *L.henrii*, and *L.umbellatum*; macerated bulbs were treated with methanol to remove mono- and oligosaccharides and amino-acids, dried, and ground. The glucomannans were extracted with cold water, and precipitated and reprecipitated with alcohol. The yields, based on the dry weight of the bulbs, were 14% from *L.candidum*, 20% from *L.henrii*, and 5% from *L.umbellatum*. After purification by means of the copper complex, the glucomannans were insoluble in water, but soluble in sodium hydroxide solution and formic acid; they gave no colour with iodine. Hydrolysis of all three polysaccharides give glucose and mannose in the approximate ratio 1 : 2. Exhaustive methylation of the polysaccharides from *L.umbellatum* and *L.henrii* gave yields of 56% and 34% respectively of the methylated derivatives. Methanolysis of the trimethylglucomannans and hydrolysis of the glycosides formed gave mainly trimethylhexoses and very small amounts of tetra- and dimethylhexoses. The trimethylhexoses were not separable by chromatography, but from its rotation the mixture appeared to contain 2,3,6-tri-*O*-methyl derivatives of glucose and mannose in the ratio 1 : 2. Separation was achieved by oxidation to the corresponding lactones, which were separated on cellulose and converted to crystalline derivatives. Thus, 2,3,6-tri-*O*-methylmannose (I, below) was characterised as the crystalline 2,3,6-tri-*O*-methylmannonamide (II), which hypochlorite cleaved to a crystalline derivative of the cyclic ureide (III). Later hydrolysis gave 2,5-di-*O*-methylarabinose (IV).



On methylation, the glucomannan from *L.umbellatum* yielded 3.7% of tetramethylhexoses, that from *L.henrii* yielded 1.3%. The tetramethylhexose fraction appeared to be mainly 2,3,4,6-tetra-*O*-methylglucose, identified in particular in the crystalline form and by convertion to crystalline *N*-phenyl-D-glucopyranosylamine tetramethyl ether. It must be borne in mind that after demethylation of the tetramethylhexoses a trace of mannose was detected chromatographically together with the glucose.

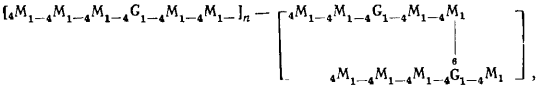
The dimethylhexose from the trimethylglucomannan of *L.umbellatum* was mainly 2,4-di-*O*-methylglucose; that from *L.henrii* was a mixture of glucose and mannose derivatives, but the quantities obtained of these were too small for exact characterisation. These data show the glucomannans of *L.umbellatum* and *L.henrii* to be fairly similar; the slightly branched chains of each are composed of glucopyranosyl and mannopyranosyl residues in the ratio 1 : 2, joined by β-1,4-glycoside links. The non-reducing end-residues are mainly of glucose. The branching-points in the glucomannan from *L.umbellatum* are apparently glucose residues linked at $C_{(1)}$, $C_{(3)}$, and $C_{(6)}$. The mean chain length of the glucomannan from *L.umbellatum* is 27 hexose units; for that from *L.henrii*, it is 75 hexose units.

Periodate oxidation was fruitless on account of the continuous production of formic acid.

4. The glucomannan from *Licoris radiata* bulbs; this, also called "Khiganbana mannan" from the Japanese name for the plant, was isolated and examined by Hayashi and coworkers[52]. Water extraction and purification by means of the copper complex gave a yield of about 2% of pure product, based on the dry weight of the bulbs. Acid hydrolysis[52] gave glucose and mannose in the ratio 1 : 4.

[§] Thus, indications of glucuronic acid in konjac mannan were not confirmed[51].

Methylation and hydrolysis gave 2,3,6-tri-*O*-methylmannose (66.2%), 2,3,6-tri-*O*-methylglucose (13.9%), 2,3,4,6-tetra-*O*-methylmannose (11.3%), and 2,3-di-*O*-methylglucose (8.6%). Partial hydrolysis yielded mannobiose, mannotriose, glucomannotriose, and glucomannotetrose. From these data, and periodate oxidation, Mizuno and Hayashi[53] proposed this structure:



$$[{}_4M_{1-4}M_{1-4}M_{1-4}G_{1-4}M_{1-4}M_{1-}]_n-\left[\begin{array}{l} {}_4M_{1-4}M_{1-4}G_{1-4}M_{1-4}M_1 \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\quad {}_4M_{1-4}M_{1-4}M_{1-4}\overset{6}{G}_{1-4}M_1 \end{array}\right],$$

M and G denoting mannose and glucose residues; $n \simeq 49$. The difficulty of access to the original report precludes knowledge of methods used to separate and identify the methylated sugars, etc.

5. The glucomannan from *Eremurus regelii* rhizomes; this, eremuran, was separated by us[54] by means of extraction with cold water from the dried and ground roots, precipitation with alcohol, and reprecipitation from 5% trichloroacetic acid with alcohol. The eremuran content in roots of plants growing in Central Asia exceeds 30% of the dry weight. Very viscous solutions of this polysaccharide give with iodine a red coloration with an absorption maximum at 530 mμ, near to that of rabbit liver glycogen (500 mμ) but much less intense. The components are glucose (1 mole) and mannose (2 moles), which were identified crystallographically, by conversion to crystalline mannose phenylhydrazone and the *N*-glucoside of *p*-nitroaniline, and by fermentation with special strains of yeast. The homogeneity of eremuran was investigated by fractionation with ethanol, by electrophoresis[55,65], and by deposition of the copper complex. Fractions were obtained by precipitation with one and two volumes of alcohol respectively; they differed in reducing power and intensity of coloration with iodine, but had identical glucose and mannose contents and identical infra-red spectra. They were, therefore, apparently, homologues of different degrees of polymerisation. Electrophoresis in a borate buffer in Tiselius' apparatus yielded two components, of which the faster-moving constituted most of the polysaccharide and contained glucose and mannose. The other component has not yet been investigated on account of the very small quantities available. Eremuran, precipitated as the copper complex and then regenerated, still contains glucose and mannose in the ratio 1 : 2, but becomes insoluble in water, probably on account of the changed conformation of the hexose residues. The flocculent aqueous suspension gives a dark red-brown colour with iodine, however. Eremuran is not hydrolysed by α- and β-amylases. Methylation of eremuran or its tetra-acetate yields di-, tri-, and tetra-methylhexoses. Preliminary data indicate the quantity of trimethylhexoses to exceed that of the tetramethylhexoses by more than ten times; a mixture is obtained of 2,3,6-tri-*O*-methylglucose and tri-*O*-methylmannose. The di- and tetra-methylhexoses have not yet been identified.

Partial hydrolysis of eremuran yields three oligosaccharides, one of which is a disaccharide consisting of glucose and mannose residues and apparently being 4-β-glucopyranosidylmannose; its structure is being studied. The data so far available therefore indicate that eremuran is a branched polysaccharide with a backbone of glucose and mannose residues, mainly joined by 1,4-glycoside links. Optical activity and infra-red data[57] indicate that these are β-links.

On account of the rich supply of *Eremurus*, eremuran has great economic potentiality for the Soviet Union as (*a*) an emulsifier as good as gum arabic, (*b*) a source of mannose, which is imported at present, and (*c*) as a possible substitute for blood, after partial hydrolysis.

6. The glucomannan of iris seeds; Andrews and coworkers[58] investigated *Iris ochroleuca* and *I.sibirica.* The polysaccharides were extracted with 10% NaOH solution, precipitated with alcohol, and purified by means of the copper complex and repeated precipitation with alcohol. They gave no blue colour with iodine. Both polysaccharides were hydrolysed to approximately equal quantities of glucose and mannose, comprising 97% of the polysaccharide from *I.ochroleuca* and 98% of that from *I.sibirica.* The remainder was galactose; it is not certain whether this is a component of the polysaccharides, or whether some galactomannan impurity remained despite purification. Methanolysis of the trimethylated polysaccharides gave tetra-, tri-, and di-methylhexoses in the ratio 1 : 24 : 1.3 for *I.ochroleuca* and 1 : 30 : 0.8 for *I.sibirica.* The trimethyl derivatives formed a mixture, inseparable by chromatography, of 2,3,6-tri-*O*-methylglucose, identified in the crystalline form, and 2,3,6-tri-*O*-methylmannose, identified as the phenylhydrazide of trimethylmannonolactone. The tetramethylhexoses (3 and 3.2%) were largely 2,3,4,6-tetra-*O*-methylgalactose, with small amounts of glucose and mannose derivatives. The dimethylhexoses were mainly mannose and glucose derivatives, but were not fully identified. These data indicate that both polysaccharide chains are little branched, and are composed of glucose and mannose residues with 1,4-links. All the galactose is present as end-residues, and may be part of an admixture of galactomannan. The methylation data, and reducing power, show the polysaccharide from *I.ochroleuca* to have a significantly higher molecular weight than that from *I.sibirica.*

7. The polysaccharides from seeds of the Japanese kaki tree (*Diospyros kaki*) were obtained by Hayashi[59] by means of extraction with hot water and then with 5% NaOH solution. The two fractions thus obtained were purified by means of the copper complexes. Both contained mannose (predominantly), glucose, and a little pentose. It is not certain whether this polysaccharide is a glucomannan containing some pentose, or a "pentoglucomannan" as the authors suggest. Triacetyl derivatives of both polysaccharides have been made.

VII. DERIVATIVES

The 2-cyanoethyl ethers of galacto- and gluco-mannans and the carboxymethyl ether of guaran[60] have been obtained; they form very stable gels with salts of heavy metals[61]. A patent exists for the etherification of galacto- and gluco-mannans with di-2-chloroethyl ether and a dihalogenohydrin derived from glycerol, the residues of which cross-link polysaccharide molecules[62]; the products are very viscous.

The conditions needed to produce nitro-derivatives of konjac mannan, and their properties, have been studied[63].

VIII. SOME BIOCHEMICAL PROBLEMS

Although the biological significance of galacto- and gluco-mannans as reserve carbohydrates, disappearing as the seeds grow, is realised, the mechanism of the biosynthesis and cleavage of these compounds is hardly known. Saccharose and raffinose were detected in a study of lucerne seeds[40], and it was therefore suggested that during galactomannan synthesis galactopyranosyl residues from raffinose were converted into a polymer of mannose; and that cleavage of galactomannans involved conversion of these residues into saccharose. On this hypothesis, the synthesis of galactose end-residues is a way of "reserving" the highly mobile galactose. The established variation of galactose content in glucomannans accords with the hypothesis[41]. The presence of guanosine diphosphate mannose in yeasts[64] and its possible role in the synthesis of yeast mannans suggests a similar synthesis of the polymannoside backbone in plant galactomannans and, possibly, glucomannans.

The high content of galactomannan-cleaving enzymes in germinating guar seeds[38] was used to hydrolyse guaran to oligosaccharides, but no attempt was made to fractionate the enzymes. An impure enzyme hydrolysing konjac mannan was apparently isolated[65]. In the human body 95.5% of konjac mannan is digested, but this occurs by virtue of intestinal bacteria, since pancreatic extract has no effect on mannans[66].

Caroban and guaran have the interesting property, along with some other galactans and other polysaccharides containing galactose residues, of serological activity; they precipitate the antibodies of antipneumococcus serum (type XIV)[67].

IX. APPLICATION

This has been mentioned above (p.271); a series of reviews deals with the industrial use of some galacto- and gluco-mannans. In ripe seeds there have recently been found, galactomannans able to replace caroban, the demand for which is not fully satisfied[69]. The treatment of seeds containing galactomannans to give good raw materials for industrial glues has been described[70,71]. The preparation of "dry", rapidly swelling galactomannan gums is described in a patent[72]. A comparative study of guar gums, with particular reference to viscosity, is described[73] (see also p.271), as is a comparison of galacto- and gluco-mannan "slimes"[74]. A number of works deal with the use of galactomannan gums in the paper industry[75,76], particularly together with starch[77]; their great use in the tobacco industry is also demonstrated[78,79]. Their use has been suggested in pharmacy for preparing gels[80] and as thickeners[81]. Their use in the food industry[82] has led to development of methods of food analysis for galactomannans[83,84].

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THE RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS

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CONTENTS

INTRODUCTION

The study of the action of different forms of radiation on aqueous solutions is important chiefly because of the marked similarity in the behaviour of the primary products of the radiolysis of aqueous solutions and biological systems. On practical application is the construction of chemical dosimeters, which are not only air-equivalent but also simulate tissue behaviour. Moreover, the present development of atomic energy makes it important to take account of processes initiated by radiation and to examine possible methods of carrying out various redox reactions in inorganic and organic synthesis in aqueous solution. It is important to make maximum use of the energy absorbed when carrying out these processes.

These more general problems require the study of the nature of the primary products, the ways in which the energy absorbed by the solution can be transferred, and the mechanism of the reaction of the primary products with one another and with dissolved substances.

Although the effect of ionising radiation in aqueous solutions has been known for more than 50 years, there is as yet no single theory of the radiolysis of aqueous solutions. In this paper we have tried to show the main directions of development of the radiation chemistry of aqueous solutions, to examine modern theories of the mechanism of radiolytic changes, and to present what is in our opinion some of the most interesting effects of radiolytic reactions. We have taken into consideration the fact that the experimental material on the radiolysis of aqueous solutions has been presented fairly completely in a number of reviews on radiation chemistry[1-17].

1. MAIN STAGES IN THE DEVELOPMENT OF THEORIES OF RADIOCHEMICAL PROCESSES IN AQUEOUS SOLUTIONS

The decomposition of water to O_2 and H_2 when radium salts are dissolved in it was first observed in the nineteen-hundreds[18,19]. It was subsequently found that in aqueous solutions radium salts yield hydrogen peroxide as well as oxygen, the sum of the quantities of O_2 and H_2O_2 evolved being equivalent to the quantity of hydrogen formed[20,21]. At that time it was considered that radioactive elements (Ra, Rn) catalysed the decomposition of H_2O to H_2, O_2, and H_2O_2, but it was not suggested that radiation supplied the energy. In a review of data published up to 1907, Bragg[22] established that when the same quantity of radon acts on water and on air, the number of water molecules decomposed almost coincides with the number of ions formed in air. In 1913 Duane and Scheuer[23] studied the action of α-rays on water and formulated a general principle of radiation chemistry, according to which the main process in aqueous solutions is the action of the radiation on water. It was implied that all radiochemical reactions in solution take place as a result of the interaction of molecules of "activated water" with the dissolved substances. The nature of the activated water, however, remained unknown.

The formation of H_2 and H_2O_2 in pure, thoroughly degassed, water treated with X-rays and γ-rays remained undetected for a long time. This was apparently due to the low sensitivity of the analytical methods employed. Later Allen and Toulis showed that the steady-state concentration of these products is extremely small (10×10^{14} molecules × × ml^{-1} for the action of 2 MeV electrons and X-rays)[28,29].

Debierne (1914) and later Risse (1929) suggested that the action of ionising radiation on water produces H and OH radicals which participate in reactions[30,31]. In 1944, Weiss used the theory that H and OH radicals are formed when aqueous solutions are irradiated to explain the oxidation and reduction of a number of substances[32]. In 1948 Dainton analysed an aqueous solution of acrylonitrile irradiated with ultra-violet light, X-rays, and γ-rays, and detected the presence of OH groups in the polymer formed. Dainton concluded that in this case the OH radical is the chain initiator[33]. The existence of H atoms in liquid water has not yet been confirmed by direct experiment. Such data are available, however, for gaseous and solid phases, where the existence of atomic hydrogen has been shown. For example, the conversion of para-hydrogen to ortho-hydrogen under the influence of α-radiation takes place *via* H atoms[34].

In the nineteen-fifties, the e.p.r.† spectra of irradiated, frozen water and aqueous solutions were recorded at different temperatures. In some cases the presence of atomic hydrogen was established[35-41]. The e.p.r. spectra of frozen solutions are important in the chemistry of aqueous solutions since the form of the primary products of radiolysis (ions and excited molecules) and their distribution in the track of the ionising particle in the initial moment are evidently independent of the state of aggregation of the system (solid or liquid)[9].

All theories of the production of radicals during the radiolysis of water are based on the assumption that the formation of a pair of ions when the ionising particle and water molecule collide requires the same amount of energy in the liquid and gaseous phases. From mass-spectrometric data[42] it is known that when an electron collides with a water molecule, H_2O^+, OH^-, H^+, and H_3O^+ are formed, together with small quantities of O^- and H_2^+. A minimum of about 12.5 eV is required for the removal of an electron from a water molecule. After a thorough survey of all available data, Gray[43] took the average value of the energy necessary to form one pair of ions as 32.5 eV for X-rays and γ-rays and 35 eV for α-particles. This shows that approximately three pairs of ions are formed for every 100 eV absorbed by the solution.

The positive and negative ions produced (after a number of collisions with water molecules, the velocity of the displaced electron falls to thermal values and the electron is captured by a water molecule with the formation of H_2O^-) can be hydrated (the energy evolved is sufficient for the rupture of an O–H bond) and converted to OH and H radicals in times of the order of 10^{-11} sec[44] according to the scheme‡:

$$\begin{array}{ll} (a) & H_2O \rightsquigarrow H_2O^+ + e \\ (b) & H_2O^+ + H_2O \rightarrow H_3O^+ + OH \\ (c) & e + H_2O \rightarrow H_2O^- \\ (d) & \underline{H_2O^- + H_2O \rightarrow OH^-aq + H} \\ & H_2O \rightsquigarrow H + OH \end{array} \qquad (1)$$

According to this first theory of radical formation, they should be formed at some distance from one another (Dale, Gray, and Meredith[47] have estimated this distance as equal to 70 times the diameter of the water molecule).

According to the theory put forward by Magee and coworkers[48,49], the electron very rapidly gives up its energy to the surrounding water molecules and thus cannot overcome the force field of the H_2O^+ ion§. As a result of the subsequent neutralisation of the H_2O^+, the excited water molecule which is produced should "break down" into H and OH radicals. According to Magee, this neutralisation step takes not more than 10^{-13} sec. The energy evolved on neutralisation of the ions is sufficient to enable the H and OH radicals to overcome the cell effect and to move a considerable distance apart.

According to the second theory, any radiochemical reaction involves the reaction of excited water molecules, and the radicals formed by their dissociation, with the molecules of dissolved substances; ions do not take part in the reaction since their lifetime is extremely small (10^{-13} sec).

These theories of radical formation give different pictures of the initial distribution of the product radicals. According to the first theory, the H and OH radicals from ionised water molecules in an irradiated system are formed initially at a considerable distance from one another, and according to the second theory they are formed in the same place. According to the first theory, for strongly-ionising radiation (α-particles), the track after the hydration of the ions formed from the water molecules can be pictured as a beam of radicals (1000 per 1 μ of path) surrounded by a "diffuse" cloud of H atoms. For weakly-ionising radiation,

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† Electron paramagnetic resonance.

‡ According to the most recent data[45,46], the lifetime of the H_2O^+ ion in the liquid phase is 1.6×10^{-14} sec. Reaction (1*b*) can take place in $\sim 10^{-13}$–10^{-14} sec.

§ Here no allowance is made for the fact that the movement of the electron takes place in the force field of polar molecules, which may weaken its interaction with the H_2O^+ ion.

the distance between the H and OH formed from one initially-ionised water molecule is greater than 15 $m\mu$. These radicals are more uniformly distributed along the track (from 3 to 1 per 1 μ of path) and their concentration in the region of the axis of the beam does not exceed 10^{-4} M (for 60 kV electrons[50]).

According to the second theory, the OH and H radicals are uniformly distributed in the volume of the track, that is, the average concentration of H and OH is the same throughout its volume, irrespective of the form of the ionising radiation. It is difficult to verify either theory since our knowledge of the nature of the product radicals and the kinetics of their interaction is incomplete. To solve this complex problem various theories of the properties of the intermediate particles and their reactivity, based on the behaviour of free radicals in the gaseous phase, are being used. A further complicating feature is that an examination of the distribution of radicals in space and with time inside the spur¶ is required, with allowance for the distribution of the spurs relative to one another and for their interaction with one another with time. Thus it is necessary to allow for the fact that their distribution in the volume of the track changes with time as a result of diffusion and recombination of the radicals.

By limiting the conditions of the problem, results have been obtained which agree satisfactorily with experimental data only in a few cases. Thus Ganguly and Magee, starting from a model giving uniform distribution of radicals in the tracks and assuming that the distribution of radicals in the spurs remains unchanged during the reaction (a doubtful simplification), found that 80–100% of the radicals are removed in reaction with the acceptors† at acceptor concentrations of the order of 1–10 M for weakly-ionising radiation[51]. Schwarz and coworkers showed that Ganguly and Magee's calculations agree with the results of experiments on the determination of the number of recombining radicals and radicals removed in reaction with acceptors for the irradiation of aqueous solutions of KBr, KNO_2, and C_2H_5OH by γ-rays, deuterons, and helium ions[52,53]. This agreement between theoretical and experimental data is observed, however, only at intermediate values of the concentration of radical acceptors. At high and low acceptor concentrations, discrepancies between theory and experiment appear[54], indicating either that the model is not completely satisfactory or that the assumptions made in simplifying the problem are incorrect.

Armstrong, Collinson, and Dainton[55] established a difference in the values and in the directions of change in the yield of radical and molecular products of radiolysis on going from solutions of acrylamine in ordinary water to solutions in heavy water. This phenomenon may be related to a difference in the initial distribution of the oxidising and reducing components of radiolysis.

Filinovskii and Chizmadzhev solved the problem of the recombination of H and OH radicals in the track for the case of uniform distribution of these radicals in the track ($r \sim 1$ Å) and for the case of "broad" distribution of H radicals ($r \sim 100$ Å). They allowed for the change of the distribution of the radicals with time as a result of their recombination: in their calculations they assumed that the rates of radical reactions are identical[56]. Other workers[57] obtained a solution for the case of the Samuel–Magee–Burton model for the action of fast electrons on concentrated acceptor solutions.

Final verification of one or other of the theories of radical distribution in the track can be made by accumulating sufficient experimental data on the concentration dependence of the conversion yields of H and OH radical acceptors and balancing all the radiolysis products over wide ranges of radical acceptor concentrations.

Even at this stage, data from an analysis of the yields in the formation of the products of the "molecular decomposition of water" with change in the concentration of radical acceptor give interesting information on the geometry of the track. It has been established, for example, that the order of the reactions involved in the formation of the molecular products H_2 and H_2O_2 in solutions depends on specific features of the radiation (the density of ionisation and the energy of the ionising particles) and hence on the spatial distribution of the product radicals‡.

A number of other concepts have been put forward and are still used in one form or another to explain the nature and distribution of the products formed in the radiolysis of water.

The basis of theories of H atom formation is the assumption that a thermal electron (whose energy is lower than the excitation potential of water) is captured either by a water molecule (Lea *et al.*'s mechanism) or by the H_2O^+ ion from which it was "torn" (Magee, Samuel, *et al.*'s mechanism), in a time less than that required for reaction with dissolved substances. According to Platzman and Fröhlich's data[60], however, these two processes take place slowly. A free electron is assumed to have a lifetime of the order of 10^{-5} sec. In this time the electron can move from one water molecule to another (time of transfer 10^{-15}–10^{-14} sec; the dissociation of the H_2O^- ion requires $\sim 10^{-11}$ sec), since the energy levels of the electrons in the water molecules are close and overlap. In this case, the electron, when captured by a molecule of dissolved substance, would act as a weak reducing agent. This might explain the predominant oxidising action of irradiated water (since an OH radical is formed in the bulk of the solution at the same time as the electron). No convincing indications that this model is completely satisfactory have yet appeared, however.

From the conclusion that irradiated water has a high redox potential, Dainton and Collinson[2] suggested that the formation of H and OH radicals is accompanied by the formation of OH^+ radical ions which are hydrolysed in time. According to Weiss[61], the high redox potential is caused by reaction of atomic hydrogen with a proton to produce H_2^+. This, of course, could only be the case for acid solutions. It is known, however, that the predominant oxidising action of X-rays and γ-rays is independent of the pH of the solution[62] and therefore cannot be due to formation of H_2^+ according to the scheme

$$H + H^+ = H_2^+. \tag{2}$$

¶ Spur — the track of the secondary electron, sometimes called the δ-ray (Editor).

† The term *scavenger* is used in place of *acceptor* by Western radiochemists (Ed. of Translation).

‡ This is reflected in the order of the equation giving the dependence of the yield of molecular products on the acceptor concentration. As pointed out by Magee and co-workers,[58,59], the order in acceptor concentration may vary from 0 to ½, depending on the density of ionisation and the energy of the particles. When γ-rays with energies of the order of 1 MeV are used, the order is 1/3.

According to Haissinsky and Magat[63], H atoms are not formed when aqueous solutions are irradiated (or at least do not exist independently) and the decomposition of the H_2O^- ion takes place according to the mechanism

$$\begin{aligned} &H_2O^- \rightarrow O^- + H_2 \\ &O^- + H_2O \rightarrow OH + OH^- \end{aligned} \tag{3a}$$

or

$$\begin{aligned} &H_2O^- \rightarrow H^- + OH \\ &\underline{H^- + H_2O \rightarrow OH^- + H_2} \\ &H_2O^- + H_2O \rightarrow H_2 + OH + OH^- \end{aligned} \ . \tag{3b}$$

This scheme for the radiolysis of water assumes the formation of two OH radicals for every hydrogen molecule (that is, eight OH radicals from four ionised water molecules) and might explain the high conversion yields for dissolved substances (~8 equiv /100 eV) reacting with the free hydroxyl.

The formation of molecular hydrogen from H_2O^- is inconsistent, however, with the experimentally observed dependence of the yield of molecular products H_2 and H_2O_2 on the concentration of H and OH radical acceptors[52,64-72]. Moreover, Proskurnin and coworkers have found conditions under which, as a result of a decrease in the yield of formation of molecular products, there is an increase in the yield of the products of conversion of the dissolved substances[73-76].

To illustrate the development of the theories of the formation of primary radical products, we must examine a recently proposed mechanism for the molecular decomposition of water.

In 1935, Fricke postulated the existence of two types of activated water molecule[77], $(H_2O)'_{act}$ and $(H_2O)''_{act}$, to explain conversion yield differences for substances in aqueous solutions when irradiated with X-rays. The first forms molecular products H_2 and H_2O_2 with a yield of 0.49, and the second type of activated water molecule exhibits the unique properties of activated oxygen and is formed with a yield of 1.96. By irradiating water with ultra-violet light corresponding to the absorption band of water below 2000 Å, Fricke and coworkers initiated reactions which they believed were characteristic only of $(H_2O)''_{act}$.

In 1948, Allen[28] suggested that the conversion of the products of the interaction between the ionising particle and the water molecule involved two processes which yield molecular products (H_2 and H_2O_2) and H and OH radicals§

$$H_2O \rightsquigarrow {}^1/_2\, H_2 + {}^1/_2\, H_2O_2 \tag{F}$$
$$H_2O \rightsquigarrow H_2 + OH\ . \tag{R}$$

At the points of intense ionisation (hot points), the molecules have energy in excess of that required for the formation of H and OH, so that the reaction H + OH = H_2O may be accompanied by recombination reactions

$$H + H = H_2 \tag{4}$$
$$OH + OH = H_2O_2\ . \tag{5}$$

The yield of "molecular" products changes on going from one system to another. Allen and Johnson[79] attributed the lack of agreement between the "molecular" yields for the irradiation of different solutions to a difference in the conditions for the back reactions

$$H + H_2O_2 \rightarrow OH + H_2O \tag{6}$$
$$OH + H_2 \rightarrow H + H_2O\ . \tag{7}$$

To explain the "high" yields of hydrogen peroxide observed in the radiolysis of acidic solutions of iron sulphate, Dainton and Sutton[80], in 1953, proposed a third general reaction (E) for the decomposition of water molecules

$$H_2O \rightsquigarrow H + {}^1/_2\, H_2O_2, \tag{E}$$

which means essentially a new distribution of radical and molecular products. At the same time, Allen, on the basis of a critical survey of data obtained by different authors on the kinetics of the radiolysis of certain systems, also concluded that reactions F, R, and E take place[81].

From the above it may be concluded that the action of rapid particles on water and aqueous solutions leads to the formation of ionisation products and excited states of the water molecules, both of which may produce H and OH radicals. Thus, although the nature of the primary products has not yet been established by direct experiments, we can, when considering radiolytic processes, speak of the primary chemical interaction of H and OH radicals with one another and with dissolved substances leading to the formation of molecular products H_2 and H_2O_2 and products of conversion of the dissolved substances. The subdivision of the processes involved in the formation of the products into reactions F, R, and E, and the mechanism proposed by Haissinsky, should, in our opinion, be regarded merely as a method of balancing the radiolytic products, since $G(H_2)$ and $G(H_2O_2)$ change on going from one system to another. These considerations can also to some extent be applied to cases of radiolysis under the influence of α-radiation. There is no fundamental difference between the processes involved in the formation of the primary product radicals on ionisation by α-rays and by γ- and X-rays. The only difference is in the density of ionisation in the track in α-ray radiolysis, where the recombination processes (4) and (5) have a higher probability.

H and OH radicals are formed in water in equivalent quantities and may initiate both oxidation and reduction. The fact that irradiated water has a predominantly oxidising action is apparently due firstly to the difference between the "effective" concentrations of the OH and H radicals, arising from the difference in the distribution of these radicals in the track of the ionising particle¶, and secondly to the difference between the reactivities of the H and OH radicals. For a long time no allowance was made for the effect of the reverse reaction, which increases with increase in the radiation dose, and the attainment of equilibrium between the original substances and the products of their conversion in a number of systems (for example, nitrate, nitride[82], was attributed to the definite redox potential of irradiated water (+0.96 V)[2]. It was assumed that a reversible equilibrium exists between the hydrogen atoms and OH radicals.

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§ A number of workers[48,78] believe that molecular hydrogen and hydrogen peroxide, together with H atoms, are formed as a result of changes in the excited water molecules in the spurs, according to the following reactions:

$$H_2O^* + H_2O^* \rightarrow H_2 + H_2O_2 \tag{8}$$
$$H_2O^* + H_2O^* \rightarrow 2H + H_2O_2 \tag{Ea}$$
$$H_2O^* + H_2O \rightarrow 2H + H_2O_2 \tag{Eb}$$

¶ In the estimation of the oxidising properties of irradiated water in early studies on solutions saturated with air, no allowance was made for the fact that the O_2, an energetic H atom acceptor, facilitates the removal of the reducing component of the radiolysis of water from the reaction and thus prevents the reduction of other dissolved substances[2,5].

This theory excludes the possibility of formation of reduction products whose potential is more negative than +0.95 V. Moreover, it is inconsistent with experimental observations on the conversion of a number of substances (for example, methylene blue) which are capable of being oxidised and reduced under conditions where competing acceptors (oxygen) are absent[2]. As a result of the absence of reversible equilibrium between the oxidising and reducing components of the products of the radiolysis of water, it is possible, using selective electrodes, to obtain values for the redox potentials of the products of the conversion of each of these components[83,84]. It has been found that the potential of a platinum electrode in irradiated 0.8 N H_2SO_4, corresponding to the appearance of the products of conversion of H atoms, is close to that of the normal hydrogen electrode[83].

It has been shown[74,76,83-86] that when one of the radicals, for example H, is removed by an acceptor, the conversion yield of another substance which is an acceptor of the conjugate radical (OH) increases. The absence of reversible equilibrium between the products of oxidation and reduction of a given acceptor (for example, in the case of the nitrate–nitrite system) means that the ratio of the concentration of its oxidised and reduced forms depends on the experimental conditions. The decrease in the accumulated yield of products with time of irradiation in such systems is due to an increase in the rate of the reverse processes. With the introduction of conjugated acceptors it is possible to suppress the reverse processes completely, in which case the conversion yield of one of them reaches a value equivalent to the utilisation of the products of conversion of all the radiolysed water molecules[75]. The reactivity of the radical products of radiolysed water molecules will now be considered.

2. THE CONCEPT OF RADICALS AS INTERMEDIATE PRODUCTS IN THE RADIOLYSIS OF WATER

A. OH Radicals as the Oxidising Component of Radiolysis

As we have seen, OH radicals are evidently formed in the dissociation of H_2O^+ to H^+ and OH as a result of hydration of the positive hydrogen ion, since the time necessary for this process has been calculated[46] to be much less than the time required for the neutralisation of H_2O^+†. The OH radicals have not yet been detected by direct methods in irradiated water. However, in a number of radiolyses[89-91] of frozen aqueous solutions, the e.p.r. method and luminescence analysis have established the existence of intermediate products at temperatures below -160° (one type of radical) and -120°, and in a number of cases it may be assumed that OH radicals have been observed[36,90,92]. It has not yet been possible, however, to identify OH radicals precisely from these spectra. Kaitmazov and Prokhorov[93] have described an attempt to obtain the e.p.r. spectrum of the OH radical during the photolysis of aqueous H_2O_2 solution. The identification of the OH spectrum reported cannot be taken as conclusive, since OH radicals react readily with H_2O_2 to form HO_2, whose spectrum is superimposed on that of the OH. It was not until 1959 that the OH radical was identified in irradiated ice and the kinetics of its conversion in the temperature range 77°–108°K studied by the e.p.r. method[94,95].

By recombining with one another, OH radicals are able to form hydrogen peroxide, whose steady-state concentration[96] cannot exceed 10^{-3} M. Increase in the pH of the solution from ~0 to 12 decreases $G(H_2O_2)$ by a factor of 2.5–3, in irradiation by X-rays[97]. A sharp decrease in the H_2O_2 concentration at pH ~2.5 and a slight increase in the H_2O_2 concentration at pH ~12 has been reported[98,99]. This phenomenon is attributed to the possibility of dissociation of the OH radical to O^- and H^+ under these conditions and its removal from the reverse reaction of peroxide oxidation (6). The possibility of dissociation of OH radicals in alkaline medium and the stability of O^- at pH 13.9 has been reported by other authors[100-103]. The e.p.r. spectra of frozen nitrate solutions has revealed that on going from alkaline solutions (1 M and 0.1 M NaOH) to neutral solutions, one radical disappears and another is produced, which may correspond to the process

$$\underset{\text{(I)}}{OH} + OH^- = \underset{\text{(II)}}{O^- H_2O} \; . \qquad (9)$$

The radicals (I) and (II) can exist only at temperatures $\leqslant$ -160°.[104]

It is generally assumed that the fate of the free hydroxyl in the radiolysis of water is its dimerisation with the formation of hydrogen peroxide, but it is also necessary to allow for the possibility of disproportionation of OH radicals to H_2O_2 and O_2.[105] Kazarnovski and coworkers, using potassium ozonide as a source of free hydroxyl radicals, showed that the disproportionation of OH in aqueous solutions should play a more important role than the dimerisation process.

The OH radicals have a high electron affinity (free energy = 40 kcal mole^{-1} [106,107]) and hence may act as oxidising agents. The electron affinity plus the solvation energy is 147.6 kcal mole^{-1}.[108] This may explain the radiolytic oxidation of, for example, halide ions‡ Cl^-, Br^- and I^-, salts of uranium(IV),[111-117] tin(II),[117-119] and iron(II),[120,121] oxy-anions such as SeO_3^-, TeO_3^-, AsO_2^-, NO_2^-, and PO_3^{3-},[122-127] the gases CO, NH_3, H_2S, N_2O, and N_2 dissolved in water[128-132] (Table 1), and a large number of organic compounds (alcohols, acids, ketones, aldehydes, aromatic compounds, etc.). The oxidising power of OH radicals is determined by the redox potential of the system and depends on the acidity of the medium, decreasing with increase in pH.[132-135]

It has been observed in a number of cases (the radiolysis of solutions of ferrous salts, the dye methylene blue, etc.) that there is a sharp decrease in the conversion yield of the substances in the pH range 2–3, due to a decrease in the oxidising power of the OH radicals[111,136,137]. In approximately the same pH range there is an increase in the reducing power of H radicals[134]. Since these two radicals can be considered to have opposing effects, and both are always present in solution, it is possible that the apparent decrease in the oxidising power of OH and reducing power of H is due to the same factor. It would be interesting to examine this question for a large number of systems with the action of the conjugated radical excluded in each case.

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† Weiss and coworkers[87,88] believe that in strongly acidic medium H_2O^+ exists for a longer period (up to 10^{-11}–10^{-10} sec), as does H_2O^- in alkaline medium. These ions may react with dissolved substances if the concentration of the latter is sufficiently high.

‡ The reaction of ordinary OH radicals with Cl^- would be accompanied by an increase in free energy (17 kcal mole^{-1}), so that it is assumed that excited OH radicals take part in this reaction[106,109,110].

A number of workers believe that OH radicals may exhibit reducing properties towards strong oxidising agents. Thus, Haissinsky and Lefort[138] consider that the reduction of Ce^{4+} and $Cr_2O_7^{2-}$ [138-140] involves reaction between OH and these ions. It must be remembered, however, that the reduction of these compounds is caused not by the direct action of OH radicals but by the formation and decomposition of intermediate compounds of the peroxide type produced as a result of the addition of hydroxyl to these ions[131]. Proof of this is provided by the fact that apparent participation of OH radicals in reduction processes are characteristic only of compounds capable of forming more highly oxygenated derivatives.

B. The Participation of H Atoms in Radiolytic Reactions

H atoms, formed in aqueous solutions as a result of reaction (1*d*) and also, in acid medium, by the reaction[53,141]

$$H_3O^+ + e = H + H_2O, \qquad (10)$$

are able to reduce a number of substances (Tables 1 and 2).

There is every reason to suppose that atomic hydrogen (H radicals) in the condensed phase are present in the hydrated state, that is, as H_3O. We must also remember that the hydrogen atom is able to form hydrogen bonds. This may explain the rapid displacement of H and OH radicals within the volume by the so-called relay mechanism of active particle transfer and may thus explain the absence from the e.p.r. spectrum of H atoms and OH radicals in irradiated frozen aqueous solutions at low temperatures (above -196° and -160°) when diffusion of the radicals is hindered[142]. It is only comparatively recently that the e.p.r. method has made it possible to detect H atoms in pure frozen water at the temperature of liquid helium[35]. In frozen solutions of oxy-acids, the doublet belonging to H can be observed at higher temperatures[37-39]. No attempt has been made to observe directly H radicals in the liquid phase, since their steady-state concentration during irradiation is extremely low.

Zalkind and Veselovskii suggested that the decrease in the electrode potential of a smooth platinum electrode in acidified irradiated water was caused by the setting-up of a redox potential corresponding to a definite concentration of H atoms in the solution[83,84,143]. Assuming that the lifetime of the H atoms in water is of the order of several minutes, it is possible to estimate the steady-state concentration of H atoms in the volume, the value found being $\sim 3 \times 10^{-5}$ M;[143] when an oxidising-component acceptor (oxalic acid) is present in the solution, the steady-state concentration of H is several times greater. This conclusion for liquid solutions at ordinary temperatures, however, is inconsistent with the diffusion picture of the track of the ionising particles and the recombination reactions of H atoms. From a study of the isotopic exchange between H_2 and D_2 in aqueous solutions, initiated by γ-rays, and assuming that the rates of the processes

$$H + H_2 = H_2 + H \qquad (A)$$

$$H + D_2 = HD + D, \qquad (B)$$

in the liquid phase are the same as in the gaseous phase, Friedman and Zeltmann[144] estimated the steady-state concentration of H atoms and obtained the value 2×10^{-8} M for a dose power of 10^{18} eV cm^{-3} sec^{-1} §. In our opinion, this value for the steady-state concentration of H corresponds more closely to the real value, although the assumption that the rate constants of processes (*A*) and (*B*) in the gaseous and liquid phases are equal is a considerable simplification.

The decrease in the electrochemical potential of a platinum electrode in an irradiated acid may be due to the accumulation of molecular hydrogen in the solution and resultant supersaturation, or to the accumulation in the solution of intermediate products (whose formation is possibly related to the fate of the H atoms) which exist for a comparatively long time.

The hydrogen atoms take part in recombination reactions with one another and with OH radicals, forming H_2 and H_2O. For the action of strongly-ionising radiation (for example, α-particles) on water and aqueous solutions, G_{H_2} remains almost constant, irrespective of the composition of the solution in the range of intermediate values of the concentrations. This is due to the high values of the local concentrations of radical products in the track. In the case of γ-radiation, the introduction of H-atom acceptors into the irradiated water in comparatively small quantity may lead to a sharp decrease in G_{H_2} through competition for H atoms in the recombination process H + H.[75] In the presence of the conjugate OH-radical acceptor, the conversion yield of the H-atom acceptor increases and remains constant over a wide dose range, through a decreased recombination of H with OH radicals[75] and the reverse oxidising processes[73,86,132,137]. In this case G_{H_2} shows almost no change compared with its value in the absence of OH acceptor, if the concentration of H-atom acceptor ensures removal of the latter from the recombination reaction H + H, that is if it is equal to or greater than ~1 M.

The reducing power of the H atoms is determined by the reactivity of the H-atom acceptor, and also by the pH of the medium in which the reaction takes place. However, the dependence of the reactivity of the dissolved substance on the pH of the solution must be taken into account. This dependence may be more clearly defined than in the H atom case and the effect may exceed that in the latter, as, for example, in the reduction of dichromate ion[123,135]. The reducing power of the H atoms increases with increase in the pH of the solution[145-147].

Some workers[148] attribute oxidising properties to the H atom in acid solutions. For example, Weiss suggests that in acid medium, H atoms present in the form H_2^+ take part in the oxidation of iron(II) ions and organic compounds according to the scheme

$$RH_2 + H_2^+ \rightarrow RH + H^+ + H_2 \qquad (11)$$

The theory that H atoms have an oxidising action is supported by experiment[149-151]. Atomic hydrogen, prepared by electrical discharge in H_2, was passed into acidic solutions of Fe^{2+} and Fe^{3+}, and the kinetics of the oxidising and reducing reactions of the Fe^{2+}–H_2O and Fe^{3+}–H_2O systems were studied. Under these conditions, however, the data[149] show that intermediate products of the conversion of sulphuric acid and H atoms, and not H_2^+, may take part in the reactions.

Cottin studied the oxidation of phosphite and considers that H atoms are capable of oxidising phosphite ions by the formation of an H–H bond, which is stronger than the H–HPO bond[127].

The question of the existence of the molecular hydrogen ion H_2^+ in acid medium (pH = 1 – 4) is of interest since in

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§ The effective lifetime of the H atoms under these conditions, according to Friedman and Zeltmann, is 0.2 sec.

TABLE 1. Examples of radiolytic processes involving oxidation and reduction of inorganic compounds in aqueous solution.

System studied (suggested reactant in brackets)	Experimental conditions	Concentration range studied, M*	Maximum value of conversion yield of original substance, molecules (or ions) / 100 eV	References**
$Fe^{2+} \rightarrow Fe^{3+}$ (OH)	acid medium in the presence of O_2	$2\cdot10^{-6}$—$1\cdot10^{-2}$ (10^{-4}—10^{-2})	15.6 (15.6)*	136,181—197,80 67,120
	acid medium, without O_2	$1\cdot10^{-4}$—$1\cdot10^{-2}$	~8	136,182,155
$Fe^{3+} \rightarrow Fe^{2+}$ (H)	pH = 0.8 (without O_2)	$1\cdot10^{-3}$	0.07	140,147
	pH = 2.46 (with O_2)	$2.2\cdot10^{-4}$—$3.86\cdot10$-4	15	198,199
$Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-}$ (OH)	pH = 2–11 (without O_2)	$1\cdot10^{-4}$—$1\cdot10^{-1}$ (10^{-4}—10^{-1})	1.02 (1.02)	122
$Fe(CN)_6^{3-} \rightarrow Fe(CN)_6^{4-}$ (H)	pH = 0.5–7 (with O_2)	$2\cdot10^{-4}$—$5\cdot10^{-3}$	5 4	133
	pH = 12 (without O_2)		0.95	133
Fe^{2+} 2, 2′-bipyridyl (OH)	0.8 *N* H_2SO_4	$1\cdot10^{-3}$	15.6	200
Fe^{3+} 2, 2′-bipyridyl (H)	pH ⩽ 7	$1\cdot10^{-3}$	9.4	200,201
Fe^{3+} 1, 10-phenanthroline (H)	pH = 0.4–3.5	$1\cdot10^{-4}$	9.6	201
	pH = 6 (with O_2)	$1\cdot10^{-4}$	4.0	198
$Ce^{4+} \rightarrow Ce^{3+}$ (H)	0.8–1 *N* H_2SO_4 in the presence of O_2	$1\cdot10^{-4}$—$4\cdot10^{-3}$ ($1\cdot10^{-3}$—$4\cdot10^{-3}$)	2.2—2.4 (2.36)	203,199,202,82,204,205
		$2\cdot10^{-4}$—$1\cdot10^{-3}$	5.2	140
$Ce^{3+} \rightarrow Ce^{4+}$ (OH)	3 *M* K_2CO_3 (alkaline solution)	$1\cdot10^{-3}$	1.7—1.9	138
$Cl^- \rightarrow Cl$ (OH*)	pH = 11	$1\cdot10^{-2}$—7	3.2	109,206—208
$Br^- \rightarrow Br$ (OH)	pH ≃ 7	$1\cdot10^{-5}$—4.5 ($1\cdot10^{-3}$—$1\cdot10^{-1}$)	0.66	111,66,109,207,122
$I^- \rightarrow I$ (OH)	pH = 2–11	$1\cdot10^{-7}$—5 ($1\cdot10^{-5}$—$1\cdot10^{-3}$)	3 (3)	111,122,112,209
$BrO_3^- \rightarrow Br_2 + O_2$ (H)	0.1 *N* H_2SO_4	$6\cdot10^{-4}$	2.0	202,210
$IO_3^- \rightarrow I_2$ (H)	pH = 12.5	$5\cdot10^{-4}$—$1\cdot10^{-3}$	~1.7	211,209,202
	pH ≃ 0	$5\cdot10^{-4}$—$1\cdot10^{-3}$	~0.6	211
$Sn^{2+} \rightarrow Sn^{4+}$ (OH)	4 *N* HCl, 1 *N* NaOH	$1\cdot10^{-2}$—1 ($1\cdot10^{-2}$—$1\cdot10^{-1}$)	0.5; 0.6 (~0.5)	118,119
	pH ≃ 0.1	$3.6\cdot10^{-1}$	0.49	212
$Sn^{2+} \rightarrow Sn^0$ (H)	weakly alkaline medium, vacuum	$1\cdot10^{-2}$	~0.03—0.01	119
$Ti^{3+} \rightarrow Ti^{4+}$ (OH)	1—4 *N* HCl	$1\cdot10^{-2}$—$1\cdot10^{-1}$ ($1\cdot10^{-2}$—$1\cdot10^{-1}$)	5 (5)	119
	1—4 *N* H_2SO_4	$1\cdot10^{-2}$—$1\cdot10^{-1}$	4.2 (4.2)	119
$Co^{3+} \rightarrow Co^{2+}$ (H)	pH ~ 0.4	$1\cdot10^{-3}$	2.3	82
$Tl^{3+} \rightarrow Tl^+$ (H)	pH ~ 0.4	$1\cdot10^{-4}$—$2\cdot10^{-3}$ ($1\cdot10^{-4}$—$2\cdot10^{-3}$)	1.18 (1.18)	213,82,214
$U^{4+} \rightarrow U^{6+}$ (OH)	3 *N* H_2SO_4	$5\cdot10^{-4}$—$5\cdot10^{-2}$ ($2\cdot10^{-2}$—$5\cdot10^{-2}$)	2,0 (2,0)	113—116
$SeO_3^{2-} \rightarrow SeO_4^{2-}$ (OH)	pH=2÷11	$1\cdot10^{-4}$—$1\cdot10^{-1}$ ($1\cdot10^{-4}$—$1\cdot10^{-1}$)	0.6 (0.6)	122,111
$TeO_3^{2-} \rightarrow TeO_4^{2-}$ (OH)	pH=2÷11	$1\cdot10^{-4}$—$1\cdot10^{-1}$ ($1\cdot10^{-4}$—$1\cdot10^{-1}$)	0.6 (0.6)	122
$AsO^-_2 \rightarrow AsO^-_3$ (OH)	pH=2.5; 7	$1\cdot10^{-4}$—$1\cdot10^{-2}$ ($1\cdot10^{-3}$—$1\cdot10^{-2}$)	1.75; 2.2 (with O_2) (1.75)	124,111,122,215
	pH=10.5	$1\cdot10^{-4}$—$1\cdot10^{-2}$ ($1\cdot10^{-2}$—$5\cdot10^{-2}$)	3.25; 15 (O_2) (3.25)	124
$H_2PO^-_3 \rightarrow PO_4^{3-}$ (OH)	pH=0.4; 3	$2\cdot10^{-5}$—$1\cdot10^{-1}$ ($5\cdot10^{-3}$—$1\cdot10^{-1}$)	3.8; 3 (3.8; 3)	127,216
$PuO_2^{2+} \rightarrow Pu^{4+}$ (H)	0.5 *N* H_2SO_4	$2.8\cdot10^{-5}$—$9\cdot10^{-3}$ ($1\cdot10^{-3}$—$9\cdot10^{-3}$)	1.7 (1.7)	217,218
$VO^+_2 \rightarrow VO^{2+}$ (H)	pH~0.4	$3\cdot10^{-4}$—$1-10^{-2}$ ($3-10^{-4}$—$1-10^{-2}$)	2.7 (2.7)	134
$HClO_4 \rightarrow ClO^-_3 + Cl^-$	acid medium (with and without O_2)	$1\cdot10^{-3}$—8.4	1.34	127,219
$NaClO_4 \rightarrow ClO^-_3 + Cl^-$	pH = 5.4–4.6 (with and without O_2)	1—8	~2.42	127
$NH_2OH \rightarrow N_2 + NH_3 + N_2O_2H_2$	pH = 4, vacuum	$1\cdot10^{-3}$—$5\cdot10^{-3}$ ($1\cdot10^{-3}$—5.10^{-3})	6.8 (6.8)	111,220
$NH_2OH \rightarrow NH_3 + NO^-_3$	pH = 3.3 in the presence of O_2	$1\cdot10^{-3}$	3.5	111
$N_2H_4 \rightarrow NH_3 + N_2 + H_2$ (H+OH)	pH = 0.3–12.3	$5\cdot10^{-5}$—$5\cdot10^{-2}$ ($1.5\cdot10^{-2}$—$5\cdot10^{-2}$)	5.2 (5.2)	221,111
$NH_3 \rightarrow NO^-_2$(OH)	pH = 6.9–9.6 (with O_2)	$5\cdot10^{-4}$ $1\cdot10^{-1}$	1.3 (pH = 12.5)	129
$NO^-_3 \rightarrow NO^-_2$ (OH)	pH = 2–11 (vacuum)	$1\cdot10^{-4}$—$1\cdot11^{-4}$ ($1\cdot10^{-4}$—$1\cdot10^{-1}$)	0.91 (0.91)	122,126,132
$NO^-_2 \rightarrow NO^-_3$ (OH)	pH = 6 (vacuum)	$1\cdot10^{-4}$—$1\cdot10^{-3}$	1.6	112
$NO^-_3 \rightarrow NO^-_2$ (H)	pH = ~ 1.5–14	10^{-7}—5 ($5\cdot10^{-1}$—10^{-2}); (2—6)	4.4 (2,2: 4.4)	75,70,208,222
Reduction of MnO_4^- (H + OH)	pH = 0.4–12	$7.7\cdot10^{-4}$—$2.6\cdot10^{-1}$	8.5 (pH = 0.4); *G* (—Mn^{VII})	223—226, 205
Reduction of $Cr_2O_7^{2-}$ (H + OH)	pH = 1–12	$1\cdot10^{-4}$—$1\cdot10^{-3}$ ($1\cdot10^{-4}$—$1\cdot10^{-3}$)	3.8	139,135,140
	pH ≃ 0.4, with O_2	$2\cdot10^{-4}$	0.78 (Cr^{3+})	226
$CO \rightarrow CO_2$ (OH)	pH = 3.5	$1\cdot10^{-6}$—$1\cdot10^{-4}$	4	128
$H_2S \rightarrow S$ (OH)	acid medium in the presence of O_2	$2.4\cdot10^{-3}$—$6\cdot10^{-3}$	high	111,25,130

* The figures in brackets in column 3 give the concentration range (M) with the observed constant conversion yield of acceptor given in brackets in column 4.

** The first references are to papers giving the most complete data.

this range of pH values reaction (7) is possible, and this is associated with "conversion" of OH radicals to H atoms and participation of the latter in reactions involving oxidation, for example, of Fe^{2+} ions[136], or reduction, for example, of V^V and Ce^{4+}.[82,134]

Let us examine this question briefly.

In a study of the kinetics of radiolytic reactions in systems containing H_2O, H_2, O_2, and H_2O_2 in various combinations, Allen *et al.*[152,153] generalised the results of a series of investigations and concluded that two forms of H, differing in chemical character, exist. The H atom formed directly during radiolysis appears rather to be a solvated electron. The H atom exists in acidic or basic form, depending on the pH of the medium; this can be represented as follows

$$e \overset{H^+}{\rightleftarrows} H \overset{H^+}{\rightleftarrows} H_2^+ . \tag{2a}$$

The solvated electron (H_2O^-) can be captured by an atom, molecule, or radical with a high electron affinity (for example, O_2 or OH). It has been suggested[87] that at a sufficiently high pH, H_2O^- exists in solution for at least 10^{-11}–10^{-10} sec and may react with a dissolved substance if the concentration of the latter is sufficiently high. Allen[144] suggests that the H atom is able to take part in one of the reactions (6) or (7), which decrease the accumulation yield of molecular products

$$H + H_2O_2 = H_2O + OH \tag{6}$$

$$OH + H_2 = H_2O + H + 11.6\ \text{kcal mole}^{-1}\ ¶ \tag{7}$$

A characteristic feature of the second form of H atom produced according to reaction (7) is that kinetic data[152,153] shows them to react more readily with oxygen than with

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¶ From data given by Kondrat'ev[154].

TABLE 2. Characteristics of some conjugated radiation-chemical reactions.

Type of reaction and conditions	Conjugated acceptors		Accumulation yield, molecules 100 eV	Number of H_2O molecules converted	Note: increase in yield compared with conditions when one of the conjugated acceptors is absent	References
	of H atoms	of OH radicals*				
Reduction of Ce^{4+} ions in the presence of air 0.1 N H_2SO_4	Ce^{4+} ($\sim 3\cdot 10^{-4}$)	benzene (0.02) acetic acid (2×10^{-2}–1×10^{-1})			~ 2.3 times greater than without acceptors	202
Reduction of Ce^{4+} ions in the presence of NO_3^- and Tl^+ 0.8 N H_2SO_4	Ce^{4+} ($4\cdot 10^{-4}$) $NaNO_3$ (0.5)		11	11		228
Reduction of Ce^{4+} ions 0.8 N H_2SO_4	Ce^{4+} ($10^{-4}\div 10^{-2}$)	benzene (10^{-5})	8.2	8.2	3.4 times	82
Reduction of Tl^{3+} ions 0.8 N H_2SO_4	Tl^{3+} ($1\cdot 10^{-3}$)	benzene (10^{-5})	8.1	8.1	3.5 times	82
Reduction of Cr^{6+} ions 0.8 N H_2SO_4	$Cr_2O_7^{2-}$ ($1\cdot 10^{-3}$)	benzene (10^{-5})	8.2	8.2	3.4 times	82
Decomposition of AET** in neutral solutions in the presence of O_2	O_2 ($H+O_2\rightarrow HO_2$)	AET	~18	9	2 times	170
Oxidation of Fe^{2+} ions in acid medium (0.8 N H_2SO_4) in the presence of oxygen	($p_{O_2}=70$—150 atm)	Fe^{2+} (0.001)	~23	11.5	~3 times	137
Reduction of $C(NO_2)_4$	$C(NO_2)_4$ ($4.2\cdot 10^{-3}$)	ethyl alcohol 1–80%	5.85	5.85	1.6 times	136
Oxidation of ammonia in the presence of oxygen at pH = 11	O_2 (from air)	$NH_3\rightarrow NO_2^-$ (0.15)	1.3(6.8 equiv)	6.8	no reaction without O_2	129,245
Decolorisation of methylene blue (oxidation)	$Fe(NO_3)_3$ ($2.4\cdot 10^{-4}$)	methylene blue (2.4×10^{-4})	3.9	7.8	~100*** times	242
Decolorisation of methylene blue (reduction)	methylene blue 2.2×10^{-4}	glucose, sodium benzoate, ethyl alcohol (0.5)	5.2	10.4	~10 times	242,247,248
Oxidation of the leuco-form of indigo in the presence of nitrate	$NaNO_3$ (1)	leuco-form (2×10^{-3})	5.0	10	10 times	74
Reduction of nitrate ion in the presence of glucose and glycerol	$NaNO_3$ (2)	glycerol, glucose (1×10^{-2})(1 M KOH)	6	12	2.6 times	75,86
Reduction of U^{6+} 5×10^{-3} M in acid medium	$UO_2^{2+}\rightarrow U^{4+}$	glycerol, glucose (0.5)	5	10	20 times	249
Formation of nitrite ion in the oxidation of ammonia and reduction of sodium nitrate	$NaNO_3$ (1)	NH_3 (0,15) (KOH—1)	6 3	10.5	2.3 times	245
Oxidation of the leuco-base of methylene blue at pH $\leqslant 2$	$NaNO_3$ (1)	the leuco-base of methylene blue (2×10^{-3})	9	12	12 times	76
Oxidation of the leuco-base of malachite green in the presence of oxygen	O_2	the leuco-base (1.4×10^{-2})	4.7	9.4	almost no reaction without O_2	250
Reduction of methylene blue 22.9 N H_2SO_4	methylene blue (1.6×10^{-4})	ethyl alcohol (0.5)	3.4	3.4	no reaction	141,251
Oxidation of indigo-carmine in the presence of oxygen, 1 N H_2SO_4	O_2 ($p_{O_2}=70$ atm)	indigo-carmine (2×10^{-4})	12	12	1000*** times	168
Reduction of indigo-carmine to the leuco-base 1 N H_2SO_4	indigo-carmine (2×10^{-5})		1.7	3.4	17 times	168
Oxidation of dye at pH ~ 4	sodium nitrate (1)	indigo-carmine (2×10^{-5})	2	4	200 times ***	168
Reduction of Fe^{3+}, pH = 3	Fe^{3+} (10^{-2})	glycerol (1), glucose (1)	10—12	10—12	20 times	252
Reduction of UO_2^{2+} and oxidation of U^{4+} in 0.8 N H_2SO_4	UO_2^{2+} ($5\cdot 10^{-3}$)	UO^{2+} ($5\cdot 10^{-3}$)	4	4	—	253

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* Concentrations expressed in M.

** AET denotes S-(2-aminoethyl)-thiuronium dinitrate.

*** The value given represents the increase in the yield under conditions where the back reaction is suppressed.

hydrogen peroxide, unlike the H atoms formed directly on radiolytic breakdown of the water molecules. In the latter case no selectivity of action of the H atoms with respect to O_2 and H_2O_2 is observed. Allen concludes that the process involved in reaction (7) is the removal of an electron from the H_2 molecule, and not rupture of the H–H bond, so that the "H atom" is in fact H_2^+.

Experiments on the role of reaction (7) in the oxidation of phosphite[127] and iron(II) ions[155] and the reduction of nitrate[156] in solutions at pH 0.4 and 2–14 respectively show that saturation of the solutions with hydrogen and even increase in the H_2 pressure above the solution to 180 atm[155,156] has almost no influence on the conversion yield for these substances. Cottin, and also Shubin and Dolin, assuming that reaction (7) occurs at a high rate, concluded that atomic hydrogen, like OH, takes part in oxidation reactions. It is interesting that Dainton and Hardwick[157], in a kinetic study of the action of Fenton's reagent (a source of OH radicals) and Shubin and Dolin, in a radiation study of systems with Fe^{2+}, H_2O_2, O_2, and H_2 or CO, obtained almost identical relative rate characteristics for the fundamental reactions. Essentially identical initial assumptions were made. This might indicate that the kinetic characteristics of radicals obtained by different methods are identical. $G(-Fe^{2+})$ does not change with increase in the pressure of hydrogen above the system from 1 atm to 180 atm. Shubin and Dolin suggest that the fundamental reactions in the system are

$$OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \tag{12}$$

$$\left.\begin{array}{l} OH + H_2 \rightarrow H + H_2O \text{ and } H + H^+ \rightarrow H_2^+ \\ Fe^{2+} + H_2^+ \rightarrow Fe^{3+} + H_2 \end{array}\right\} . \tag{13}$$

The small change in the value of $G(-Fe^{2+})$ (5%) on going from degassed solutions to solutions saturated with H_2 indicates that the rates of processes (12) and (13) are of similar order of magnitude. This is also indicated by studies[129] of the oxidation of Fe^{2+} in solutions of pH 0.2–3.0†, if allowance is made for the displacement of equilibrium (2a) to the right. The oxidation yield of salts of the Sn^{2+} and Ti^{3+} type depends little on the acidity of the solution and in these cases oxidation by H atoms (in the form of H_2^+, at least) may be less probable[118,119].

In an examination of the part played by reaction (7) in the radiolytic Fe^{2+} conversion, a suggestion of Hart and Lefort[103,159] is of interest. They state that, in contrast with gas phase behaviour, where reaction (7) takes place *via* H atoms, the oxidising action of H atoms (and not H_2^+ directly) in the liquid phase can be represented, owing to the presence of the hydration shells, by the scheme

$$Fe(H_2O^{2+})_n + H = H_2 + Fe^{2+}OH + (H_2O)_{n-1}\,. \qquad (14)$$

As well as these examples on the oxidation of Fe^{2+}, other experimental features can be interpreted by taking into account the appreciable velocity of reaction (7) and the reducing properties of H atoms. Thus in acid solutions (pH ⩾ 1) saturated with hydrogen, the conversion yield of Ce^{4+} and V^V is greater than that for solutions saturated with air[82,134]. However, the oxygen molecule in the solution is an active H-atom acceptor and may produce a sharp change in the processes of radiolytic conversion of dissolved substances (Table 1). This effect of dissolved oxygen should be particularly marked with solutions of substances at relatively low concentrations‡.

Generalisation of published data on the possible oxidising properties of H atoms or the conversion of OH radicals into H atoms according to reaction (7), or the similar reaction (15) studied by Dainton and Hardwick[157],

$$OH + CO = CO_2 + H_2 + 21.2\ \text{kcal mole}^{-1}\S\,. \qquad (15)$$

indicates that there is insufficient experimental proof of these theories. All the proofs are based on the results of the kinetic study of complex systems from the initial and final products. The nature of the intermediate is not yet clear. It is possible that as a result of certain characteristics, *e.g.* ability to form "bulky" hydration sheaths, the iron ion may facilitate the transfer of the excitation from the H_2O molecules in solution to the molecules in the hydrate sheath. Some chemical reactions, including the capture of an electron from an iron(II) ion by an oxidising agent[131,161], may involve participation of the molecules of the hydration sheath.

C. The Part Played by HO_2 Radicals

At the 2nd Geneva Conference, Allen and Schwartz emphasised that one of the greatest recent achievements in radiation chemistry is the conclusion reached by Hart[162] and by Donaldson and Miller[163] that HO_2 can be regarded as a primary product of the decomposition of water molecules in the track of an ionising particle. This radical is formed in the case of γ-radiation with a yield of 0.02 and in the case of irradiation of solutions with α-particles from polonium with a yield of 0.25,[163] by a reaction involving three OH radicals

$$\begin{array}{l} OH + OH = H_2O_2 \\ H_2O_2 + OH = HO_2 + H_2O \\ \hline 3OH = HO_2 + H_2O \end{array} \qquad (16)$$

The HO_2 radical apparently may also be formed in solutions containing molecular oxygen[96]:

$$H + O_2 = HO_2. \qquad (17)$$

since the latter has a high electron affinity¶. Thus, in mechanistic studies of solutions saturated with oxygen, it is necessary to consider the possibility of reactions with HO_2. Direct methods of observing intermediate radical products (e.p.r. and luminescence analysis) have not yet enabled this radical to be identified in liquid media. In the solid phase, however, this radical has been detected[95,164]. The form of the spectrum of this radical is analogous to that of the spectrum observed in the salt NaO_2. The HO_2 radicals may reduce or oxidise dissolved substances, depending on the pH of the medium and the redox potential of the system. It has been estimated[108] that the sum of the electron affinity of HO_2 and its solvation energy is 106–136 kcal. Lefort[13] concludes that if the redox potential of the system is greater than 1.0 V, HO_2 may take part in a reduction reaction, so that its action does not differ from that of H atoms, for example, in acid solutions (0.8 *N* H_2SO_4) of Ce^{4+}. Cottin considers that in acid solutions HO_2 oxidises the intermediate product of the oxidation of phosphite to phosphate ion, whereas in neutral medium O_2^- and PO_3^{3-} (HO_2 dissociates[128] to O_2^- and H^+) do not react, due to electrostatic repulsion of the ions[127]. The possibility of dissociation of the HO_2 radical is indicated by observations by Kulkes-Pujo[98] and Dolin[102], on the formation of hydrogen peroxide in aqueous solutions at pH values from ~0 to ~14. These authors suggest that the decrease in the yield of hydrogen peroxide with increase in pH is due to conversion of the HO_2 radical to a more stable ionic form. The reducing power of the HO_2 radical increases with increase in pH[134,165,166]. The HO_2 radicals recombine to give hydrogen peroxide and molecular oxygen, and the hydrogen peroxide may act as an oxidising agent or reducing agent, depending on the pH of the medium and the reactivity of the substrate. Thus it is difficult to determine, from the nature of the final products, which reagent (HO_2 or H_2O_2) has reacted with different substances. In a number of cases, however, it has been shown that HO_2 apparently does not take part in oxidation reactions. Thus, in the oxidation of benzene[167] and the oxidation of indigo-carmine[168,169], it has been established that HO_2 does not play a direct part in the oxidation processes. Of particular interest is the study of the role of this radical in the oxidation of iron(II) ions. According to Krenz and Dewhurst's scheme, HO_2 should have three equivalents of oxidising power and should thus increase the

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† Rothschild and Allen[158] believe that the oxidation of iron(II) ions by H_2^+ ion takes place at a pH of 0.4–2.

‡ It may be concluded that molecular hydrogen plays a part in determining the conversion yield of a given substance only by comparison with the results of vacuum experiments (or with solutions saturated with inert gases).

§ From data given by Elbe[160].

¶ According to calculated data[108], the electron affinity of O_2 is 15.8 kcal $mole^{-1}$ (calculated for compounds of the KO_2 type) and the sum of the solvation energy and electron affinity for molecular oxygen is 85.8 kcal $mole^{-1}$.

oxidation yield of iron in solution in the presence of oxygen by a factor of 4 compared with the case when oxygen is absent[121]†.

$$\begin{aligned}
&Fe^{2+} + OH + H^+ \rightarrow Fe^{3+} + H_2O\\
&H + O_2 \rightarrow HO_2\\
&Fe^{2+} + HO_2 \rightarrow Fe^{3+} + HO_2^-\\
&HO_2^- + H^+ \rightarrow H_2O_2\\
&Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\\
&\underline{H^+ + OH^- \rightarrow H_2O}\\
&4Fe^{2+} + OH + HO_2 + 4H^+ = 4Fe^{3+} + 3H_2O \quad .
\end{aligned} \qquad (18)$$

In the oxidation of iron(II) ions (Fricke's dosimeter solution) in the presence of oxygen, however, $G(Fe^{3+})$ is ~1.9 times greater than *in vacuo*. Proskurnin[131] suggested the following reaction scheme

$$\begin{aligned}
&Fe^{2+} + OH + H^+ \rightarrow Fe^{3+} + H_2O\\
&H + O_2 \rightarrow HO_2\\
&2HO_2 \rightarrow H_2O_2 + O_2\\
&2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O.
\end{aligned} \qquad (19)$$

In Zansokhova and Orekhova's experiments with solutions of Fe^{2+} and O_2 of different concentrations, it was shown that at $p_{O_2} = 75$ atm, $G(Fe^{3+})$ reaches a value of ~24 equiv. and remains constant with further increase in p_{O_2} to 150 atm, that is, it corresponds to the complete utilisation of the radical products from 12 radiolysed water molecules. The decomposition of *S*-(2-aminoethyl)-thiuronium dinitrate in the presence of oxygen under the influence of γ-rays from ^{60}Co takes place with a conversion yield corresponding to the use of ~8.6 pairs of H and OH radicals at acceptor concentrations of 2×10^{-3}–5×10^{-3} M ‡.[170]

Thus, some workers suggest that the oxidising power of HO_2 radicals is realised only indirectly *via* hydrogen peroxide formed by radical recombination.

Summarising our discussion of the characteristics of the intermediate radical products controlling radiolytic reactions, we must note the following points. Since there are no direct experiments confirming the existence of H, OH, and HO_2 radicals in the liquid phase in the exact form in which they have been represented here, and since the hydration of radicals is a problem in physical chemistry which has been only slightly studied, all conclusions regarding their chemical characteristics should be regarded as hypothetical. In our opinion, the further development of radiation chemistry will depend on how well the intermediate products are studied by a combination of kinetic methods and such methods as ultra-violet, infra-red, and radiowave spectroscopy, measurement of the magnetic properties of the intermediate products, and electrochemical measurements. Kinetic studies, which by themselves give information on the disappearance of the original radiolysis products and the accumulation of the final products, cannot give unambiguous results on the intermediate stages of the process.

By generalising data for different systems, efforts are being made to reduce all kinetic characteristics of the conversion of substances in the liquid phase to the characteristics of several (perhaps even one) well-studied reactions in the gaseous phase. It is assumed that a given reaction is characterised by the same parameters in both the liquid and gas phases. Undoubtedly, with greater precision, by reducing the parameters of all radiolytic processes to one "standard", it may be possible to convert the relative rate constants to absolute values, after studies have been made of the characteristics of this "standard" reaction in the liquid phase, for example the reaction $H + D_2 = HD + D$, chosen by Riesz and Hart[171].

3. IONISED AND EXCITED WATER MOLECULES IN RADIOCHEMICAL REACTIONS OF DISSOLVED SUBSTANCES

A. Routes for the Redistribution of the Energy Absorbed by a Solution

If it is assumed that the average value of the energy of formation of one pair of ions for γ- and X-rays is 32.5 eV and the ionisation potential of the water molecule is 12.59 eV,[172] then only ~40% of the absorbed energy is used in the ionisation step. Approximately 50% of the absorbed energy is used in the excitation step. From ultra-violet spectroscopy it is known that water vapour absorbs light in the wavelength ranges 1785–1550 Å and 1392–1000 Å with absorption maxima at ~1650 Å and 1350 Å, corresponding to excitation of the bonding and non-bonding electrons[173,174]. Moreover, according to data obtained by the electron collision method, there is a further excitation level of the water molecule, corresponding to an excitation energy of 5.6 eV.[42]

A definite quantity of energy is removed by electrons whose energy is less than the first excitation potential of water for electron collision. The fraction removed by these electrons has been estimated by Platzman[60] to be approximately 15% of the absorbed energy and by others [59,175] to be ~10%.

To excite water vapour (bonding electron) in optical studies requires ~7.5 eV. If allowance is made for the fact that rupture of the H–OH bond requires ~5.2 eV,[42] it may be concluded that in both cases (excitation of the molecules to the 7.5 eV and 5.6 eV levels with corresponding redistribution of energy) the water molecule may dissociate to H and OH, so that for each ionisation step there are approximately two excitation steps.

If the radical products are to react with the dissolved substances, it is necessary, firstly, that the latter have a sufficiently high chemical activity, and secondly, that they are present in the solution in concentrations which at least exceed the concentration of radicals in the track of the ionising particle. The concentration of H and OH radicals ensuring conversion of the dissolved substances depends on the dose power of the radiation (the number of particles in unit time) and on the density of the ionisation (the number of ions per unit length of track of the ionising particle). For aqueous solutions of Ce^{III} and Fe^{III} it has been shown that the conversion yields of these substances change under the action of accelerated electrons and high dose powers reaching 10^{24} eV ml^{-1} sec^{-1}. This is due to overlap of the

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† Here no allowance is made for the oxidation of Fe^{2+} by atomic hydrogen. The oxidising properties of H atoms have been confirmed by experiments in which the atomic hydrogen was prepared by methods other than radiation methods [149,150] (Editor).

‡ Anderson and Joseph[170] suggest that the conversion of the original substance takes place by a chain mechanism, which does not, however, explain the attainment of "limiting" values of the conversion yields for the substances.

tracks and an increase in the role of radical recombination[176–178]. The ionisation density and the recombination yield for the radicals increase[48] with decrease in the path length of different types of ionising particle with the same energy.

Analysis of data on the effect of the dissolved substance concentration on its conversion yield shows that with strongly-ionised radiation the initial conversion yield for the substances increases with increase in the concentration of reagent in the range of "intermediate" concentrations ($\sim 10^{-4}$–10^{-1} M) and reaches limiting values G_{ion} (ionised) corresponding to the utilisation of the radical products from the ionised water molecules. It has been shown, in a study of the influence of ionisation density on the conversion yield for a number of dissolved substances[13,179] in the concentration range 10^{-6}–10^{-2} M, that for electromagnetic forms of radiation (γ- and X-rays) $G(-H_2O)$ is of the order of 4.5. The number of radiolysed water molecules drawn into the reaction depends on the pH of the solution, as Schwarz and coworkers have shown on the basis of their own work[52,53] and that of Schuler and Allen. In neutral medium $G(-H_2O) = 3.62$ and in acid (0.8 N H_2SO_4) ~ 4.5, which Schwarz attributes to a change in the mechanism of electron capture in the track of the ionising particles§.

We have compared the results of various studies of the dependence of the conversion yields of substances on their concentration (Table 1). We assumed that the dissolved substances are only acceptors for one or other of the radicals, irrespective of the way in which the authors of the studies regarded the conversion mechanism of a given substance. The data given in Table 1 lead to the following important conclusions.

1. With increasing concentration, the conversion yield of the dissolved substances at first increases and then, in a definite concentration range (10^{-4}–10^{-1} M) reaches "limiting" values [the first "step" on the curve giving the dependence of $G(-\text{Ac})$ on the acceptor concentration], irrespective of the nature of the dissolved substance. In most cases the conversion yield of the substances in this concentration range varies from 3 to 5 equiv. per 100 eV, that is, it corresponds to the utilisation of the conversion products from the ionised water molecules (in Table 1 the values of the yields are given per 100 eV).

2. It may be supposed that the limiting conversion yield of a dissolved substance will be reached earlier the more reactive the substance. The lack of data on the concentration dependences of the yields makes it impossible to observe this directly, except in 2–3 cases. Subsequently, by collecting analogous concentration dependences of $G(-\text{Ac})$, we may be able, by extrapolating them to the curve for the most active acceptor of H and OH radicals, to estimate in this purely chemical way the concentration of H and OH radicals avoiding recombination in the track.

3. The presence in the solution, in addition to the acceptor, of a second substance which is also a radical acceptor, for example molecular oxygen, has a considerable influence on the conversion yield for the first acceptor. The influence of the second acceptor may be competitive or sensitising, depending on the type of acceptor (see Table 2 for the sensitising effect). To obtain information on the conversion mechanism for a given acceptor then, it is necessary to make allowance for the nature of the gas saturating the solution. Unfortunately, until recently, research workers often did not attach particular importance to the presence of O_2 in the solution.

From published data it can also be concluded that in some cases, particularly in concentrated solutions and in solutions of certain substances, the conversion yield for the reagents exceeds the utilisation of the radical products from the ionised water molecules. With radical acceptor concentrations from 1 M upwards, the conversion yield of the substances sometimes also reaches limiting values of 8–9 equiv. per 100 eV. Until recently, some workers attributed this increase in the yield of radiolytic decomposition to an increase in the part played by the direct action of radiation on the dissolved substance[206,207,227,228]. A number of non-Russian scientists also attributed this phenomenon to "direct action", but they signified by this term the transfer of excitation energy from the water molecule of dissolved substance, *i.e.* they were considering the utilisation of the energy of excited water molecules. Strictly speaking, the term "direct action of radiation" should signify the effect of the interaction between the ionising particle and the molecule, accompanied by excitation or ionisation of this molecule. This is equally true of the molecule of the solvent and the molecule of the dissolved substance. The effect of direct action is directly proportional to the electronic fraction of the substances and allowance must therefore be made for it in concentrated solutions. In the estimation of this effect, the solutions are often frozen, since in this case the rate of diffusion of the radicals decreases and the part played by the direct action is reduced to a minimum. It is also assumed that the distribution of the primary products of the radiolysis of water is independent of the state of aggregation of the system (solid or liquid). Available data appear to confirm the first assumption. For example, Duane and Scheuer and Bonet-Maury observed a decrease in the yield of gaseous products from ice irradiated with α-rays, compared with that for the liquid phase. According to Haissinsky and Lefort's data[124], the oxidation yield of arsenite on irradiation of its frozen solutions (10^{-2}–10^{-1} M, -196°) by α- and X-rays is from one-thirtieth to one-half of the yield in the liquid phase. An analogous phenomenon is also observed in the irradiation of frozen nitrate solutions by γ-rays[142,230,231].

Even in frozen solutions, however, we cannot neglect the diffusion of intermediate products and the possibility of radical reactions, which have been shown to depend on the temperature of the frozen system. Lefort found that almost no H_2O_2 is detectable between -196° and -120° on irradiation of ice with X-rays. Increase in the temperature to -4° increases $G(H_2O_2)$ slightly, and it increases sharply on melting (0°).[232] In the work cited, the conversion yield for the substances was determined after the solutions had been thawed, so that during thawing, diffusion and recombination of the radical products is possible. A fundamental error has thus been introduced in the "estimation" of the effect of direct action. Moreover, it has been shown by a number of methods (radio- and optical spectroscopy) used directly under low-temperature conditions that in frozen aqueous solutions the H and OH and possibly HO_2 radicals

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§ It may be expected, contrary to Schuler and Allen's suggestion[180], that the electric fields of the ions should also influence the process of electron capture, since the introduction of ions (particularly polyvalent ions) into the solution creates a high local intensity and thus changes the trajectory of the emitted electron.

formed can move freely at temperatures of -196° (H) and -160° to -120° (OH and HO_2)[¶] and react with one another and with dissolved substances[90][†].

It has been found that the larger radicals formed from the dissolved substances disappear rapidly at a higher temperature (-70° to -90°).[104,142,231] It should be noted that the method of freezing the solutions, even with analysis of the conversion products (under conditions where the temperature at which the irradiation was carried out is maintained), is suitable for "estimating" the effect of the direct action of irradiation only if the structure of the solutions remains unchanged on freezing.

The increase in the conversion yields of dissolved substances in concentrated solutions should, in our opinion, be attributed to the part played by excited molecules, in addition to the radical products formed from ionised water molecules.

As already mentioned, an average of two excitation steps take place for every ionisation step. Obviously, when suitable conditions obtain, there may be a directed transfer of excitation energy from the solvent molecules to the dissolved substances, increasing the efficiency of the action of the radiation on the dissolved substances.

The excitation energy absorbed by the water molecules can be transferred to the dissolved substances in various ways: (1) by direct collision between an excited water molecule and a molecule of dissolved substance; (2) by direct transfer of a quantum of energy (emission and absorption); (3) by resonance transfer; etc.

The first method of energy transfer is possible since the excited water molecules formed on radiolysis are present in a higher excited state and may, in a time of the order of 10^{-13} sec and without altering their multiplicity, move to a lower excited state. The molecules exist for a considerable time in the lower triplet excited state[59] (for some substances the lifetime may reach 1 sec). In this time these molecules, by diffusing and colliding with molecules of dissolved substance, may transfer the excitation energy to the dissolved substances and thus bring about their conversion. Some workers[206,208] atribute the increase in the conversion yield for substances in concentrated solutions to the collision between excited solvent molecules and molecules of dissolved substances. The resonance transfer of excitation energy from one solvent molecule to another requires a time of the order of 10^{-13} sec.[78] Resonance transfer of energy (related to the transfer of electronic excitation energy) may take place over a distance of up to 50 Å.

These methods of transferring the excitation energy from the solvent molecules to the molecules of the dissolved substances are not, in the final analysis, related to the dissociation of the molecule to H and OH radicals and hence cannot, in our opinion, explain why additives, in solutions of certain substances which are radical acceptors, influence their conversion yields. Nevertheless, certain additives have a marked influence on the conversion yields of substances which are radical acceptors, increasing or decreasing the yield by a considerable factor, sometimes amounting to several orders of magnitude (Table 2). The surprising feature of the sensitising action of additives is that it is shown in solutions containing the additives in concentrations of $\sim 10^{-4}$ M. Change in the viscosity or temperature of the solution in this case does not influence the magnitude of the limiting yield of a given radical acceptor.

In our opinion, these effects are satisfactorily explained by Voevodskii's suggestion[236] that the transfer of excitation energy in aqueous solutions can take place along systems of hydrogen bonds or by a relay mechanism of active particle transfer.

The time required for the energy transfer is obviously determined by the stability of the excited water molecule (to H–OH bond rupture) and should apparently be of the order of $\sim 10^{-13}$ sec. An interesting feature of Voevodskii's mechanism of directed transfer of energy along a "chain" at the ends of which there are conjugated acceptors (in the terms of Proskurnin's conjugated acceptor theory) is that the H and OH radicals formed from a single excited water molecule appear at two different points in the volume of the solution. Due to the high probability of formation, by the water molecules, of different combinations of hydrogen bonds, there are a large number of chains which might transfer the excitation energy; the one chosen is that at whose ends are situated an H-radical acceptor and an OH-radical acceptor (conjugated acceptors). Thus one of the conjugated acceptors may, at a considerable distance from the other[‡], facilitate the reaction between the conjugated aqueous radical and its acceptor. It thus becomes clear why a low concentration of one of the conjugated acceptors is so effective in the process of conversion of the other and why subsequent increase in the concentration of the first acceptor in the solution does not change the conversion yield for the second.

It may be assumed, following Proskurnin[131], that in the solutions there is directed transfer of excitation energy from a water molecule in the depth of the solution to a water molecule in the hydration sheath of a given radical acceptor. At the same time it is assumed that the directed transfer of energy takes place as a result of the fact that the electronic levels of the water molecules are displaced under the influence of the forces of interaction and decrease in the direction towards the molecules of dissolved substances. According to this mechanism, the excited water molecule formed in the hydration sheath dissociates under the influence of the forces of the hydrolysed ion-acceptor to H and OH radicals which then react with it.

In the transference of energy of the excited water molecules by the radical method, it is necessary to take into account the Frank–Rabinowitch cell effect[237]; the H and OH radicals in this cell exist for approximately 10^{-13} sec[238] (time of one vibration). Thus if the recombination of H and OH radicals is to be suppressed, the radical acceptor must

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[¶] Matheson and Smaller[90] erroneously attribute the observed spectra to combined atomic hydrogen (magnitude of the hyperfine splitting ~30 G) and the OH radical. The spectrum of free atomic hydrogen (splitting between doublet lines ~ 500 G[37]) in pure ice disappears below -196°[36]. Comparison of various data[91–95,233–235] indicates that the spectrum observed[90] is probably due to the presence of OH and HO_2 radicals.

[†] By gradually increasing the temperature of the specimen[95], Siegel *et al.* were able to detect the successive disappearance of the doublet lines ($g = 2.008 \pm 0.002$) due to the presence of the OH radical at 100°K and the single broad line ($g = 2.08$) of a radical identified as HO_2 at 145°K.

[‡] The distance is obviously determined by the probability of formation of a system of hydrogen bonds *via* water molecules at a given concentration of radical acceptors in the chain: H-radical acceptor..... OH-radical acceptor, that is, the chain along which the energy transfer can take place.

be present in the solution in high concentration[238].

According to Firestone's data[239] the yield of H and OH radicals in water vapour is 11.7 per 100 eV of absorbed energy. In the gas phase the Frank–Rabinowitch cell effect is excluded and the recombination of H and OH is less probable, so that G(H,OH) corresponds to the limiting value of the decomposition yield for the water molecules $G(-H_2O) \sim$ ~ 12.

B. Proskurnin's Concept of Conjugate Radiochemical Reactions

According to Proskurnin *et al.*[86], conditions for the suppression of the recombination of H and OH in the liquid phase are produced when two conjugated H- and OH-radical acceptors are introduced simultaneously into the solution[§]; the concentration of one of the acceptors may differ from that of the other by 2–4 orders of magnitude. It is assumed that the conjugated acceptors act as follows. In their presence it becomes possible for the H and OH radicals formed as a result of the "breakdown" of the excited water molecules to overcome the cell effect and react with dissolved substances. Experiments on a number of systems of conjugated acceptors have shown that with change in the concentration of one of the conjugated acceptors (the concentration of the other should obviously be not less than the concentration of radical in the track), given values of the conversion yields of substances are reached at lower concentrations of the first acceptor than under conditions where the conjugated acceptors were not introduced[75].

It is necessary to note that the introduction of the conjugated acceptors should first of all apparently also facilitate the removal, into the reaction, of radical products from the ionised water molecules as a result of the favourable conditions for the suppression of the reverse process — reactions (4) and (5). In this case the depence of G(acceptor) on the acceptor concentration should also show characteristic "levels" of constant yields due to utilisation of the radical products from the ionised water molecules; this has been studied for the case of the glycerol–nitrate, nitrate–glycerol, and glycerol (or glucose)–methylene blue systems[75,86,241–246].

According to this theory, substances which have different individual chemical properties are identical as far as their radiolytic behaviour as acceptors of H and OH radicals is concerned. As a result, the limiting conversion yield for a dissolved substance cannot (if this is not a chain process) exceed the total conversion yield of the radiolysed water molecules, that is, 12[¶].[74,131,137,168,242] This theory can be proved, however, only from the results of an analysis of the products of the conversion of the oxidising component and the products of the conversion of the reducing component.

The results of experiments carried out in the presence of conjugated acceptors are given in Table 2, which also gives data on the conversion of certain substances in the presence of a number of organic and inorganic compounds[66,82,170,202]. The authors of these papers explain their results on the basis of various other mechanisms differing from the conjugated acceptor mechanism[†].

In our opinion, the processes in the various systems can be readily incorporated in a general scheme of conjugated radiolytic reactions without any further particular assumptions. The correctness of this suggestion will be discussed in more detail for the case of the $Tl^+–NO_3^-–Ce^{4+}$ system studied by Sworski[228], who established that in sulphuric acid ($[Ce^{4+}] = 4 \times 10^{-4}$ M) in the presence of the thallium ion (Tl^+) as OH-radical acceptor ($[Tl^+] = 10^{-5}–10^{-2}$ M), $G(Ce^{3+})$ increases by a factor of 2.5. The introduction of nitrate into the solution in sufficiently high concentration (up to 0.5 M) increases $G(Ce^{3+})$ by 3 equivalents, both in the presence and in the absence of Tl^+ ($G(Ce^{3+})$ equals 11 and 5 respectively). The nitrite ions formed from NO_3^- reduce Ce^{4+} to Ce^{3+}. The curves giving the dependence of $G(Ce^{3+})$ on the NO_3^- concentration are symbathic [change in the same sence], and Sworski concludes that the reduction of the nitrate is independent of the radiolytic conversion of the Ce^{4+} and Tl^+ ions. The mechanism of radiolysis of the NO_3^- ion involves the transfer to the nitrate ion of the excitation energy from water molecules on collision, and also from the superthermal electrons[254]. The possibility that radical products from the excited water molecules take part in the reduction of the nitrate was not considered by Sworski, although the concentration of the radical acceptor (NO_3^-) is fairly high. Sworski states that the formation of intermediate products of reduction and oxidation of the nitrate as a result of its reaction with H and OH radicals, and the participation of these intermediate products in the reduction of Ce^{4+} and oxidation of Tl^+, would lead finally to the same result as the action of H and OH on Ce^{4+} and Tl^+, that is, to a result for which allowance is already made by the action of the ionised water molecules. This conclusion is incorrect in this respect, that if the nitrate ion is not capable of oxidising Tl^+, and thallium of oxidising nitrite, because the Tl^{2+}/Tl^+ potential is lower than the NO_3^-/NO_2^- potential, then neither can the intermediate products of the oxidation bring this about.

The effect of the direct action of radiation on the nitrate ion under these conditions (up to 0.5 M $NaNO_3$), in accordance with the electronic fraction of the nitrate, does not exceed 2% (in 0.5 M) of the total absorbed energy and, as can be seen from the curve giving the dependence of $G(Ce^{3+})$ on $[NO_3^-]$, the most effective concentration range is that up to 0.2 N; subsequently, the shape of the curve is typical of that showing saturation. As far as the role of superthermal electrons in the reduction of nitrate ion is concerned, their

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[§] Another method of utilising the radicals produced from excited water molecules, which normally recombine with one another as a result of the cell effect, is by increasing the temperature of the irradiated mixture. Barelko and coworkers showed that with increase in the temperature of an irradiated benzene–water mixture, the initial rate of the yield of phenol formation increases (that is, there is an increase in the probability of removal of radicals from the cell into the reaction)[240]. In the temperature dependence, as in the case of the concentration dependence[75], G (conversion of radical acceptor) should not be greater than the utilisation of 12 radiolysed water molecules.

[¶] Clark and Coe studied the action of conjugated acceptors as early as 1937. They suggested that additives (benzene, acetic acid, etc.) by removing the energy of the activated water molecules, facilitate, for example, the reduction of Ce^{4+} [202].

[†] For example, the OH radical oxidises an organic substance according to the reaction $RH + OH \rightarrow H_2O + R$. The radical R, by reacting with another dissolved substance S, increases the conversion yield for the latter according to the scheme: $\left.\begin{matrix} S + R \\ S + H \end{matrix}\right\} \rightarrow$ reduction product.[148]

fraction corresponds to the utilisation of about 10–15% of the total quantity of absorbed energy. This shows that the superthermal electrons cannot play a very important part in the reduction of the nitrate.

In our opinion, the system studied by Sworski can be regarded as an example of the action of conjugated acceptors of H atoms (Ce^{4+}) and OH radicals (Tl^{+}) as a result of which a further quantity of H atoms are drawn from the excited water molecules into the reduction reaction of Ce^{4+} due to suppression of the recombination reaction $H + OH = H_2O$. This is indicated by the sharp increase in $G(Ce^{3+})$ when very small quantities of Tl^{+} (from 10^{-5} M) are added. $G(Ce^{3+})$ remains constant with change in the thallium ion concentration from 10^{-5} M to 10^{-2} M (compare, for example, the nitrate–glycerol system [74,110], where change in the concentration of the latter in the range 5×10^{-4} M to 0.1 M has no influence on $G(NO_2^-)$. With the introduction of the second H-atom acceptor, the nitrate ion, in concentrations greater than $[Ce^{4+}]$, the conversion yield of the latter increases due to the nitrite ions formed. In 0.5 M nitrate solution, the value reached by $G(Ce^{3+})$ coincides with data on the yield of nitrite[¶] in the presence of glycerol [74,110] corresponding to the combination of 10.5–11 H atoms from the ionised and excited water molecules.

This theory of the mechanism of action of conjugated acceptors may be confirmed only on the basis of an analysis of the products of the conversion of both the oxidising and the reducing components of the radiolysis of water. There are at present a number of reports of the attainment of limiting conversion yields of 12 for water molecules. Thus Zansokhova and Orekhov have shown that under certain conditions (high O_2 pressure above the solution), H atoms take part in the formation of products (HO_2 or H_2O_2) which are capable of oxidising Fe^{2+} ions, so that in the radiolytic reactions ~24 equivalents of oxidising power are realised, that is 12 pairs of H and OH radicals [137]. An analogous picture has also been observed for the oxidation of indigo-carmine [168].

The limiting conversion yield, that is, with the participation of 12 radiolysed water molecules, can also be reached in the radiolysis of solutions of substances which are vigorous acceptors of both radicals (H and OH), such as $ON(SO_3)_2^{2-}$ [246,255] or α,α-diphenyl-β-picrylhydrazyl-*p,p'*-disulphonic acid [256].

C. The Participation of Two Types of Excited Water Molecule in the Reactions

In some cases it has also been possible, without the presence of conjugated acceptors, to observe a limiting conversion yield for an ordinary acceptor of one of the radicals equal to the utilisation, for example, of H atoms from 12 radiolysed water molecules. Thus in the case of the irradiation of molar nitrate solutions with γ-rays from ^{60}Co at low dose powers, the yield of nitrite reaches 12 equivalents per 100 eV, whereas at ordinary dose powers $G(NO_2^-)$ = 8–9 equivalents per 100 eV. [142] It may be assumed that the lifetime of the excited water molecules (~4) taking part additionally in the reaction at low dose powers is sufficient for the purpose under these conditions. In the range of high dose powers, these molecules are probably deactivated by collision with one another. It may be concluded that in aqueous solutions two types of excited water molecule are formed, differing apparently in the level and form of their excitation (dissociating or not dissociating in the liquid phase to H and OH radicals). One type of excited water molecule reacts in the general case in highly-concentrated solutions of radical acceptors on in dilute solutions at high temperatures [75,243,244]. A characteristic feature of this type of excited water molecule is that the radicals formed at the moment of its dissociation may move apart to a considerable distance from one another and react with solute. For the second type of excited water molecule to be drawn into the reaction, the solution must contain conjugated radical acceptors or substances which are simultaneously acceptors of H atoms and OH radicals [246,255,256]. However, in concentrated solutions of nitrate, which is an acceptor of one of the radicals (H atoms), as already mentioned, it is possible, in irradiation with γ-rays of low[§] intensity [142], to attain yields which also correspond to the utilisation of approximately 12 H atoms from ionised and excited water molecules.

Data have been published indicating that the excited water molecules formed during radiolysis exist in an upper excitation level for times of the order of 10^{-13}–10^{-14} sec and then move to a lower excitation level without altering their multiplicity. The lifetime of an excited water molecule in the lower triplet excitation level is of the order of 10^{-8} sec. The comparatively long lifetime of these molecules evidently facilitates their reaction with dissolved substances.

It is also possible that a slight additional interaction, for example, a magnetic interaction, between the triplet-excited water molecule and the dissolved substance (nitrate ion) becomes sufficient for reaction to take place in concentrated solutions and with irradiation with γ-rays of low intensity. It may therefore be assumed that excited water molecules of the second type are in a triplet state. The total number of excited water molecules reacting is thus 8.

Confirmation that the excited water molecules take part in the reactions by a radical mechanism is provided by experiments on the measurement of the yield of the "molecular products" of the decomposition of water with change in the concentration of an acceptor of one or other of the radicals; in particular, the yield of H_2 with change in the concentration of nitrate ion.

As already mentioned, in the case of irradiation of aqueous solutions with γ-rays from ^{60}Co, the formation yield of the products of the radical reactions in the presence of a competing acceptor is proportional to the acceptor concentration to the power $\frac{1}{3}$. The nature of this dependence is not yet clear. The generally-accepted qualitative interpretation given by Sworski [66] is that when the concentration of radical acceptor in solution is sufficiently high (Sworski studied Br^- solutions saturated with oxygen), the acceptor, by capturing the radicals (OH) in the region of high ionisation density, decreases their recombination yield. Sworski concludes that the rate of the reaction of the bromide ion with OH radicals should be related to the average distance separating the bromide ion from the region of high ionisation density.

[‡] At the most effective glycerol concentration (5×10^{-4} M to 0.1 M) and $[NO_3^-]$ = 0.5–1 M.

[§] In very concentrated solutions of NO_3^- ions, heated to ~70°–90° and irradiated at ordinary (moderate) power doses, $G_{NO_2^-}$ also reaches ~12 equiv. per 100 eV.

It may be assumed, on the basis of general theories of reaction kinetics in the volume of the track, that in this case the rate of molecular product formation depends on the rate of the competing processes; the product of the rate constants of the main competing reactions and the corresponding reagent concentrations evidently appears in the general expression for the reaction rate, to the power 3, and the conditions for the competing reactions are averaged Thus the rate of the reaction R + R depends on the concentration of one of the competing reagents to the power $\frac{1}{3}$. In the general form

$$G_{R-R} = A + B\,[\mathrm{Ac}]^{1/3}, \qquad (a)$$

where B obviously characterises the probability of the reaction of the acceptor (Ac) with the radical product R, and A is the accumulation yield of the product of recombination of the radicals under conditions where the acceptor does not influence the formation of molecular products in the track.

As Mahlman's observations on the NO_3^-–Br^-–H_2O system[257] have shown, the relationship (a) may remain linear, that is the value of B does not change over a wide concentration range, if the concentration of dissolved substance is replaced in the expression by its activity. The value of A corresponding to the yield of molecular products under conditions where $[\mathrm{Ac}] = 0$ has been shown to depend on the composition, acidity, and temperature of the solution[66,67]. Further study of this type of dependence, in which a mutual relationship between the chemical (activity, pH, and temperature of the solution) and physical (the specific properties of the radiation and the energy of the ionising particles) factors is found, together with a physical picture of the interaction between ionising radiation and matter (described by the previously-proposed models, which do not make allowance for the chemistry of the radiolytic processes and suffer from this fundamental shortcoming) should make it possible to gain an insight into the nature of the reactions in the track and radiolytic processes in general.

In connection with the reactions by radical products formed not only from the ionised water molecules but also from the excited ones, it is interesting to consider experiments in which the relationship $G_{R-R} \propto [\mathrm{Ac}]^{\frac{1}{3}}$ was studied over a wide range of concentrations of radical acceptor (nitrate ion). With increase in the concentration of radical acceptor in the solution, as we have seen, conditions are produced for the withdrawal, into the reaction, of radical products first from the ionised and then from the excited water molecules. Since the distributions of the radical products for these cases are different, the conditions of competition between the processes H + Ac and H + H change with increase in the acceptor concentration. This also explains the inflection on the curve for the above relationship[69][¶], where the slope of the straight sections in this case should correspond to the introduction of H atoms formed from the ionised (at $[NO_3^-] < 1$ M) and excited (at $[NO_3^-] > 1$ M) water molecules. The fact that the section of the curve in the range of high nitrate ion concentrations is linear indicates that the conditions for the radical–radical and radical–acceptor reactions do not change, although the electronic fraction of the acceptor changes by approximately 2–1.5 orders of magnitude; in other words, the mechanism of nitrate reduction is retained in solutions of concentrations of 1–15.9 M.

The fairly detailed data given here on the radiolysis of the nitrate–water system, which is one of the most widely studied, indicate that the method involving the G_{R-R} *vs.* $[\mathrm{Ac}]^{\frac{1}{3}}$ relation may be useful in a particular case in the examination of the distribution in the tracks of different forms of excited water molecule.

This review shows that the interpretations given by a number of authors to explain radiolytic processes do not yet explain unambiguously the accumulated experimental data on different radiolytic processes.

Radiation chemists in recent years have begun to acknowledge the decisive part played by the reactions of the primary radical products of the radiolysis of water with the dissolved substances. At the same time the urgency of the problem of the molecular decomposition of water has disappeared.

One of the fundamental problems in radiation chemistry is the part played by excited states in the processes of radiation conversion and methods for the transfer of absorbed energy between molecules in solution.

[¶] Agreement is observed, within the limits of experimental error, between the experimental data on the yield of hydrogen obtained by Sowden[69] for the case of mixed $n + \gamma$ radiation and data for γ- and X-irradiation[70,243] of neutral and alkaline nitrate solutions at 80° and 20° with change in the dose power of the radiation over a range of about 8 orders of magnitude. This apparently indicates that the reaction taking place is the recombination of H atoms, and not the recombination of other products which then yield H atoms (for example H_2O^- in alkaline medium).

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APPLICATION OF SIMILARITY THEORY TO CHEMICAL PROCESSES

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CONTENTS

I. SIMILARITY CRITERIA IN CHEMICAL PROCESSES

Design of reaction vessels for chemical processes requires in general the simultaneous examination of the following set of differential equations, for an infinitesimal element of the vessel: (1) equation for mass balance; (2) equation for the energy balance; (3) fundamental equation of hydrodynamics or equation of motion; (4) rate equation for the reaction; and (5) equations defining the conditions for single-valuedness. Since even in the absence of chemical reactions it is impossible to solve this set of equations for the general case, similarity theory is widely used for such problems.

The application of similarity theory to chemical processes requires the simultaneous consideration of all the differential equations enumerated above supplemented by terms taking into account the presence of point sources of energy and mass, which considerably complicate this problem. The complexity lies in the fact that in general it is impossible to observe simultaneously the hydrodynamic, thermal, diffusion, and purely chemical similarity of processes accomplished in apparatus differing in size. It is characteristic of chemical processes that one system cannot be simulated by another, as would be the case with physical processes.

Thus although in the case of hydrodynamic similarity we can maintain the Reynolds number Re constant in the model and in the prototype by changing the system, we cannot do this in the case of chemical similarity since a chemical reaction of a given group of compounds cannot in general be reproduced in compounds of a different group.

As a result of this and other difficulties, similarity theory is comparatively rarely used at present for the simulation of chemical processes. It is quite widely used, however, in the generalisation of experimental results for a great variety of such processes[1].

Transformations of the set of differential equations have yielded the following criteria of chemical similarity:[2-5]

Damköhler's Group I

$$\mathrm{Da}_{\mathrm{I}} = \frac{Ul}{cw}, \tag{1}$$

where U is the reaction velocity in kmole $\mathrm{m}^{-3}\ \mathrm{h}^{-1}$, l a linear dimension in the direction of flow in metres, w the linear rate of flow in metre h^{-1}, and c the concentration of the reactant in kmole m^{-3}.

Since l/w measures the time of flow through the reaction vessel, the ratio c/U will measure the duration of the reaction at constant velocity. Consequently Da_{I} can be defined as the ratio of the residence time of the flow in the reaction vessel to the duration of the reaction occurring at a constant rate until the reactant is completely exhausted. This dimensionless group can, of course, be treated also as the ratio of the reaction velocity to the rate of flow, both expressed in the same units†, as the ratio of the concentration of substance which has reacted to the concentration introduced by the flow, or finally as the ratio of the actual

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† The group $W = w_x/U_k$, deduced by Matz,[6] in which the reaction velocity U_k is expressed in flow-rate units, or for a first-order reaction, as a rate constant; it follows from the definition of Da_{I} that the Matz number is identical with it.

length of the reaction vessel to the length which would be necessary for completion of the reaction at a constant velocity of the latter.

Damköhler Group II

$$\mathrm{Da}_{\mathrm{II}} = \frac{Ul^2}{cD}, \tag{2}$$

where D is the coefficient of molecular diffusion in m^2 h^{-1}. $\mathrm{Da}_{\mathrm{II}}$ gives the ratio of the velocity of a chemical reaction to the rate of molecular diffusion. By analogy with Da_{I}, this group can also be interpreted in terms of other quantities, as was shown above.

Damköhler Group III

$$\mathrm{Da}_{\mathrm{III}} = \frac{qUl}{c_p \gamma w \Delta t}, \tag{3}$$

where q is the heat of reaction in kcal kmole^{-1}, c_p the specific heat at constant pressure in kcal kg^{-1} deg^{-1}, γ the density of the medium in kg m^{-3}, and Δt a characteristic temperature difference, which may be, for example, the difference in temperature between the wall of the vessel and the centre of the flow or the change in temperature along the length of the reaction vessel.

It follows from Eqn. (3) that the Damköhler group III expresses the ratio of the quantity of heat evolved in the reaction to the quantity of heat transported by the flow.

Damköhler Group IV

$$\mathrm{Da}_{\mathrm{IV}} = \frac{qUl^2}{\lambda \Delta t}, \tag{4}$$

where λ is the thermal conductivity of the reaction mixture in kcal m^{-1} h^{-1} deg^{-1}.

The Damköhler group IV represents the ratio of the quantity of heat evolved by the reaction to that transferable* by thermal conduction.

Equilibrium or Steady-State Group[3]

$$\mathrm{Eq} = \frac{U_r}{U_f} = \frac{k_r c_{B_1}^{\beta_1} c_{B_2}^{\beta_2}}{k_f c_{A_1}^{\alpha_1} c_{A_2}^{\alpha_2}}, \tag{5}$$

where k_f, k_r, are the rate constants for the forward and reverse reactions respectively, and U_f, U_r the corresponding reaction velocities; c_{B_1}, c_{B_2} are the concentrations of the reaction products B_1, $B_2 \ldots$, and c_{A_1}, c_{A_2} the concentrations of the initial components A_1, A_2; β_1, β_2 are the stoichiometric numbers of the reaction products, and α_1, α_2 those of the components A_1, A_2.

The equilibrium group expresses the ratio of the absolute rates of the chemical reaction, *i.e.* of the velocities of forward and reverse reactions.

Contact Group

$$Ko = \frac{U_f}{U} = k_f c^{\Sigma a - 1} . \tau, \tag{6}$$

where τ is the residence time of the reaction mixture in the reaction vessels, and $\Sigma\alpha$ the sum of the stoichiometric numbers on the right-hand side of the rate equation. The contact group represents the ratio of one of the individual reaction rates to the overall reaction velocity.

With an irreversible reaction, for which the rate of the reverse reaction is practically zero, the constant group is identical with Da_{I}, as can be seen on expressing the reaction velocity U in the latter group in terms of the concentrations of the reactants.

It has also been proposed[3,6] that the dimensionless equilibrium constant should be used as a criterion of similarity

Arrhenius Number

$$\mathrm{Ar} = \frac{E}{RT}, \tag{7}$$

where E is the activation energy and R the gas constant. Ar represents the ratio of the activation energy to the internal energy of the system.

Radiation Group[7]

$$K_{r_1} = \frac{qcw}{C_0 e T^4}, \tag{8}$$

$$K_{r_2} = \frac{T_1}{T_2}, \tag{9}$$

where C_0 is the constant in the Stefan–Boltzmann radiation equation, e is the emissivity in this equation, and T_1 and T_2 are the temperatures of the more and the less strongly heated surfaces respectively.

Criteria (8) and (9) are obtained not from the main set of differential equations but from the Stefan–Boltzmann equation, and should be used if the reaction temperature is so high that allowance has to be made for the heat transmitted by radiation.

The radiation group (8) represents the ratio of the quantity of heat evolved by the reaction to that transmitted by radiation, while group (9) represents the ratio of the temperatures of the radiating surfaces.

Hydrodynamic-Acceleration Group:[8]

$$K_h = \frac{w}{lU\Delta V}, \tag{10}$$

where ΔV is the increase in volume accompanying the reaction, in m^3 kmole^{-1}.

The hydrodynamic-acceleration group K_h expresses the ratio of the volume of reaction mixture passing through the vessel in unit time to the change in volume due to the occurrence of the chemical reaction. It takes into account the acceleration of the motion of the reaction mixture in the vessel resulting from the chemical reaction. Like the radiation and some other groups, it specifies the conditions under which the process takes place.

Generalised Thermal Group.

$$K_t = \frac{qcw}{q_{st}}, \tag{11}$$

where q_{st} is the heat flow across unit area of the heat-exchange surface in kcal m^{-2} h^{-1}. This group expresses the ratio of the quantity of heat evolved in the reaction to that which is evolved or is supplied through the heat-exchange surface. The usefulness of introducing the group K_t is due to the fact that the flow of heat through unit heat-exchange surface is an independent variable, which the experimenter can change independently of the scale.

In the analysis of chemical processes dimensionless groups are quite often employed which are analogous to those considered above but somewhat modified for application to particular processes. Thus the following criterion has been introduced:[9,10]

$$K_{int} = \int_0^\tau c^{n-1} k_n [T(\tau)]\, d\tau\,, \tag{12}$$

where k_n is the rate constant for a reaction of the n-th order, represented as a complicated function of time (it is assumed that the temperature varies with time according to a definite law). The criterion K_{int} is obviously a modified form of Da_I, in which the velocity of the chemical reaction, which varies with time, is taken in integral form. This latter method of representing dimensionless groups is useful in all cases in which the properties of a chemical system change with time (or in space, when integration is carried out with respect to volume).

For the case of a heterogeneous chemical reaction, the following group was introduced:[11]

$$K_{het} = \frac{k'_n \delta}{D} c^{n-1} = \frac{k'_n l}{D} c^{n-1} f(\mathrm{Re},\ \mathrm{Pr})\,, \tag{13}$$

where k'_n is the rate constant of the heterogeneous chemical reaction per unit area of interface, and $\mathrm{Pr} = wl/a\mathrm{Re}$ is the Prandtl number, in which $a = \lambda/c_p\gamma$ is the thermal conductivity. This group uses as linear dimension and thickness of the diffusion layer δ:

$$\delta = l/\mathrm{Nu} = lf(\mathrm{Re},\ \mathrm{Pr}).$$

It is readily seen that the group K_{het} is a modified form of Da_{II} in which δ is used as l and the reaction velocity is based on unit surface separating the phases.

The dimensionless multiplier φ used in calculations on absorption processes belongs to the same type of modified groups:[12]

$$\varphi = \frac{x}{\tanh x}, \tag{14}$$

where

$$x = \delta \sqrt{k_1/D} \tag{15}$$

Eqn. (14) is obtained by the simultaneous solution of the diffusion and rate equations for a first-order reaction. The dimensionless group (14) is called the Hatta number (Ha). It is readily shown that Ha is a quantity which is functionally related to Da_{II}:

$$\mathrm{Ha} = \frac{x}{\tanh x} = \frac{\delta \sqrt{k_1/D}}{\tanh \delta \sqrt{k_1/D}} = \frac{\sqrt{k_1 \delta^2/D}}{\tanh \sqrt{k_1 \delta^2/D}} = \frac{\sqrt{Da_{II}}}{\tanh \sqrt{Da_{II}}}\,. \tag{16}$$

Dimensionless ratios are often used as defining criteria. Among these the following may be mentioned:[3,6,13]

$$X_1 = \frac{c_i}{c_0} \tag{17}$$

$$X_2 = \frac{c}{c^*}, \tag{18}$$

where c_1 and c_0 are the concentrations at the inlet and the outlet respectively of the reaction vessel, c is the concentration actually reached in a given reaction vessel, and c^* is the equilibrium concentration. Eqn. (17) represents the ratio of the concentrations at the inlet and the outlet of the reaction vessel, and (18) is a measure of the relative yield of product.

Instead of concentration ratios, use can be made of the ratios of any other physical properties[10] characteristic of the system and linked with the concentration, such as viscosity, density, etc. This method can be employed to specify conditions for the control, regulation, and automation of the process.

Apart from the similarity criteria enumerated above, deriving from the original set of differential equations, the general dimensionless-group equation should include criteria characterising hydrodynamic similarity $\mathrm{Re} = wl/\nu$, thermal similarity $\mathrm{Pe} = wl/a$, diffusion similarity $\mathrm{Pe_d} = wl/D$, etc. In the case of irreversible reactions, the general dimensionless-group equation for a chemical process then has the form.

$$Da_I = f(Da_{II},\ Da_{III},\ Da_{IV},\ \mathrm{Pe},\ \mathrm{Pe_d},\ \mathrm{Re},\ K_i \ldots), \tag{19}$$

where K_i are groups specifying the conditions under which the process takes place [see Eqns. (8)–(10)]. Instead of Da_I, the dimensionless ratios (17) and (18) can also be used.

In the case of reversible reactions the dimensionless-group equation is of the form

$$\mathrm{Eq} = f(\mathrm{Ko},\ Da_{II},\ Da_{III},\ Da_{IV},\ \mathrm{Pe},\ \mathrm{Pe_d},\ \mathrm{Re},\ K_i)\,. \tag{20}$$

(The Ar groups should not increase the number of groups in the general dimensionless-group equation, since it characterises the change with temperature of quantities already occurring in groups $Da_I - Da_{IV}$ considered earlier).

Since several of the dimensionless groups in Eqns. (19) and (20) contain the same parameters, the number of groups can be reduced by combining them.

Da_{II}, for example, can be represented as the product $Da_I\,\mathrm{Pe_d}$:

$$Da_{II} = \frac{Ul^2}{cD} = Da_I\ \mathrm{Pe_d} = \frac{Ul}{cw}\ \frac{wl}{D} = \frac{Ul^2}{cD},$$

and Da_{III} as the product $Da_I\ qc/c_p\gamma\Delta t$:

$$Da_{III} = \frac{qUl}{c_p\gamma w\,\Delta t} = Da_I\ \frac{qc}{c_p\gamma\,\Delta t} = \frac{Ul}{cw}\ \frac{qc}{c_p\gamma\,\Delta t} = \frac{qUl}{c_p\gamma w\,\Delta t}\,.$$

The expression $qc/c_p\gamma\Delta t$ was defined by D'yakonov[3] as a criterion establishing the proportionality of the temperature and concentration gradients. Let us denote this group as follows‡:

$$K_{tc} = \frac{qc}{c_p\gamma\,\Delta t}\,. \tag{21}$$

Da_{IV} can be represented as the product $Da_I \mathrm{Pr} K_{tc}$:

$$Da_{IV} = \frac{qUl^2}{\lambda\,\Delta t} = Da_I \mathrm{Pe} K_{tc} = \frac{Ul}{cw}\ \frac{wl}{a}\ \frac{qc}{c_p\gamma\,\Delta t} = \frac{qUl^2}{\lambda\,\Delta t}\,.$$

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‡ In some papers[14] the group K_{tc} has been termed the Boltzmann number (Bo).

TABLE 1. **Scheme for the derivation of the fundamental criteria of chemical similarity.** *

Equation for the conservation of mass				
rate of change with time	rate of change due to convection	rate of change due to diffusion	rate of change due to chemical reaction	
$-\partial c/\partial\tau$	$-(w\ \mathrm{grad})\ c$	$+D\ (\mathrm{Div\ grad})\ c$	$+U$	$=0$
c/τ	wc/l	Dc/l^2	U	
	←	$\mathrm{Da_I} = \frac{Ul}{cw}$	→→	
		← $\mathrm{Da_{II}} = \frac{Ul^2}{cD}$	→→	

Equation for the conservation of energy				
rate of change with time	rate of change due to convection	rate of change due to thermal conduction	rate of change due to chemical reaction	
$-\partial t/\partial\tau$	$-(w\ \mathrm{grad})\ t$	$+a\ (\mathrm{Div\ grad})\ t$	$+qU/c_p\gamma$	$=0$
t/τ	wt/l	at/l^2	$qU/c_p\gamma$	
	←	$\mathrm{Da_{III}} = \frac{qUl}{c_p\gamma w\Delta t}$	→→	
		← $\mathrm{Da_{IV}} = \frac{qUl^2}{\lambda\Delta t}$	→→	

Rate equation for reaction			
net reaction velocity	rate of forward reaction	rate of reverse reaction	
$-dc/d\tau$	$+k_f\ c_{A_1}^{\alpha_1} c_{A_2}^{\alpha_2} \cdots$	$k_r\ c_{B_1}^{\beta_1} c_{B_2}^{\beta_2} \cdots$	$=0$
c/τ	$k_f\ c^{\Sigma\alpha}$	$k_r\ c^{\Sigma\beta}$	
← $\mathrm{Ko} = k_f c^{\Sigma\alpha-1}\cdot\tau$	→→		
	← $\mathrm{Eq} = \frac{k_r\ c^{\Sigma\beta}}{k_f\ c^{\Sigma\alpha}}$	→→	

* A single arrowhead points to the denominator, and a double one to the numerator.

Since Pe and $\mathrm{Pe_d}$ can be represented by the products RePr and $\mathrm{RePr_d}$, division of $\mathrm{Da_{II}}$, $\mathrm{Da_{III}}$, and $\mathrm{Da_{IV}}$ by $\mathrm{Da_I}$, $\mathrm{K_{tc}}$, and Re brings Eqns. (19) and (20) to the form

$$\mathrm{Da_I} = f(\mathrm{K_{tc}}, \mathrm{Pr}, \mathrm{Pr_d}, \mathrm{Re}, \mathrm{K}_i), \quad (22)$$

or

$$X_1 = \frac{c_i}{c_0} = f(\mathrm{Da_I}, \mathrm{K_{tc}}, \mathrm{Pr}, \mathrm{Pr_d}, \mathrm{Re}, \mathrm{K}_i), \quad (23)$$

and

$$\mathrm{Eq} = f(\mathrm{Ko}, \mathrm{K_{tc}}, \mathrm{Pr}, \mathrm{Pr_d}, \mathrm{Re}, \mathrm{K}_i), \quad (24)$$

or

$$X_2 = \frac{c}{c^*} = f(\mathrm{Ko}, \mathrm{K_{tc}}, \mathrm{Pr}, \mathrm{Pr_d}, \mathrm{Re}, \mathrm{K}_i). \quad (25)$$

In the case of heterogeneous chemical processes, some groups (*e.g.* Re, Pr, and $\mathrm{Pr_d}$) can be repeated as many times as there are phases involved in the process. However, the presence of a large number of dimensionless groups, and hence of the relevant physical quantities, in Eqns. (21)–(24), makes it difficult to keep all the criteria constant.

It is impossible, for example, to maintain simultaneous constancy of Re and $\mathrm{Da_I}$ in the model and in the prototype, since the linear velocity which occurs in both these groups varies in different ways with the linear dimension which also is present in both groups. It follows from the condition for the constancy of Re that the linear velocity is inversely proportional to the linear dimension, whereas from the corresponding condition for $\mathrm{Da_I}$ it should be directly proportional to the linear dimension. Thus the direct simulation of chemical processes by obtaining the general dimensionless-group equation proves to be impossible in practice§. This has led to the necessity for approximate simulation. The derivation of the main chemical criteria is shown in the accompanying scheme (Table 1).

II. APPROXIMATE SIMULATION

Approximate simulation is based on the principle of including in the dimensionless-group equation only those groups which relate to the slowest stage of the process. A thermodynamic treatment of this question has been given by D'yakonov[3] showing that these equations need include only those groups related to the non-equilibrium or steady-state stages of the process.

A result of isolating the rate-determining stage in the general dimensionless-group equation is the disappearance of incompatible groups (*e.g.* $\mathrm{Da_I}$ and Re), so that it becomes theoretically possible to find a functional relationship between the groups. The theoretical possibility of isolating the rate-determining stage is based on the fact that in many cases a complex process consists of several successive stages. The slowest of such stages is rate-determining.

In the kinetics of chemical reactions complicated by heat and mass transfer it is usual to distinguish[16] reactions occurring in the kinetic range, where the rate-determining step is the chemical reaction itself, reactions occurring in the diffusion range, in which the rate-determining stage is the diffusion of reactants to the reaction zone, and finally reactions occurring in the diffusion–kinetic range, where the rates of diffusion and of chemical change are comparable in magnitude. The last is the most difficult case to simulate. Heat exchange within the system takes place at the same time as the chemical changes, and therefore cannot be rate-determining. The methods for ascertaining the rate-determining state[17, 18] are indicated below.

1. From the temperature coefficient of the overall rate of process. If a 10° change in temperature causes a two- or threefold change in the overall velocity of the process (as follows from the Arrhenius law), the chemical reaction itself is the rate-determining step. If, however, a 10° change in temperature causes an overall change in rate of 30%, material transfer is rate-determining. In intermediate cases the reaction occurs in the diffusion–kinetic range.

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§ An artificial decrease in the activity of the catalyst in the simulation of heterogeneous chemical processes[15] is of no practical significance.

2. From the apparent reaction order. If the reaction order differs from unity, the chemical reaction is rate-determining. If, however, the order of reaction is unity, the nature of the rate-determining step remains uncertain since mass transfer also depends on the first power of the concentration.
3. From the dependence of the overall rate of the process on the hydrodynamic conditions under which it is carried out. If the velocity of the process does not depend on the hydrodynamic conditions, the chemical reaction itself is rate-determining; but if there is such a dependence, the rate-determining step involves either mass transfer or both mass transfer and chemical change together (*i.e.* the reaction takes place in the diffusion–kinetic range).

1. Simulation of Processes Occurring in the Kinetic Range

For a process occurring in the kinetic range, the dimensionless-group equation contains only chemical dimensionless groups, and for irreversible chemical reactions Eqns. (22)–(25) become

$$\mathrm{Da_I} = \frac{Ul}{cw} = \text{const.}, \qquad (26)$$

or

$$\mathrm{X_1} = \frac{c_i}{c_0} = f(\mathrm{Da_I}) \; . \qquad (27)$$

As noted above, the concentration ratio can be replaced by the ratio of a suitable physical property of the system.

For reversible chemical reactions, Eqns. (24) and (25) become

$$\mathrm{Eq} = f(\mathrm{Ko}), \qquad (28)$$

$$\mathrm{X_2} = f(\mathrm{Ko}) \; . \qquad (29)$$

Two methods have been suggested[3] for generalising experimental data on chemical reactions whose mechanism is unknown. In the first method the experimental data are used to plot a graph of Eq against τ (the residence time). It is then found that experimental results relating to different temperatures and pressures fall on quite definite curves.

The discovery of a functional relationship (28) is equivalent to combining all the curves into a single curve. Remembering that $\mathrm{Ko} = k\tau c^{\Sigma\beta-1}$ and that $k = f_1(T)$, and assuming that the reaction takes place in the gas phase, *i.e.* that $c = f_2(p)$, we can find the activation energy and the order of the reverse reaction by measuring the distance between these curves. From these values we can find the group Ko and plot the relationship Eq = f(Ko), *i.e.* combine all the curves into a single curve.

The other method of generalisation consists in finding a functional relationship between the reaction velocity and the thermodynamic potential, used in this method as a driving force: *i.e.* it consists in establishing experimentally a relationship of the form $u = k^* f(G/RT)$, where k^* is a coefficient having the dimensions of reaction velocity, which in many cases can be regarded as constant. The expression G/RT is analogous to the Arrhenius number, G being the thermodynamic potential.

It follows from Eqns. (26)–(29) that, when a process occurs in the purely kinetic range, it is independent of the geometrical shape and size of the system, provided that the time in the reaction vessel remains constant, *i.e.* that l/w = constant. (This conclusion, however, is no longer valid in the case of a chain reaction in which initiation or termination of the chains take place on the walls of the apparatus, or if the chemical reaction is accompanied by considerable evolution of heat.)

The effect of heat exchange on reactions occurring in the kinetic range can be allowed for by introducing the criteria $\mathrm{K_{tc}}$ and $\mathrm{K_t}$, so that the dimensionless-group equation for the kinetic range becomes

$$f(\mathrm{Da_I}, \mathrm{K_{tc}}, \mathrm{K_t}) = 0 \; . \qquad (30)$$

As noted above, heat exchange cannot be isolated as a rate-determining stage. In passing from one scale to another in the case of a strongly exothermic reaction it is desirable to avoid complications due to the formation of a temperature gradient in the reaction vessel. An element of a large reaction vessel is therefore usually taken as the model, with the provision that the large reactor consists of several identical elements (*e.g.* if the latter is a system of tubes filled with catalyst, one of these tubes is used as such an element).

Although there is no need to maintain geometrical similarity in the simulation of chemical processes occurring in the kinetic range, nevertheless, in several cases this is done for purely technical reasons (*e.g.* in the modelling of stirrers[12]).

When reactions accompanied by the evolution or the absorption of a large quantity of heat take place in geometrically similar apparatus, a complication arises from the fact that the ratio of the heat-exchange surface to its volume decreases with increase in size of the vessel, and hence the conditions for the supply and removal of heat are impaired. In order to achieve approximate simulation in such cases, it is recommended[7] that the flow of heat through unit heat-exchange surface of the model reactor should be artificially reduced by making the vessel more adiabatic. This can be achieved either by increasing the thickness of the layer of insulation on the heat-exchange surface of the laboratory vessel or by providing additional heating. In this way it is possible, in spite of the difference in the heat-exchange surface in the model and in the prototype, to ensure that the same quantity of heat is supplied in unit time to unit volume in both.

A further difficulty in the simulation of continuous reaction vessels is that in many forms of continuous apparatus, different portions of the reaction mixture reside for different periods of time, *i.e.* a definite residence-time distribution is established in such apparatus. It has a particularly adverse effect on the course of the process when the main chemical reaction is complicated by subsequent secondary reactions. In the simulation of continuous chemical processes, therefore, it is necessary to keep the residence-time distribution the same in order to obtain the same yield in the model and in the prototype.

In the study of heterogeneous chemical reactions (determination of reaction mechanisms, optimum temperature conditions, etc.) it is important to eliminate or minimise resistance to diffusion in the laboratory apparatus, *i.e.* to ensure that the reaction should take place in the kinetic range. In this case it is very important to be able to estimate how effectively such diffusion resistance has been eliminated, and hence the accuracy of the experimental values for the reaction velocity.

Application of similarity theory enables the following method[20] to be used. The variation of the overall reaction velocity U with the mass flow rate G is determined for a constant residence time in the reaction zone¶. It follows from the above that the kinetic range should correspond to that portion of the curve $U = f(G)$ along which U becomes constant and does not depend, or depends only slightly, on further increase in G. In the latter case the proportion of diffusion resistance can be estimated as follows. On equating U to the quantity of matter transported through the diffusion layer, we obtain

$$U = k_g F_m \Delta p_A, \tag{31}$$

where U is the reaction velocity expressed as the number of moles of component A which react in unit time per unit mass of catalyst, k_g the coefficient of mass transfer in the gas phase, F_m the surface area per unit mass of the catalyst, and Δp_A the difference in the partial pressures of component A across the diffusion layer.

On the other hand, the mass-transfer coefficient k_g occurs in the generalised equation of Chilton and Colburn[21] as modified by Hougen[20] for application to heterogeneous reactions:

$$j_d = \left(\frac{k_g\, M_m p}{G}\right)\left(\frac{\mu}{\rho D_{Am}}\right)^{2/3} = a_0\left(\frac{\sqrt{F_p}G}{\mu}\right)^{-n}. \tag{32}$$

On solving Eqns. (31) and (32) simultaneously for $\Delta p_A/p_A$ we obtain

$$\frac{\Delta p_A}{p_A} = \frac{1}{a_0}\left(\frac{\sqrt{F_p}U\, M_n p}{p_A \mu F_m}\right)\left(\frac{\mu}{\rho D_{Am}}\right)^{2/3}\left(\frac{\sqrt{F_p G}}{\mu}\right)^{n-1}. \tag{33}$$

In the above equations p is the total pressure, p_A the partial pressure of component A, M_m the mean molecular weight of the gas passing through which has a dynamic viscosity μ and density ρ, D_{Am} the mean diffusion coefficient of component A in the gas phase, a_0 a proportionality coefficient, $(F_pG)^{\frac{1}{2}}/\mu$ a modified Re groups, and F_p the surface area of a single catalyst particle.

The first of the groups on the right-hand side of Eqn. (33) is a modified form of Da_I. In fact

$$p_A/p = c'\sqrt{F_p} = l$$

(where c' is the concentration in mole fractions); and $\mu F_m \propto v^*$ m sec^{-1} is some characteristic velocity, since the units of μ are kg sec m^{-2} and those of F_m are m^2(kg$_{\text{mass}}$)$^{-1}$ = = m^3(kg$_{\text{force}}$)$^{-1}$ sec^{-2}. Thus Eqn. (33) can be reduced to the form

$$\frac{\Delta c'}{c'} = \frac{1}{a_0}\,\mathrm{Da_I Pr_d^{2/3} Re}^{n-1}, \tag{34}$$

where a and n depend on Re, their values being as follows:

$$\text{for } \mathrm{Re} < 620 \quad a_0 = 2.44 \quad n = 0.51,$$
$$\text{for } \mathrm{Re} > 620 \quad a_0 = 1.25 \quad n = 0.41.$$

On the basis of Eqns. (33) and (34) $\Delta p_A/p_A$ is plotted against $\mathrm{Da_I Pr}^{\frac{2}{3}}/a_0$, the Re numbers being taken as parameter. This yields straight lines passing through the origin and having different slopes for each value of Re.

Having specified the accuracy with which the true rate of the chemical reaction should be determined, and the corresponding pressure difference $\Delta p_A/p_A$ in the diffusion layer, we can find the appropriate rate of flow for the given value of the expression $\mathrm{Da_I Pr}^{\frac{2}{3}} a$. Thus, for example, if in a particular investigation the value of the reaction velocity, allowing for the diffusion resistance, should be accurate to within 10%, we take $\Delta p_A/p_A = 0.1$; and if the accuracy is to be within 1%, then correspondingly $\Delta p_A/p_A = 0.01$. The temperature gradients in the boundary layer may be estimated in an analogous fashion.

2. Simulation of Processes Occurring in the Diffusion Range

In this case the dimensionless-group equations (22) and (23) are of the form

$$\mathrm{Da_I} = f(\mathrm{Re},\ \mathrm{Pr}). \tag{35}$$

Here, too, the ratios X_1 and X_2 can be used as defining criteria.

The simulation of processes occurring in the diffusion range thus reduces to the use of the well-known criteria of physical similarity, [1] and will not be considered here.

3. Simulation of Processes Occurring in the Diffusion–Kinetic Range

These comprise primarily heterogeneous chemical processes — catalysis and absorption accompanied by chemical reaction. Owing to the incompatibility of the groups Da_I and Re occurring in Eqns. (22) and (23), a fundamental difficulty arises here in using such equations for simulation. This is increased by the need to take account of the resistance in each phase by introducing appropriate criteria for each. This difficulty can, however, be eliminated.

Usually the same catalyst (having the same particle-size distribution) or the same packing is employed in the model and in the prototype. The volume elements formed by grains of catalyst or packing in contact therefore remain the same in the model and in the prototype. It must not be forgotten, however, that at low values of the ratio d_a/d_0 (of the diameter of the apparatus d_a to the grain diameter d_0) the effect of the walls must be taken into account. The results obtained in the model may be transferred directly to the prototype if the experimental conditions (charge per unit cross-section of the apparatus, temperature, concentration, etc.) are kept constant and if d_a/d_0 is sufficiently high.

If the reaction is accompanied by the evolution of large quantities of heat, the reaction vessel must be divided into elementary units of small diameter in order to increase the ratio of the external heat-exchange surface of the reaction vessel to its volume, and thus to prevent any possible production within the vessel of inadmissibly high temperatures. In such cases a reaction vessel comprising a system of narrow tubes is normally employed. The diameter is selected by calculating the permissible temperature difference between the centre of flow in the tube and its walls under conditions of a maximum yield[22]. In the simulation, considerations (indicated previously) relating to the use of Eqn. (30) must be taken into account.

At the present time the overall reaction velocity in the diffusion–kinetic range is determined by means of equations analogous to those employed in calculations on processes of simple (physical) mass transfer uncomplicated

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¶ Fulfilment of this last condition is equivalent to the assumption that an increase in the mass flow rate is accompanied by a proportionate increase in height of the catalyst layer.

by chemical reaction, *i.e.* the overall rate constant is determined as the reciprocal of the sum of the resistances in each of the stages. The individual mass-transfer coefficients for each phase are determined from the appropriate dimensionless-group equations for the phases.

In the case of a heterogeneous catalytic reaction, the overall reaction velocity can thus be determined from the equation[23]

$$G_a = k_e c_g = \frac{1}{\frac{1}{k_g} + \frac{C}{d_0}\frac{1}{k' F_0 \rho_a \psi}} \times c_g\ , \qquad (36)$$

where k_e is the effective rate constant of the heterogeneous reaction, c_g the concentration of the chemically active component in the gas phase, k_g the mass-transfer coefficient in the gas phase, C/d_0 the ratio of the surface area of a catalyst grain to its volume (for spherical grains $C = 6$), k' the rate constant of the reaction per square centimetre of total surface of the catalyst, F_0 the total surface per gram of catalyst, ρ_a the apparent density of the porous mass of catalyst, and ψ the degree of utilisation of the catalyst surface, which allows for the drop in concentration of a given component within the pores of the catalyst.

A very rapid reaction takes place almost exclusively on the outer surface of the catalyst grains, so that $\psi \to 0$. A very slow reaction involves the whole surface of the catalyst grains, including that within the pores, so that $\psi = 1$. Thus ψ in Eqn. (36) is always less than unity.

The second term in the denominator takes account of the resistance to diffusion within the pores of the catalyst grains in addition to the purely chemical resistance. In some papers[24] these two types of resistance are considered separately, and the denominator then comprises three terms. Such a form of the equation, however, is less convenient for practical use.

Similar equations are used for calculations on absorption processes[25,26] accompanied by chemical reactions, and also for calculations on heterogeneous catalysis in the liquid phase[24].

Thus, in the case of a slow irreversible chemical reaction of the first order occurring in the bulk liquid phase, the following equation was suggested[27]:

$$G_a = k_{og}\left(p - \frac{p_{liq}}{\cosh x}\right) = \frac{1}{\frac{1}{k_g} + \frac{1}{\varphi H k_{liq}}}\left(p - \frac{p_{liq}}{\cosh x}\right), \qquad (37)$$

where H is Henry's constant, k_{og} the overall coefficient of mass transfer for the gaseous phase, p_{liq} the partial pressure of the absorbed material in the bulk of the liquid phase.

In contrast to heterogeneous catalysis, chemical reactions accompanying absorption processes usually occur, not at the interface, but in a zone adjacent to the interface and having a finite thickness. Therefore chemical change and diffusion in the liquid phase do not occur successively but simultaneously. This leads to a continuous diminution in the diffusion flux of the component undergoing absorption as it passes through the diffusion layer in the liquid phase. This factor has led to some complication of the form of Eqn. (37) compared with Eqn. (36).

The use of the groups Ha has been proposed for calculations on absorption processes accompanied by reactions of the second and higher orders.[13,28]

III. SCALE EQUATIONS

The so-called scale equations[2,7,14,29,30] are a consequence of the application of the principles of approximate simulation. Scale equations are obtained by equating in pairs the groups characterising the conditions under which the process occurs in the model and in the prototype, and cancelling out from these groups the physical constants which have the same values in the model and in the prototype.

Let us consider the derivation of the scale equation for a chemical process occurring in the kinetic range and complicated by heat exchange. As was shown above, the general dimensionless-group equation for such a process can be written in the form

$$f(\mathrm{Da_I},\ \mathrm{K_{tc}},\ \mathrm{K_t}) = 0\ . \qquad (30)$$

To maintain similarity of the rate-determining stage in the model and in the prototype it is necessary to keep all the groups which characterise it constant. In order to obtain the scale equations, all the groups in Eqn. (30) must be equated in pairs for the model and for the prototype:

$$(\mathrm{Da_I})_m = (\mathrm{Da_I})_p\ , \qquad (38a)$$

$$\frac{U_m l_m}{c_m w_m} = \frac{U_p l_p}{c_p w_p}\ , \qquad (38b)$$

where the subscripts m and p refer to the model and to the prototype respectively.

Cancelling out the physical constants and remembering that the concentration (*e.g.* initial or final) remains unchanged in the model and in the prototype, we obtain for the groups $\mathrm{Da_I}$:

$$\frac{l_m}{w_m} = \frac{l_p}{w_p}\ . \qquad (39)$$

It follows from this equation that the residence time should be identical in the model and the prototype.

For the groups $\mathrm{K_t} = qcw/q_{st}$ we obtain

$$\frac{w_m}{w_p} = \frac{(q_{st})_m}{(q_{st})_p} = \frac{l_m}{l_p} \qquad (40)$$

The groups $\mathrm{K_{tc}} = qc/c_p\gamma\Delta t$ includes only physical constants, and therefore yields no new relationships.

Scale equations can be obtained in an analogous manner for other rate-determining stages. Thus in the case of a heterogeneous chemical reaction occurring in the purely kinetic range, the dimensionless groups of the scale equation contain the activity of the catalyst α and the space velocity s sec^{-1}. In this case we have

$$(\mathrm{Da_I})_m = (\mathrm{Da_I})_p \quad \text{or} \quad \frac{k'_m f(c_m)\,\alpha_m}{w_m} = \frac{k'_p f(c_p)\,\alpha_p}{w_p}\ , \qquad (41)$$

where k' is the rate constant for the heterogeneous chemical reaction calculated for unit surface of the catalyst.

On introducing space velocities s sec^{-1}, we obtain

$$\frac{k'_m f(c_m)\,\alpha_m}{(d_0)_m s_m} = \frac{k'_p f(c_p)\,\alpha_p}{(d_0)_p\ s_p}\ , \qquad (42)$$

where d_0 is the grain diameter of the catalyst. With $\alpha_m = \alpha_p$ and $(d_0)_m = (d_0)_p$ (the grain size is assumed to be constant, since a change in it usually alters the activity of the catalyst), we obtain

$$s_m = s_p, \qquad (43)$$

i.e. the space velocity should be the same in the model and in the prototype. It has also been suggested[30] that, in deriving the scale equation for a chemical reaction occurring in the kinetic range, when heat exchange must be taken into account, the $\mathrm{Da_{IV}}$ groups could be used in combination with the thermal group Nu. Let us consider the derivation of such an equation applied to a homogeneous chemical reaction carried out in a tubular reaction vessel.

On equating

$$\frac{(\mathrm{Da_{IV}})_m}{\mathrm{Nu}_m} = \frac{(\mathrm{Da_{IV}})_p}{\mathrm{Nu}_p},$$

we obtain

$$\frac{q_m U_m d_m^2}{\lambda_m \Delta t_m \mathrm{Nu}_m} = \frac{q_p U_p d_p^2}{\lambda_p \Delta t_p \mathrm{Nu}_p}, \tag{44}$$

where d_m and d_p are the diameters of the tubular reactors employed as model and as prototype respectively. If the amount of material processed in the prototype is n times greater than in the model, we obtain the following relationship:

$$n d_m^2 w_m = d_p^2 w_p, \tag{45}$$

whence

$$n = \frac{d_p^2 w_p}{d_m^2 w_m}. \tag{46}$$

Since it is necessary to keep the $\mathrm{Da_I}$ groups constant in the model and in the prototype, we obtain

$$\frac{U_m l_m}{c_m w_m} = \frac{U_p l_p}{c_p w_p}. \tag{38b}$$

Remembering also that identical yields can be obtained in the model and in the prototype provided that the rise in temperature ΔT is identical in the two systems, and that for a tubular reaction vessel

$$\mathrm{Nu} = \mathrm{const.Re}^{0.8}, \tag{47}$$

we obtain from Eqn. (44)

$$\frac{d_m^{1.2}}{w_m^{0.8}} = \frac{d_p^{1.2}}{w_p^{0.8}}. \tag{48}$$

From Eqn. (38b), it follows that

$$\frac{l_m}{w_m} = \frac{l_p}{w_p}. \tag{39}$$

Simultaneous solution of Eqns. (45), (48), and (39) finally yields

$$d_p = d_m n^{0.286}, \tag{49}$$

$$l_p = l_m n^{0.428}, \tag{50}$$

$$w_p = w_m n^{0.428}. \tag{51}$$

In conclusion, let us consider the derivation of scale equations for a homogeneous chemical reaction taking place in the gas phase in a continuously operating tubular reaction vessel. To derive the scale equations, it must be remembered that the pressure drops in the model and in the prototype should be equal, since otherwise the stream of gas would be accelerated in the reaction vessel in which the pressure drop was the greater, and the residence time in this vessel would be reduced. A difference in pressure gradients can be neglected only when the total pressure in the system is high compared with the drop. If the coefficient of drag of the gas is written in the form

$$\Delta p = c_1 \lambda \frac{l}{d} w^2, \tag{52}$$

putting

$$\lambda = c_2 \mathrm{Re}^{-m} = c_3 (wd)^{-m}, \tag{53}$$

and remembering that

$$V_{\mathrm{sec}} = c_4 d^2 w, \tag{54}$$

where $c_1 - c_4$ are constants, simultaneous solution of Eqns. (52)–(54) yields

$$\frac{l_p}{l_m} = \left(\frac{d_p}{d_m}\right)^{\frac{1+m}{3-m}}, \tag{55}$$

$$\frac{(V_{\mathrm{sec}})_p}{(V_{\mathrm{sec}})_m} = \left(\frac{d_p}{d_m}\right)^{\frac{7-m}{3-m}}. \tag{56}$$

Under conditions of turbulent flow we can put $m = 0.16$, and substitution of this value in Eqns. (52) and (53) yields

$$\frac{l_p}{l_m} = \left(\frac{d_p}{d_m}\right)^{0.41}, \tag{57}$$

$$\frac{(V_{\mathrm{sec}})_p}{(V_{\mathrm{sec}})_m} = \left(\frac{d_p}{d_m}\right)^{2.41}. \tag{58}$$

Thus the ratio of the dimensions of the model and of the prototype perpendicular to the direction of flow should be greater than the ratio in the direction of flow. Hence the model tubular reactor should have a greater length: diameter ratio than the prototype. For laminar flow in both reactors, the Poiseuille equation can similarly be used to deduce the following scale equation:

$$\frac{d_p}{d_m} = \left[\frac{(V_{\mathrm{sec}})_p}{(V_{\mathrm{sec}})_m}\right]^{1/3}. \tag{59}$$

Since the ratio of the lengths of the reaction vessels is equal to the ratio of their diameters, geometrical similarity must be maintained in this case, and since the ratio of the space velocities is equal to the ratio of the cubes of the diameters of the vessels, the space velocity should be proportional to the reactor volume.

An attempt has been made[14] to model reaction vessels with respect to geometrical and regime parameters. The fundamental parameters used were the diameter of the apparatus d_a and the linear rate of flow w. These parameters were used in the form of ratios of corresponding quantities in the model and in the prototype. The space velocity V_{sec}, the geometrical ratio d_a/l, Re, $\mathrm{Da_I}$, the pressure drop Δp, and the thermal flux through the heat-exchange surface $\pi d_a l \alpha$ or jl/d_a, where α is the thermal emission coefficient and j the heat-transfer coefficient, were used as supplementary parameters. The ratio of these in the model and in the prototype was expressed in terms of the ratio of the fundamental parameters. It was assumed that the height of the apparatus varies in direct proportion to the linear rate of flow, *i.e.* that the mean residence time in the apparatus is kept constant.

The following notation is employed in Table 2: ratio of reactor diameters $d_p/d_m = x$, ratio of reactor lengths $l_p/l_m = y$, ratio of linear flow rates $w_p/w_m = z$, and ratio of space velocities $(V_{\mathrm{sec}})_p/(V_{\mathrm{sec}})_m = \beta$. These ratios have been termed

TABLE 2.

Parameter compared	Scale factor	$x^2z=\beta\ y/z=1$	$x=1$	$x=\sqrt[3]{\beta}$	$x=\sqrt{\beta}$	$x=\beta$
d, diameter	x	x	1	x	x	x
l, length	y	β/x^2	β	x	1	$1/x$
w, velocity	z	β/x^2	β	x	1	$1/x$
$V_{sec}=\pi d^2w/4$	x^2z	$=\beta$	β	x^3	x^2	x
d/l	x/y	x^3/β	$1/\beta$	1	x	x^2
$\mathrm{Re}=\rho wd/\mu$	xz	β/x	β	x^2	x	1
$\mathrm{Da_I}=k_1l/w=$ $=k_1V/V_{sec}$	y/z	$=1$	1	1	1	1
Δp	$yz^2/x\,(xz)^m$	$\beta^3/x^7\,\mathrm{Re}^m$	β^{3-m}	x^{+2-2m}	x^{-m-1}	x^{-4}
$\pi dl\alpha$	$y\,(xz)^{1-m}$	$\beta^2/x^3\,\mathrm{Re}^m$	β^{2-m}	x^{+3-2m}	x^{-m+1}	x^{-1}
jl/d	$y/x\,(xz)^m$	$\beta/x^3\,\mathrm{Re}^m$	β^{1-m}	x^{-2m}	x^{-m-1}	x^{-2}

scale factors (see Table 2). The scale factors giving the ratios between the fundamental parameters are related by the equations

$$x^2z=\beta\cdot \tag{60}$$

It was therefore possible to obtain different scales by expressing the ratio of one of the fundamental parameters in the model and in the prototype in terms of the ratio of other parameters. Thus when $z=\beta$, we have $x=1$ (Table 2, column 4). In practice this case corresponds to constancy of diameter in model and in protype.

When $z=x$, we have $x=\beta^{1/3}$ (Table 2, column 5). This corresponds to geometrical similarity of model and prototype, since as a result of the equality $z/y=1$, also $y=x$, *i.e.* the ratio of the lengths of model and prototype is equal to the ratio of their diameters.

Similarly, when $z=1$ (Table 2, column 6), we have $x=\beta^{1/2}$. This means that model and prototype are of equal length, when the ratio of their outputs is equal to the ratio of their cross-sections.

Finally, when $z=x^{-1}$ (Table 2, column 7), we have $x==\beta$. This case corresponds to the maintenance of hydrodynamic similarity in model and in prototype. Actually the condition $zx=1$ means that the ratio of the Re in the model and in the prototype is unity (since physical constants cancel out, the ratio of the groups proves to be equal to the produce zx). Table 2 gives scale relationships showing how the ratio of the supplementary parameters in model and prototype is expressed in terms of the ratios of the fundamental parameters for each of the four examples discussed above. This attempt represents a modified method of using scale equations.

For the particular case of a heterogeneous catalytic reaction occurring in the gas phase over a fixed bed of catalyst, the following rate equation can be obtained[6]:

$$V_{sec}dy=U_k(1-y)\,dF\cdot \tag{61}$$

where y is the degree of conversion, dF a surface element of the catalyst, and U_k is the velocity of the chemical reaction expressed in flow-rate units. Eqn. (61) allows the dimensions of the apparatus to be linked with the chemical-reaction velocity and the proportion of material undergoing reaction.

This equation is valid on the following assumptions: the chemical-reaction velocity U_k is constant over the whole length (height) of the apparatus, the quantity of material undergoing change varies along the length of the apparatus in proportion to the difference between the actual composition at a given cross-section of the apparatus and that which is theoretically possible, the reaction is of the first order, and it takes place without change in volume. Integration of Eqn. (61) yields

$$1-y=e^{-U_kF/V_{sec}}\ . \tag{62}$$

Eqn. (62) can be written in the form of the following relationship between three dimensionless groups:

$$A=\Gamma W,\ . \tag{63}$$

where $A=-\epsilon/ln(1-y)$ gives the degree of conversion expected when a given fraction of the catalyst surface is utilised. The physical significance of this criterion is obviously equivalent to that of the concentration ratio X_1 or the relative yield X_2.

$\Gamma=(l\sigma)^{-1}$ is a criterion of geometrical similarity of the catalyst surface. It is equivalent in physical meaning to the criterion of geometrical similarity.

$W=w/U_k$ is a criterion of kinetic similarity, equivalent in physical significance to $\mathrm{Da_I}$, as already remarked above (see p.297). In the above equations ϵ is the fraction of catalyst surface utilised, σ the specific surface of the catalyst, and w the linear rate of flow.

The applicability of the dimensionless-group equation (63) is subject, however, to the same limitations as those postulated in deriving the original rate equation. Furthermore, it is obviously supposed here that the reaction is occurring in the kinetic range, and consequently that mass transfer has no retarding effect on it. An analogous equation for a first-order homogeneous reaction was suggested by Pozin[31] in deducing an equation for the efficiency of a chemical apparatus (by which he meant the degree of approximation, achievable in the apparatus, to the theoretically possible results). Pozin's equation for this case is

$$\eta=1-e^{-k_1fl/V_{sec}}\ , \tag{64}$$

where η is the efficiency of the chemical apparatus, f the cross-section of the flow (apparatus), and l the length of flow.

Examination of Eqns. (62) and (64) shows their similarity, since, in the case of a first-order reaction, the efficiency of the apparatus is identical with the degree of conversion, as is evident from the definition of the former; the two equations therefore have the same meaning. They relate the dimensions of the apparatus to the rate of flow and the degree of conversion. In using them it must be borne in mind, however, that neither equation takes account either of complications due to heat and mass transfer or of the distribution of residence times within the apparatus.

IV. SOME PARTICULAR CASES OF THE PRACTICAL USE OF SIMILARITY THEORY

Examples of the practical application of similarity theory to chemical processes occurring in the kinetic range are given in D'yakonov's monograph[3]. Thus generalisation of experimental data on the synthesis of ammonia at different temperatures yields the following dimensionless-group equation:

$$X_2=\left(\frac{b\,\mathrm{Ko}}{1+b\,\mathrm{Ko}}\right)^{1/2}\ , \tag{65}$$

where b is a constant. Generalisation of experimental results for this synthesis at different temperatures and pressures gave the following equation:

$$\mathrm{Eq} = \left(\frac{b\,\mathrm{Ko}}{1 + b\,\mathrm{Ko}}\right)^2 \qquad (66)$$

Similarly, experimental data on the oxidation of sulphur dioxide at different temperatures yielded the equation

$$X_2 = \frac{\mathrm{Ko}}{1 + \mathrm{Ko}} \cdot \qquad (67)$$

Using Eqn. (67), the isotherms on a so-called Knitsch diagram could be combined into a single curve represented by this equation.

Generalisation of experimental data on the thermal decomposition of calcium and cadmium salts and oxides[30] showed that all these decomposition processes follow the dimensionless-group equation

$$\frac{1}{\mathrm{Ko}} = 1 - \mathrm{Eq}. \qquad (68)$$

Generalisation of experimental results for the polymerisation of vegetable oils (in the production of drying oil[10]) gave equations of the form

$$\Phi = f(\mathrm{K_{int}}), \qquad (69)$$

where Φ is the ratio of the physical constants used to control the industrial process (viscosities, densities, etc.).

These equations were expressed graphically. Their practical application enabled the control of the process to be considerably improved and production losses to be eliminated. In addition, a scheme was proposed for the automation of this process, based on the use of Eqn. (69).

Analysis of experimental data on flame propagation in a tube filled with a fuel gas mixed with various inert gases having considerably different coefficients of diffusion and of thermal conductivity yielded[32] the following dimensionless-group equation:

$$\left(\frac{w}{\sqrt{ak_2c_2}}\right)\left[\left(\frac{qc_1}{\gamma c_pT}\right)^{3.36}\left(\frac{D}{a}\right)^{0.6}\right] = f\left(\frac{c_1}{c_2}\right), \qquad (70)$$

where w is the velocity of flame propagation, a the temperature conductivity, and c_1 and c_2 are the concentrations of the reactants (methane and oxygen). This equation was also put in a graphical form.

It is easy to show that the group $w(ak_2c_2)^{-\frac{1}{2}}$ represents the ratio $(\mathrm{Pe}/\mathrm{Da_I})^{\frac{1}{2}}$:

$$\left(\frac{w}{\sqrt{a_2kc_2}}\right)^2 = \frac{w^2l}{ak_2c_2l} = \frac{wl}{a}\ \frac{w}{k_2c_2l} = \frac{\mathrm{Pe}}{\mathrm{Da_I}} \cdot \qquad (71)$$

D/a, however, is obviously the ratio of the groups $\mathrm{Pe}/\mathrm{Pe_d}$. The remaining groups have already been discussed previously.

Thus the general dimensionless-group equation can be written in the following form:

$$\left(\frac{\mathrm{Pe}}{\mathrm{Da_I}}\right)^{0.5}\left[(\mathrm{K_{tc}})^{3.36}\left(\frac{\mathrm{Pe}}{\mathrm{Pe_d}}\right)^{0.6}\right] = f(X_3), \qquad (72)$$

where $X_3 = c_1/c_2$, or in a more general form:

$$f = (\mathrm{Da_I},\ \mathrm{Pe},\ \mathrm{Pe_d},\ \mathrm{K_{tc}},\ X_3) = 0 \cdot \qquad (73)$$

In the generalisation of experimental data on chemical reactions occurring in the diffusion range, *e.g.* in the absorption of ammonia by sulphuric acid, the processes are described by equations of the form

$$G_a = k_{og}F\Delta p_{av}, \qquad (74)$$

where $k_{og} = k_g$ is the general mass-transfer coefficient for the gas phase, and Δp_{av} is the mean driving force in the apparatus, expressed in partial-pressure units. Here, as always, the mass-transfer coefficient is found from the appropriate dimensionless-group equation for physical absorption.

In a recent paper[33], generalised equations were obtained for physical sorption in packed columns taking account of the hydrodynamic state of the two-phase system.

For readily soluble gases:

$$\mathrm{Nu}\,A\,\mathrm{Re}_g^m\mathrm{Pr}_g^n(1 + f). \qquad (75)$$

For sparingly soluble gases:

$$\mathrm{Nu}\,A_1\,\mathrm{Re}_{\mathrm{liq}}^{m_1}\mathrm{Pr}_{\mathrm{liq}}^{n_1}(1 + f), \qquad (76)$$

where f is a factor of the hydrodynamic state of the two-phase system. The values of A, m, n, and f depend on the hydrodynamic regime of the two-phase system.

Normal dimensionless-group equations for mass transfer are used to determine the velocity of chemical processes occurring in a solid–gas system. For example, similarity theory has been used to show[34] that the rate of combustion of carbon is governed by the rate of supply of oxygen through the external diffusion layer in the gas phase.

Dimensionless-group equations for diffusion can be used also for absorption accompanied by a slow chemical reaction, when the absorbed component passes through both diffusion layers (in the gas and the liquid phases) without reacting or almost without reacting, *i.e.* when the reaction takes place mainly in the bulk of the liquid phase. The reaction then affects only the vapour pressure of the component absorbed in the bulk of the liquid phase, without changing the form of the equation. An example of such a process is the absorption of ethyl formate by caustic soda solution[25].

As an example of the use of similarity theory in calculations on chemical processes occurring in the diffusion–kinetic range, we can cite the dimensionless-group equation

$$\mathrm{Nu} = C\,\mathrm{Ha}\,\mathrm{Re}^{3/4}\mathrm{Pr}^{1/3}, \qquad (77)$$

obtained in an analysis of experimental data on the absorption of carbon dioxide by solutions of alkalis — sodium carbonate and diethanolamine[12,28]. The design of a catalyst column for the production of phenol by Raschig's method[22] may be cited as an example of the partial application of similarity theory in calculations on heterogeneous catalytic processes. A method which we have already described[20] is suggested here for taking into account the diffusion resistance. A considerable number of examples of the partial use of similarity theory in calculations on chemical processes taking place in the diffusion–kinetic range using a great variety of equipment, can also be found in other papers[35–38].

As an example of the experimental verification of the possibile uses of scale equations, mention may be made of the work of Bretsznajder[30], who confirmed experimentally the possibility of simulating reaction vessels by means of scale equations. Experiments were carried out on a pseudo-homogeneous system, a suspension of zinc dust in a solution of dichromate in sulphuric acid, in two tubular reaction vessels, the dimensions of which were established in conformity with the requirements of the scale equations. The output of the two reaction vessels differed fivefold. The scale equations (49)–(51) were used as a starting point. These equations are discussed in the present review, and are obtained from the condition for a constant temperature rise in the two vessels. The experiments confirmed that, when the geometrical relationships between the dimensions of model and prototype and the flow rates found from the scale equations were used, the actual increase in temperature in the prototype coincided with the specified value within the limits of experimental error.

Conditions have been formulated for the simulation of packed apparatus for gas–liquid and vapour–liquid systems[39] where diffusion has a decisive effect, *i.e.* for processes occurring in the diffusion range. This becomes possible because the phase-inversion condition in the packing leads to definite values of (1) the velocities at every cross-section of the column, (2) the pressure drop, and (3) the distribution of liquid in the column. Thus every element of a layer of packing reproduces the layer elements arranged on either side of it.

When the same systems are being analysed in the model and in the prototype, the conditions for the simulation of packed columns reduce to the following.

For the heights of the layer of packing:

$$\frac{h_1}{h_2}=\left(\frac{\sigma_2}{\sigma_1}\right)^{1.3}\left(\frac{F_{c_1}}{F_{c_2}}\right)^{1.3} \tag{78}$$

For the column diameters:

$$\frac{D_1}{D_2}=\left(\frac{\sigma_1}{\sigma_2}\right)^{0.25}\left(\frac{F_{c_2}}{F_{c_1}}\right)^{0.75}. \tag{79}$$

For the pressure drops:

$$\frac{\Delta p_1}{\Delta p_2}=\left(\frac{\sigma_1}{\sigma_2}\right)^{0.3}\left(\frac{F_{c_2}}{F_{c_1}}\right)^{0.3}, \tag{80}$$

where σ is the specific surface of the packing (filling) in m^2/m^3, and F_c is the free cross-section or free volume of the packing in m^3/m^3.

In a recent paper[40] conditions have been found for the simulation of chemical processes by the use of Eqns. (75) and (76).

The application of similarity theory to chemical processes opens up opportunities for generalising experimental data on chemical reactions occurring in the kinetic, diffusion, and diffusion–kinetic ranges. In some cases similarity theory makes it possible to simulate chemical processes by the use of scale equations and criteria in integral form.

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CYCLIC ACETYLENES AND THEIR REACTIONS

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CONTENTS

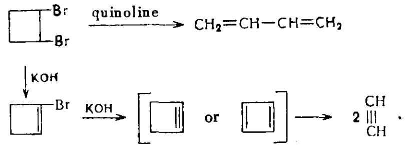
The stereochemistry of cyclic compounds has recently developed considerably. Its important achievements include the concepts of conformational analysis, non-classical strain, transannular reactions, "proximity effect", and so on. A good deal of work has also been devoted to the study of cyclic compounds with strained rings. Systems in which great strain is manifested in their chemical behaviour are particularly interesting.

Cyclic hydrocarbons containing a triple bond in the nucleus are one such group of compounds. The present review deals with the methods of synthesis, properties, and steric structure of cyclic acetylenes; it covers the literature published on this subject up to the end of 1959.

1. POLYMETHYLENE RINGS CONTAINING AN ACETYLENIC BOND

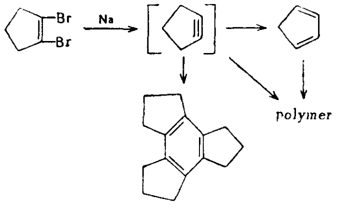
Markovnikov[1] started studying methods of preparation and structure determination of cyclic acetylenes more than sixty years ago. In 1895 he prepared a hydrocarbon, C_7H_{10}, to which he ascribed the cycloheptyne structure. As the development of stereochemistry was just beginning, this discovery aroused great interest. As a result, a number of other papers followed, which were devoted to the synthesis of cyclic acetylenes. We shall consider the subject in order of increasing number of carbon atoms in the ring.

Cyclobutyne. Willstätter[2] attempted to prepare cyclobutyne from 1,2-dibromocyclobutane:



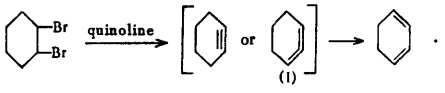
Butadiene was formed when quinoline was used in this reaction, whereas solid potassium hydroxide yielded acetylene. An unstable intermediate compound, which spontaneously undergoes rupture of the ring, is formed in this reaction, but it is impossible to say at present whether it is cyclobutyne, cyclobutadiene, or some other compound.

Cyclopentyne. Favorskii and Shostakovskii[3] studied the action of sodium on 1,2-dibromocyclopent-1-ene.



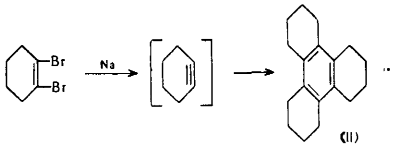
They isolated two products: tricyclopentenobenzene and cyclopentadiene, the latter only as an adduct with maleic anhydride. This indicates that the unstable cyclopentyne is formed in the reaction, but either trimerises to a benzene derivative or isomerises to cyclopentadiene.

Cyclohexyne. Crossley[4] was the first to point out the possibility of forming cyclohexyne or cyclohexa-1,2-diene (I) as intermediate products in reactions:



(I)

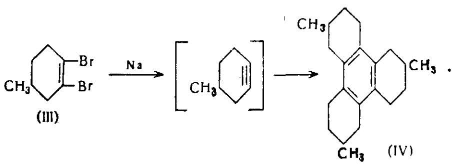
Favorskii and Bozhovskii[5] used the reaction of sodium on 1,2-dibromocyclohex-1-ene to prepare dodecahydrotriphenyl (II):



(II)
+
polymer

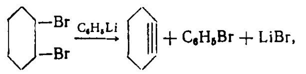
Its properties were identical with those of the material obtained previously by Mannich[6].

In his work with 1-methyl-3,4-dibromocyclohex-3-ene (III), Domnin[7] isolated a derivative of dodecahydrotriphenylene (IV), whose structure he determined by oxidation to mellitic acid:

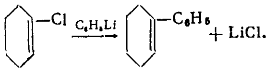


(III) (IV)
+
polymer

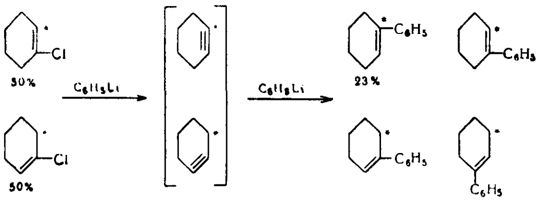
Wittig's work[8] on the reaction of phenyl-lithium with halogen derivatives of hydrocarbons also deals with cyclohexane derivatives. Phenyl-lithium does not react with fluorocyclohexane, but it removes bromine from 1,2-dibromocyclohexane:



and it substitutes phenyl for chlorine in 1-chlorocyclohex-1-ene:

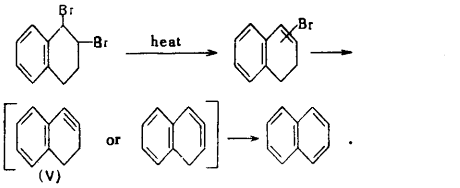


The author has not succeeded in isolating the organolithium compounds, and has ruled out the formation of cyclohexyne in this reaction owing to excessive strain. Scardiglia and Roberts[9] recently repeated the reaction of phenyl-lithium with 1-chlorocyclohex-1-ene, labelled with ^{14}C (marked in the formula by an asterisk).



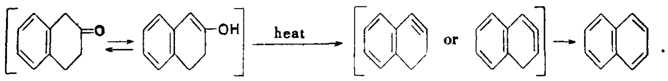
If the ^{14}C content in the starting material is 100%, then every one of the four equally probable reaction products should contain 25% ^{14}C. In fact 1-phenylcyclohex-1-ene-1-^{14}C contained 23% ^{14}C, thus confirming that the reaction proceeds through the intermediate formation of cyclohexyne.

Straus and Rohrbacher[10] explain the mechanism of the elimination of hydrogen bromide from 1,2-dibromotetralin to give naphthalene by the formation of a cyclic acetylene (V);

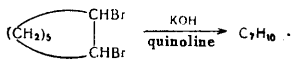


(V)

They explain Bamberger's preparation of naphthalene by distilling β-tetralone[11] in the same way:

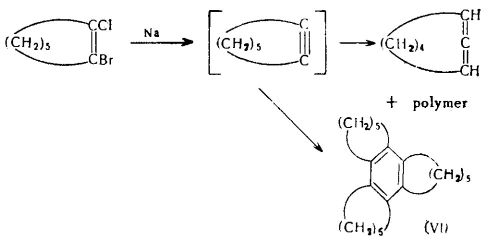


Cycloheptyne. Markovnikov[1] studied the elimination of bromine from 1,2-dibromocycloheptane by means of potassium hydroxide and quinoline:



The resulting hydrocarbon had the formula C_7H_{10} and reacted with sodium, bromine, and HI. The author ascribed to it the structure of cycloheptyne. Willstätter[12] repeated Markovnikov's experiments, but obtained only traces of hydrocarbon and was not able to determine its structure.

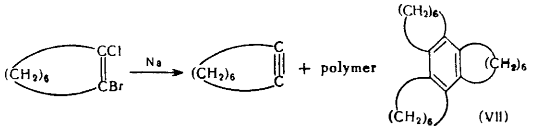
Domnin[3] used the action of sodium on 1-chloro-2-bromocyclohept-1-ene:



(VI)

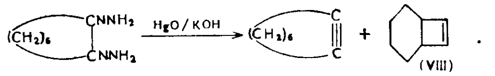
The products were cyclohepta-1,2-diene and tricycloheptenobenzene (VI), indicating that cycloheptyne is formed only as an intermediate product.

Cyclo-octyne. The first attempt to prepare cyclo-octyne, by reacting 1,2-dibromocyclo-octane with potassium hydroxide[13], failed. Cyclo-octyne was first obtained by Domnin[14,15] from the reaction of 1-chloro-2-bromocyclo-oct-1-ene with sodium:



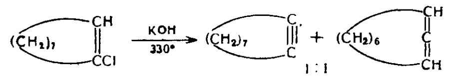
(VII)

In addition to cyclo-octyne a polymer was isolated which contained tricyclo-octenobenzene (VII). In 1953 Blomquist[16,17] also obtained cyclo-octyne. To prepare cyclic acetylenes he used the Curtius method, *i.e.*, the oxidation of α-dihydrazones by mercuric oxide in the presence of alkali:



Cyclo-octyne is a colourless liquid which oxidises in the air, and reacts explosively with azidobenzene. An isomeric hydrocarbon was also isolated which was suggested to be bicyclo[4,2,0]oct-7-ene (VIII).

Cyclononyne was first prepared by Blomquist[17]. The action of potassium hydroxide on 1-chlorocyclonon-1-ene gave a mixture of hydrocarbons which could not be separated.

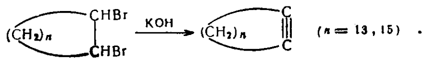


Decomposition of the cyclonona-1,2-dione dihydrazone yielded 39% pure cyclononyne. Prelog[18] obtained the same result.

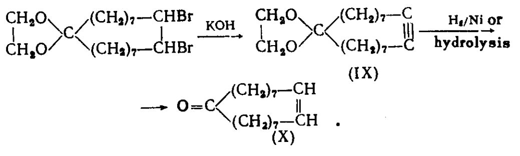
Cyclodecyne was synthesised by Blomquist[19]. Using the Favorskii method (reaction of the unsaturated chlorobromide with sodium), he obtained a 1 : 3 mixture of acetylene and allene; cyclodecyne was obtained in 67% yield by the decomposition of the dihydrazone. It was also prepared independently by Prelog[20].

Cycloundecyne and cyclododecyne were prepared by Prelog[21] by the decomposition of the corresponding dihydrazones.

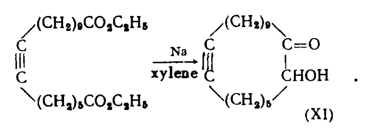
Ruzicka[13] obtained cyclopentadecyne and cycloheptadecyne by reacting the corresponding 1,2-dibromocycloalkanes with alkali:



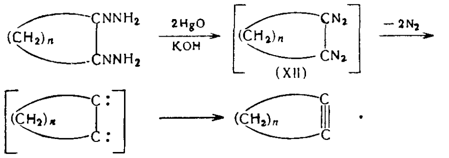
A derivative of cycloheptadecyne (IX) was used by Stoll[22] to synthesise the compound of musk odour, civetone (X):



Derivatives of cyclo-octadecyne (XI) were prepared by Epsztein by cyclisation of a diester to an acyloin[23]:



It follows from the above that there are at present three methods for the synthesis of cyclic acetylenes: 1) the classical method of elimination of hydrogen bromide from 1,2-dibromoalkanes by the action of alkali[13,22]; 2) the Favorskii method[5,14] in which halogens are removed from 1,2-dihalogenoalk-1-enes by means of sodium (the mechanism of this reaction is probably identical with that of the Würtz–Fittig reaction); 3) oxidation of the dihydrazones of α-diketones[17], a very good preparative method for pure cyclic acetylenes, giving, however, progressively smaller yields as the number of atoms in the ring decreases. A diazo compound (XII) may possibly be formed as an intermediate product in this last reaction, being subsequently converted to the acetylenic hydrocarbon with the elimination of two molecules of nitrogen:



A comparison of the reaction products obtained by the Favorskii method and by the oxidation of dihydrazones is interesting; in the former acetylenes are always formed together with isomeric allenes, but in the latter only acetylenes. Favorskii[3] considered the formation of allenes to be the result of a rearrangement caused by strain in the acetylenes. Blomquist[19] showed, however, that the Favorskii method yielded a mixture of cyclic acetylenes and isomeric allenes even in the case of cyclodecyne, which is strainless. Consequently, either the allene is formed together with the acetylene (as a side-reaction) or the acetylene formed isomerises under the action of sodium. Favorskii[24,25] observed such an isomerisation in the case of but-z-yne:

$$CH_3C{\equiv}CCH_3 \overset{Na}{\rightleftarrows} CH_3CH{=}C{=}CH_2 \overset{Na}{\longrightarrow} CH_3CH_2C{\equiv}CH.$$

The equilibrium is shifted completely to the side of but-1-yne, because it is converted in the reaction mixture into

TABLE 1. Physical properties of cyclic acetylenes.

Compound	B.p., °C	n_D^{20}	d_4^{20}	$\lambda_{C\equiv C}$ μ	Reference
Cycloheptyne	120—1				1
Cyclo-octyne	72—6/100	n_α^{15} 1.4627	0.8407	4.73*	14,15
	157.5—8/740	1.4850	0.868	4.53	16
Cyclononyne	177—8/740	1.4890	0.8972	4.54	17
	61—2/13	n_D^{23} 1.4880			18
Cyclodecyne	203—4/740	1.4903	0.8975	4.53	19
	78.5/12	1.4950	0.8973	4.41	20
				4.58	21
Cycloundecyne		1.4875			21
Cyclododecyne	106—9/11			~4.5	13
Cyclopentadecyne	158—9/14	1.4910	0.8843		13
Cycloheptadecyne	127—8/0.25	1.4869	0.8840		

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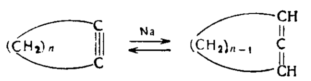
* Raman spectrum ν = 2112 cm^{-1}.

the sodium salt. It appears, therefore, that with cyclic acetylenes only the first stage of the Favorskii scheme is achieved.



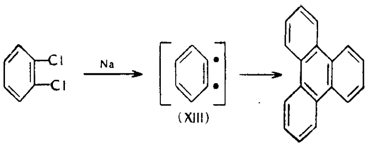
The strain in cyclic acetylenes with a small number of atoms in the ring favours isomerisation, but is apparently not a decisive factor.

The physical properties of cyclic acetylenes are given in Table 1. The cycloheptyne obtained by Markovnikov[1] was not characterised sufficiently. On the basis of boiling point (120°–121°), it could also have been cyclohepta-1,2-diene[3], b.p. 118°–119°, or cyclohepta-1,3-diene, b.p. 120°–121°.

Favorskii[3] summarised the results obtained by saying that only cyclic acetylenes with eight or more atoms can exist as monomers. Rings with fewer atoms which contain a triple bond isomerise into more stable systems. His views are, clearly, still valid.

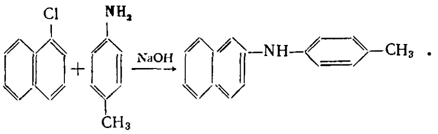
2. AROMATIC COMPOUNDS CONTAINING AN ACETYLYNIC BOND

The discovery of the triple bond in aromatic nuclei was made in connection with studies of the Würtz–Fittig reaction. In studying the action of sodium on *o*-dichlorobenzene, Bachman[26] isolated triphenylene amongst the reaction products. He considered it to result from the formation and polymerisation of the *o*-phenylene free radical (XIII):

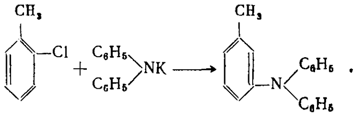


His results were confirmed by Blum-Bergman[27].

On the strength of his results with organometallic compounds, Wittig[28] later accepted the existence of benzene containing two free bonds, and suggested for this compound the name dehydrobenzene, which we shall use. The existence of dehydrobenzene as an intermediate product in reactions has been generally accepted. The concept of the transient formation of dehydrobenzene has been used to explain the reaction mechanism of certain nucleophilic substitutions in aromatic compounds. Rearrangements accompanying substitution reactions in the benzene ring were observed many years ago, the new substituent entering the position *ortho* to the group displaced. For example, Kym[29] found that the action of *p*-toluidine and alkali on 1-halogenonaphthalene gave a 2-substituted naphthalene derivative:

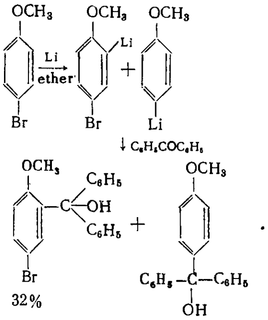


Hausermann[30] observed a rearrangement in the reaction of diphenylaminopotassium with *o*-chlorotoluene:

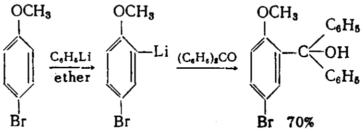


Many such examples are given in the review by Bunnet and Zahler[31]. They could not be explained using the chemical theories existing at that time, but the course of a number of such reactions is now accounted for by the properties of dehydrobenzene.

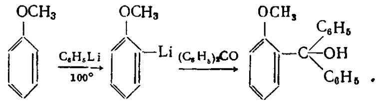
a) The discovery of dehydrobenzene arose from Wittig's observation[32] that in aromatic compounds an alkali metal is capable of replacing not only a halogen atom, but also, when the molecule contains electron-withdrawing substituents, a hydrogen atom in the position *ortho* to such substituents:



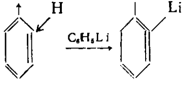
The structure of the organometallic compounds was shown by condensation with benzophenone. It was also shown that phenyl-lithium reacts more readily than lithium itself:



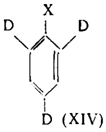
and that substitution of hydrogen is equally possible in compounds not containing a halogen:



Wittig explained the mobility of the hydrogen atom in the *o*-position of anisole by polarisation of the C–H bond under the influence of the electron-withdrawing substituent:



Roberts[33] confirmed the mobility of the *o*-hydrogen atom using exchange between hydrogen and deuterium in deuterated halogenobenzenes (XIV).

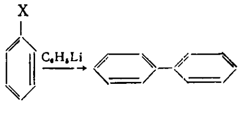


(XIV)

X = F, Cl, Br.

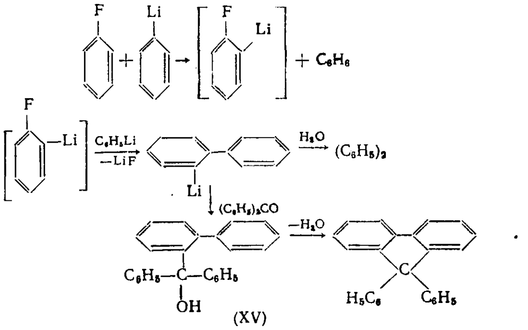
He observed that in fluorobenzene 100% of the deuterium is replaced by hydrogen, whereas under identical conditions chloro- and bromobenzene exchange only 50–70% of the deuterium. Deuterium in the *ortho*-position of fluorobenzene underwent exchange 1000 times faster than that in the *meta*- or *para*-positions[34].

Wittig verified this hypothesis[35] in the following reaction of halogenobenzenes:

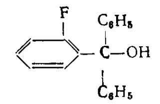


X	% $(C_6H_5)_2$
F	70
Cl	8
Br	10
I	8

The reaction with phenyl-lithium resulted in biphenyl, as would be expected from the Würtz–Fittig mechanism:



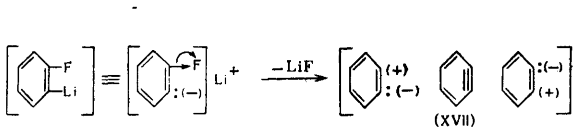
In the condensation with benzophenone, however, only (2-biphenylyl)diphenylcarbinol (XV) was isolated; *o*-fluorophenyldiphenylcarbinol (XVI), which could be expected from *o*-fluorophenyl-lithium, was absent.



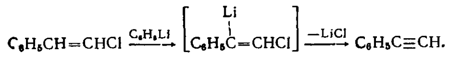
(XVI)

The unexpectedly high yield in the reaction with fluorobenzene is proof that a different mechanism is involved.

From these facts Wittig[28] suggested the formation of dehydrobenzene as an intermediate product. He considered that *o*-fluorophenyl-lithium is unstable and decomposes into lithium fluoride and dehydrobenzene (XVII).

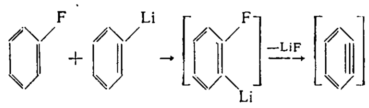


Loss of the lithium salt was assumed by analogy with his earlier work[8,36] on the reaction of β-chlorostyrene with phenyl-lithium to yield phenylacetylene:

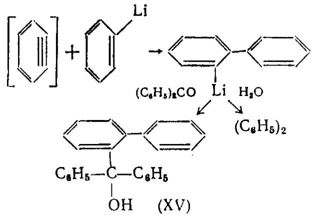


$$C_6H_5CH{=}CHCl \xrightarrow{C_6H_5Li} \left[C_6H_5\overset{Li}{C}{=}CHCl\right] \xrightarrow{-LiCl} C_6H_5C{\equiv}CH.$$

The reaction of fluorobenzene with phenyl-lithium is at present explained as proceeding in two stages — elimination and addition:

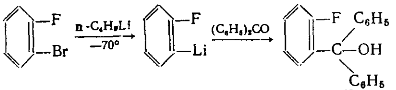


(I)



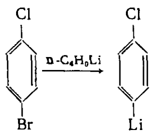
o-Fluorophenyl-lithium formed in the first stage loses lithium fluoride to yield dehydrobenzene. In the second stage dehydrobenzene adds on one molecule of phenyl-lithium giving *o*-biphenylyl-lithium, which reacts with benzophenone to give (2-biphenylyl)diphenylcarbinol (XV), and with water decomposes to biphenyl.

Gilman[37] showed that *o*-fluorophenyl-lithium is stable only at very low temperatures. At -70° a condensation product (XVIII) of *o*-fluorophenyl-lithium with benzophenone was isolated in 84% yield.

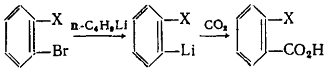


(XVIII)

It could not be obtained at -15°. However, *p*-chlorophenyl-lithium, which Gilman had prepared earlier[38], is completely stable at room temperature.



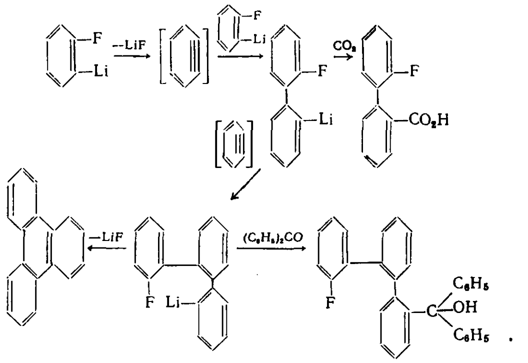
A systematic study of this reaction[39] included *o*-dihalogenobenzenes; they were reacted with butyl-lithium and the reaction product treated with solid carbon dioxide:



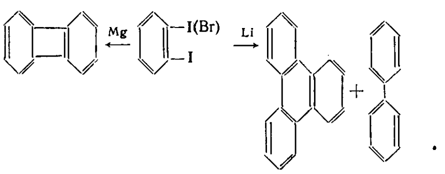
X	temp., °C	% acid
F	—60	83
Cl	—90	80
Br	—100	23

The corresponding acids were isolated in good yields. *o*-Bromophenyl-lithium proved to be very unstable even at

-100°. If the reaction mixture was heated to room temperature, 2-fluorobiphenyl and triphenylene were formed. Gilman suggested the following scheme for this reaction:

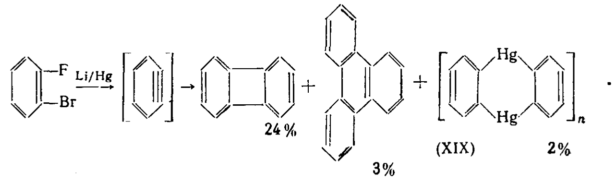


Gilman considers this stepwise formation of triphenylene more probable, from the point of view of reaction kinetics, than Bachman's mechanism, which presupposes the simultaneous interaction of three phenylene radicals. In support of his hypothesis Gilman quoted the isolation of condensation CO_2 and benzophenone, as well as the fact that in the reaction with benzophenone triphenylene was not formed. Mann and Wittig, working at about the same time as Gilman, obtained analogous results. Mann[40] used the reaction of *o*-di-iodobenzene or *o*-iodobromobenzene with lithium to obtain biphenyl and triphenylene:

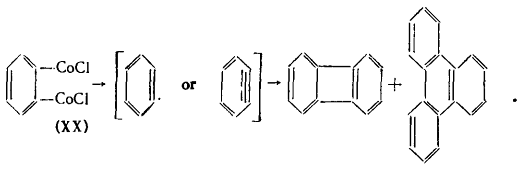


With magnesium he obtained biphenylene. The reaction with 3-bromo-4-iodotoluene gave the corresponding methyl derivatives of bi- and triphenylene[41].

From *o*-fluorobromobenzene Wittig[42] obtained biphenylene, triphenylene, and compound (XIX).

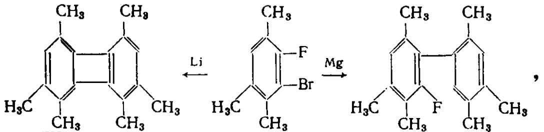


Wittig's latest work[43] showed that the Bachman mechanism cannot as yet be rejected. He isolated biphenylene and triphenylene from *o*-phenylenebiscobaltchloride (XX):



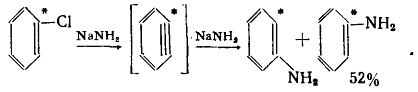
Organocobalt compounds are, of course, typical reagents which, on thermal decomposition, yield free radicals. In this case, therefore, the formation of triphenylene may well proceed by the Bachman mechanism.

Wittig[44] also studied the reaction with 1,2,4-trimethyl-5-fluoro-6-bromobenzene (XXI):



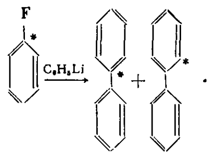
and isolated derivatives of biphenyl (XXII) and biphenylene (XXIII) but not of triphenylene. He explains the absence of a triphenylene from the reaction mixture by steric hindrance during trimerisation – the methyl groups in the triphenylene derivative would be too near to each other.

It still cannot be known for certain from the above studies whether in fact dehydrobenzene is formed in the reaction or not. Only the ^{14}C tracer studies of Roberts and his coworkers provide conclusive evidence. They studied the reaction of chlorobenzene-1-^{14}C with sodium or potassium amide in liquid ammonia[33] and analysed the resulting aniline for ^{14}C.



Two reaction products, aniline-1-^{14}C and aniline-2-^{14}C, were formed in almost equal quantities. This can only be explained by the existence of dehydrobenzene which allows for the equal probability of addition of sodium amide to either position.

The same result was obtained in the reaction of fluorobenzene-1-^{14}C with phenyl-lithium[45].

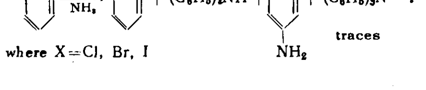


This also can be explained only as an addition of phenyl-lithium to dehydrobenzene.

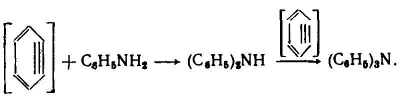
Wittig obtained further such proof in his study of the reactions of diene derivatives of dehydrobenzene[42]. The diene reactions of dehydrobenzene are reviewed below (p.317).

b) Addition to unsubstituted dehydrobenzene. We have already discussed several reactions of this type. In this section further examples are considered.

Bergstrom and coworkers[46] studied the action of potassium amide on halogenobenzenes in liquid ammonia:

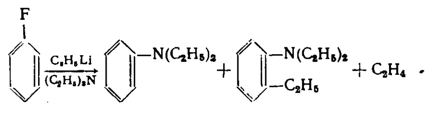


Roberts[33] accounts for the formation of aniline by addition of the metal amide to dehydrobenzene. The formation of di- and triphenylamine can be explained by addition of the corresponding amine to dehydrobenzene:

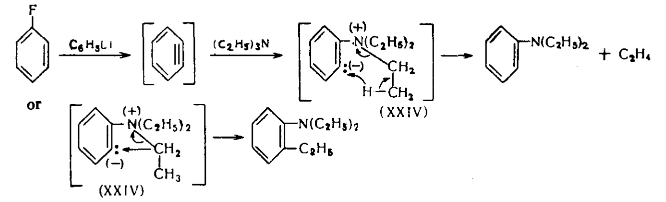


The reaction of potassium anilide with chlorobenzene can be interpreted similarly[47].

Wittig found the action of phenyl-lithium and triethylamine on fluorobenzene to be more complicated[48]:

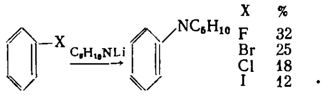


N,N-Diethylaniline, *o*-ethyl-*N,N*-diethylaniline, and ethylene were isolated. This reaction proceeds according to the following scheme:

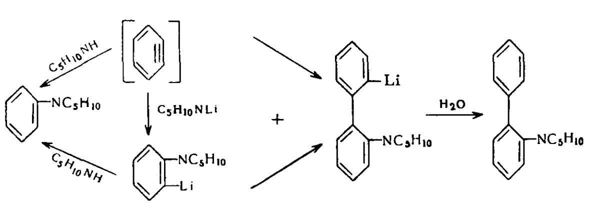


In the first stage the addition product (XXIV) is formed, and subsequently rearranges to give the final products.

Wittig[42] also studied the reaction of halogenobenzenes with lithium piperidide and found that the yield of *N*-phenylpiperidine depends considerably on the halogen present:

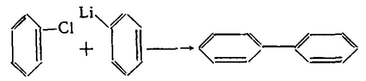


Huisgen[49] studied the amination of halogenobenzenes by lithium piperidide in the presence of piperidine and showed the yield to be independent of the halogen present; this can be taken as evidence of the intermediate formation of dehydrobenzene.



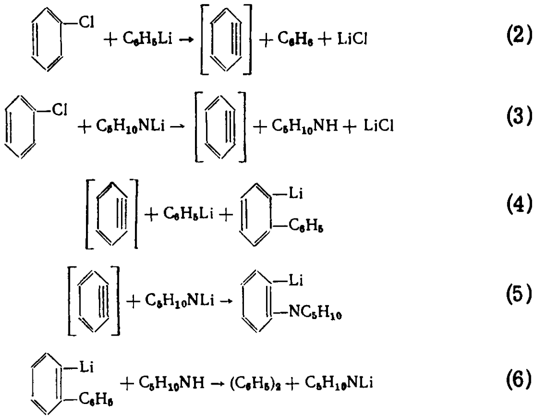
The fact that the yields were independent of the ratio of piperidine to lithium piperidide, supports the mechanism of addition of piperidine to dehydrobenzene. Similar results were obtained in the reaction with lithium diethylamide.

Huisgen[50] observed that the reaction rate of chlorobenzene with phenyl-lithium is smaller than with lithium piperidide. The addition of piperidine accelerates the former reaction and increases the yield of biphenyl form 17% to 61%.



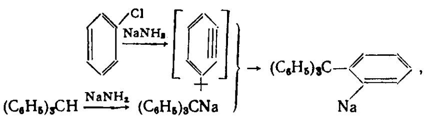
Huisgen concluded that piperidine has a catalytic effect on the reaction.

$$C_6H_5Li + C_5H_{10}NH \longrightarrow C_6H_6 + C_5H_{10}NLi \qquad (1)$$

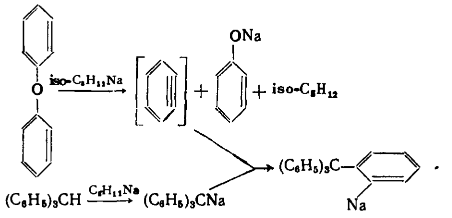


Although the concentration of phenyl-lithium in the reaction mixture is greater than that of lithium piperidide, reaction (3) is more important because it is faster. In reactions (4) and (5) phenyl-lithium reacts three times as fast as lithium piperidide, so that at high concentrations of phenyl-lithium the product is almost exclusively biphenyl. Phenyl-lithium reacts more readily because it is a stronger base than lithium piperidide.

Huisgen's recent kinetic studies[51] of the reaction of phenyl-lithium and lithium piperidide with halogenobenzenes entirely support the two-stage reaction mechanism. The formation of dehydrobenzene also explains the reaction of triphenylmethane with chlorobenzene in the presence of sodamide[52]:

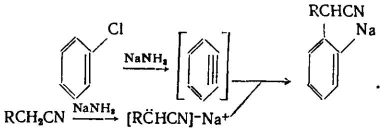


and the reaction of triphenylmethane with diphenyl ether in the presence of isopentylsodium[53]:



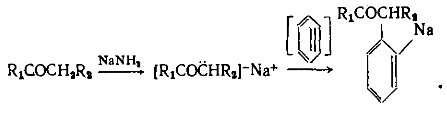
In both reactions tetraphenylmethane is formed.

Further cases of arylation by halogenobenzenes in the presence of alkali metal amides have been reported. Bergstrom[54] carried out such a reaction with nitriles:



where R = H, CH_3. Phenylacetonitrile and diphenylacetonitrile were obtained in 31 and 28% yields respectively.

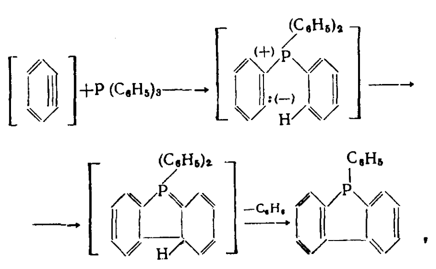
Leake[55] performed the same reaction with ketones:



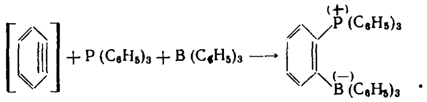
where R_1 = H or an alkyl group, and R_2 = H, alkyl, or aryl group. The esters of malonic and phenylacetic acids were also phenylated[56].

Bunnett[57] showed that the reactions of halogenobenzene with thiophenyl, piperidine, and isobutyronitrile in the presence of $NaNH_2$ gave not only aniline, diphenylamine, and triphenylamine, but also diphenyl sulphide, *N*-phenylpiperidine, and *α*-phenylisobutyronitrile, in 52, 29, and 23% yields respectively.

Wittig[58] studied the addition of triphenylphosphine to dehydrobenzene:



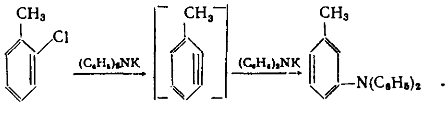
as well as the simultaneous addition of triphenylphosphine and triphenylboron:



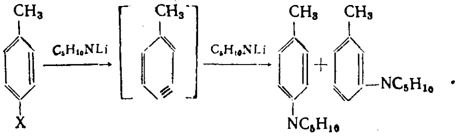
Roberts[59] compared the rates of addition of various anions to dehydrobenzene, and established that they decrease in the following order: fluorenyl anion ≃ anilide > thiophenolate ≃ triphenylmethide > acetophenone enolate anion ≃ ≃ phenylacetylide > phenolate > pyrrolate > alkoxides ≃ ≃ iodides ≃ cyanide.

c) **Addition to substituted dehydrobenzenes.** Reactions of this type are known as nucleophilic substitutions involving rearrangement ("kine-substitution"). They can easily be observed in substituted benzenes, by the formation of an isomer different from the starting compound. Many rearrangements of this type have been observed for substituted toluenes.

Hausermann[30] reported a rearrangement in the reaction of potassium diphenylamide with *o*-chlorotoluene:



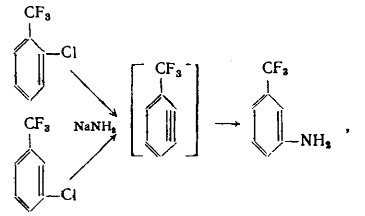
Huisgen[49] studied the reaction of *p*-halogenotoluenes with lithium piperidide and found the ratio of the resulting isomers to be independent of the halogen atom:



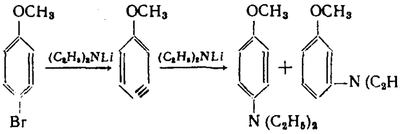
X	% meta	% para
F	53	47
Cl	55	45
Br	56	44

The constant ratio of the two isomers is evidence that the reaction proceeds *via* dehydrobenzene.

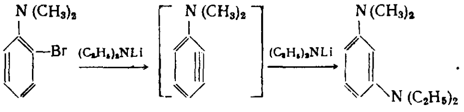
Benkeser[60] studied the reaction of trifluoromethylchlorobenzenes



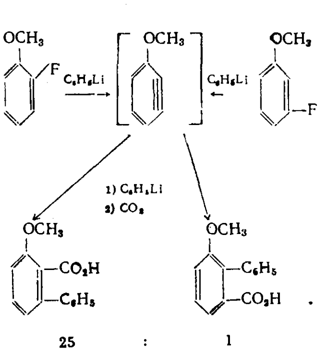
and found that rearrangement took place only in the case of *ortho* derivatives. Subsequent studies were devoted to phenolic ethers. Gilman[61] used *p*-bromoanisole



and *o*-bromo-*N*-dimethylaniline[62]:

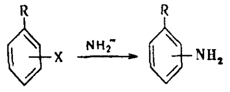


Huisgen[63] studied fluoroanisoles:



The reaction yielded very different quantities of isomers, probably owing to steric factors; the bulky phenyl group cannot enter the 2-position when both vicinal positions are occupied.

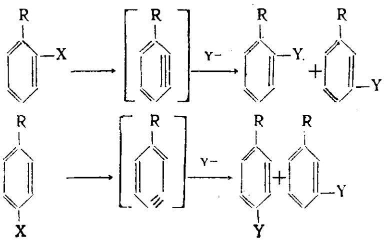
TABLE 2. Orientation in substituted halogenobenzenes.



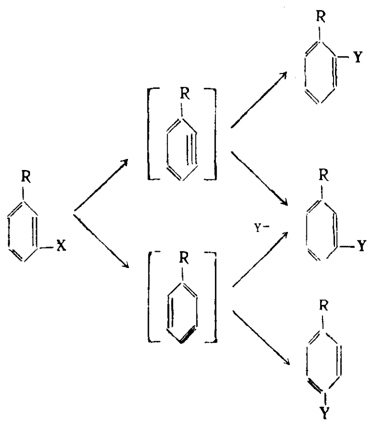
R	X	Isomer content of product, %		
		o	*m*	*p*
o-OCH_3	Br	—	100	—
m-OCH_3	Br	—	100	—
p-OCH_3	Br	—	49±1	51±1
o-CF_3	Cl	—	100	—
m-CF_3	Cl	—	100	—
p-CF_3	Cl	—	50±5	50±5
p-F	Br	—	20±1	80±1
o-CH_3	Cl	45±4	55±4	—
o-CH_3	Br	48.5±2	51.5±2	—
m-CH_3	Br	22±4	56±4	22±4
m-CH_3	Cl	40±4	52±4	8±4
p-CH_3	Cl	—	62±4	38±4

We shall discuss the reaction with diphenyl ether in the section on the synthesis of phenol by the hydrolysis of chlorobenzene.

Roberts[64] determined the quantities of the isomers formed in the above reactions and the effect of the position of the substituent on the yield of different isomers. From his results (Table 2) a number of conclusions can be drawn. First, *ortho*-isomers never give *para*-isomers, nor *vice versa*. This is explicable in terms of the formation of dehydrobenzene.

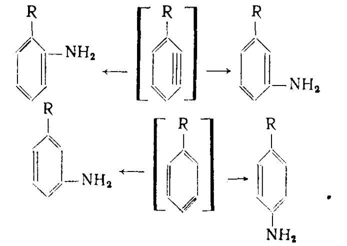


The *meta*-isomer can yield all three isomers:



The results obtained are in full agreement with theory. The fact that the *para*-isomer (which forms a dehydrobenzene without any steric hindrance) yields equal quantities of the two isomers confirms that the second stage in this reaction is an addition.

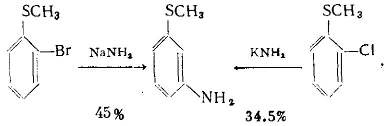
Roberts gave the following scheme for the effect of substituents on the formation of isomers:



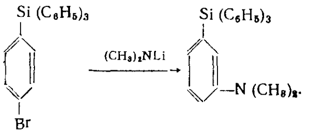
R repels electrons R attracts electrons

The decisive factor is the inductive effect of the substituent. If the substituent tends to withdraw electrons the position taken up is the further from it: in a dehydrobenzene-2,3 the NH_2^- anion enters the *meta*-position, and in a dehydrobenzene-3,4 the *para*-position. The reverse is true of substituents which repel electrons.

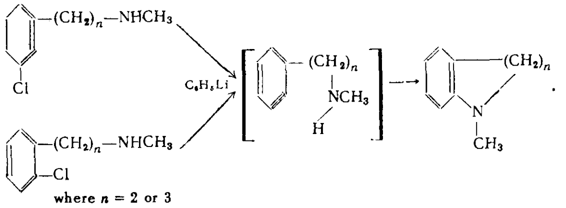
Martin[65] studied derivatives of thioanisole,



and Gilman[66] organosilicon compounds,



Addition to dehydrobenzene can also be carried out intramolecularly. Huisgen[67] accomplished the synthesis of cyclic compounds in this way.

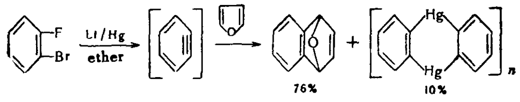


This method has recently been used for the preparation of derivatives of benzo[*b*]morpholine, tetrahydroquinoxaline, and indazoline, as well as eight- and fifteen-membered cyclic amines[68].

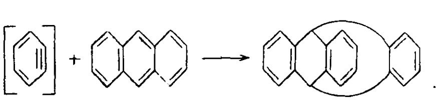
d) The behaviour of dehydrobenzene as a dienophile in the Diels-Alder synthesis supplies evidence of its structure and actual existence, and is in itself a remarkable discovery.

The acetylenic bond is involved in diene synthesis only if activated by neighbouring groups. Dehydrobenzene is very reactive, and readily takes part in diene synthesis. The reaction is carried out as follows[42]: an ether solution of *o*-fluorobromobenzene, lithium amalgam or metallic magnesium, and the reacting diene is shaken under nitrogen at room temperature for several days. The condensation product is dissolved in ether, isolated by the usual procedure and then purified by chromatography.

In the first reaction which Wittig studied, furan was the diene used.

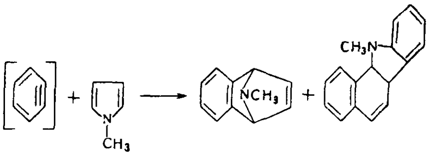


Gilman[69], as well as Müller[70] repeated Wittig's work, carrying out the reaction under conditions favourable to the stability of *o*-fluorophenyl-lithium (-70°). After heating the reaction mixture to room temperature they obtained the endo-oxide. Wittig studied diene synthesis with a number of dienes. For instance, with anthracene he obtained triptycene[71,72].



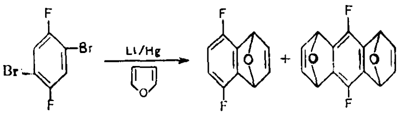
Reactions with cyclopentadiene, tetraphenylcyclopentadienone, and tetraphenylfuran were found to proceed likewise[73].

In the reaction with *N*-methylpyrrole two products were isolated[74].

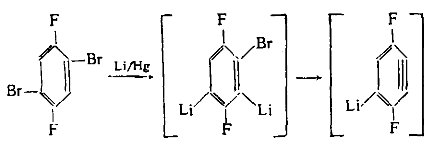


Dehydrobenzene was also treated with *N*-methylisoindole and 1,4-diphenylisobenzofuran[75]. Reactions of certain substituted halogenobenzenes with phenyl-lithium in the presence of furan were reported[44].

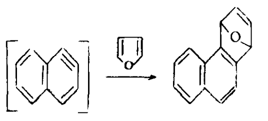
Reaction with 1,4-difluoro-2,5-dibromobenzene gave unexpected results, the fluorine atoms remaining in the molecule.



Either one molecule of lithium bromide was removed and the other bromine atom replaced by lithium, or two molecules of lithium bromide were eliminated simultaneously.

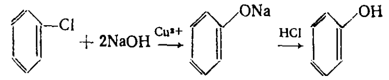


Wittig also studied the reaction of dehydronaphthalene with furan[58].



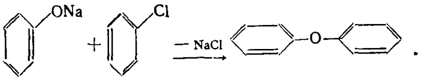
e) **Synthesis of phenol from chlorobenzene.** The hydrolysis of chlorobenzene by aqueous caustic soda is one of the most important industrial methods for preparing phenol. Since, in contrast to the foregoing reactions, it is carried out in aqueous solution, we shall deal with it separately.

The synthesis of phenol from chlorobenzene was discovered by Meyer and Bergius[76].

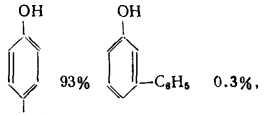


The reaction is carried out in an autoclave at 300° and 100 atm, using 10–20% NaOH solution in the presence of copper salts as catalyst. The yield of phenol is over 90%.

The first theories regarding the reaction mechanism were reviewed by Hale[77]. The mechanism is very complex, as shown by the by-products which Lüttringhaus[78] isolated. The main by-product is diphenyl ether which was earlier thought to be formed in the following reaction:

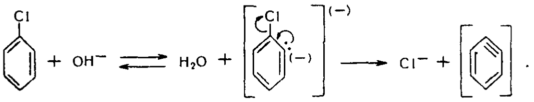


From the residue after distilling off phenol, *p*-phenylphenol and *m*-phenylphenol were isolated:



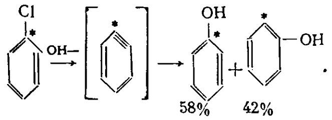
while the residue after distilling off diphenyl ether contained 30% *o*-phenylphenol, 3% *o,o*-diphenylphenol, phenyl-2-biphenylyl ether, and phenyl-4-biphenylyl ether.

Lüttringhaus proposed the following reaction mechanism involving the intermediate formation of dehydrobenzene:



The hydroxide ion attacks the hydrogen *ortho* to the chlorine atom, forming water. The equilibrium shifts to the right because the chlorobenzene anion decomposes to chloride ion and dehydrobenzene. Addition of water now yields phenol, and addition of phenoxy anion yields diphenyl ether or *o*-phenylphenol. Formation of other by-products can be explained similarly.

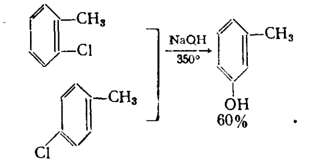
Lüttringhaus's scheme was partially proved by Roberts[79], by hydrolysing chlorobenzene labelled with ^{14}C:



A ratio of isomers close to 1 : 1 was obtained.

Lüttringhaus also studied the reaction of diphenyl ether with phenylsodium[80]. He isolated the same products as in the hydrolysis of chlorobenzene, indicating that dehydrobenzene is an intermediate also in this reaction. Wittig[42] proposed the same reaction scheme. Further proof of the intermediate formation of dehydrobenzene was the isolation of its polymerisation products, triphenylene and 4,5 : 9,10-dibenzopyrene[81] from the reaction of potassium-sodium alloy with diphenyl ether. Lüttringhaus obtained similar results in a study of phenyl-substituted diphenyl ethers and phenyl ethers derived from α- and β-naphthols[82].

The hydrolysis of chlorotoluenes was found to be accompanied by rearrangement[83,84,85]:



Roberts[79] studied the dependence of yield and isomeric composition of the reaction products on the position of the halogen atom (Table 3).

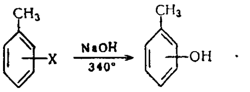
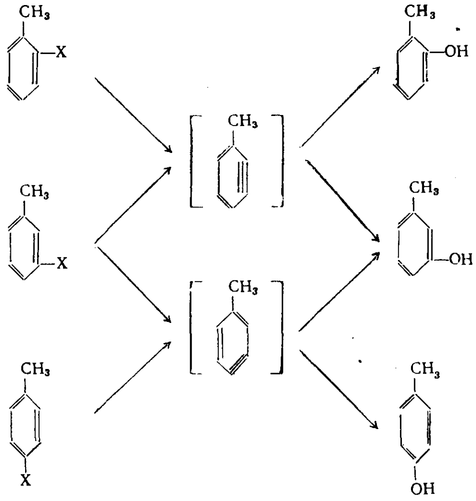


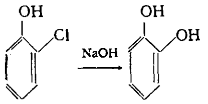
TABLE 3. Hydrolysis of isomeric halogenotoluenes.

X	Conversion, %	Product composition, %		
		o	m	p
o-Cl	68	48.2	51.8	—
m-Cl	56	21.4	63.6	15.0
p-Cl	50	—	50	50
o-Br	63	45.4	54.6	—
m-Br	60	23.9	60.2	15.9
p-Br	55	—	54.6	45.4
o-I	50	41.7	58.3	—
m-I	47	19.8	66.1	14.7
p-I	43	—	48.7	51.3

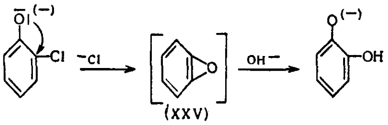
He considers two competing mechanisms possible, namely S_N2 or a dehydrobenzene mechanism. The latter is supported by the rearrangement, and the failure of o-chlorotoluene to give p-cresol (or of p-chlorotoluene to give o-cresol). Roberts suggests the following reaction scheme:



Kipriyanov[86] found that in the hydrolysis of o-chlorophenol the expected rearrangement did not take place, only pyrocatechol being formed.



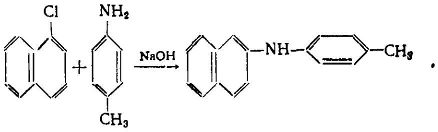
Roberts[79] explains this by intramolecular substitution resulting in "dehydrobenzene oxide" (XXV) as intermediate.



(XXV)

Rearrangement of 2- and 4-chlorobiphenyl was observed by Britton[85] and Moose[87].

f) Dehydronaphthalene. As early as 1894 Kym[29] observed a rearrangement in the reaction of p-toluidine with 1-chloronaphthalene:



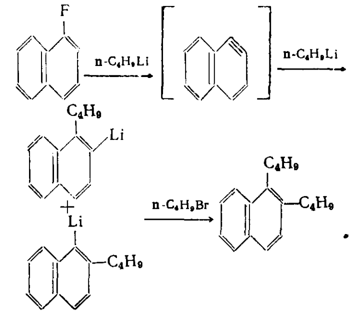
Similar rearrangements, reported in several other papers[46,62,88-90], possibly indicate the existence of dehydronaphthalene.

Huisgen[91] showed that constant ratios of isomers in the reaction products were obtained regardless of the position of the halogen attached to naphthalene. The reaction of fluoro derivatives with phenyl-lithium gave:

	Naphthalene	
	α-phenyl	β-phenyl
α-$C_{10}H_7F$	36.8	63.2
β-$C_{10}H_7F$	37.6	62.4

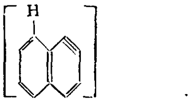
These results agree with those obtained by Bunnett[90].

Huisgen proposed addition of organometallic compounds to dehydronaphthalene for the synthesis of 1,2-dialkylnaphthalenes, which are otherwise difficult to obtain:

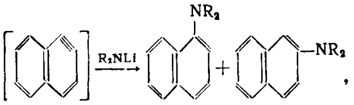


The reaction with butyl bromide gave a good yield of the expected 1,2-dibutylnaphthalene. t-Butylnaphthalenes were also prepared. The same isomer ratios were obtained whether the substituent was n- or t-butyl.

The effect of substituents on the isomer ratio has also been studied[92]. The steric effect of the hydrogen in the peri-position in dehydronaphthalene probably affects the quantity of isomers formed. For small substituents this effect is probably not important and constant ratios of isomers should be obtained. With bulky substituents the β-isomer should predominate.



The reactions of α-fluoronaphthalene with lithium alkylamides have been studied:



where R = iso-C_3H_7 or C_6H_{11}. These theoretical predictions proved correct, although it was only very bulky substituents that affected the isomer ratio.

The dependence of isomer ratio on the position and nature of the halogen has been studied in great detail[93]. In the reaction of 1- and 2-halogenonaphthalenes with lithium piperidide, constant isomer ratios were obtained for all halogens except fluorine. This can be accounted for if the reaction is assumed to proceed partly by an S_N2 mechanism.

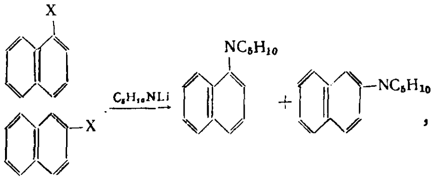
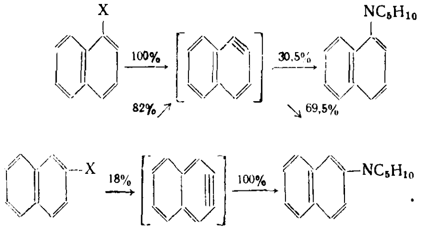


TABLE 4.

Halogenonaphthalene	Piperidinonaphthalene, %	
	1-	2-
1-F	32	68
1-Cl	30	70
1-Br	27	73
2-F	25.5	74.5
2-Cl	26.5	73.5
2-Br	23.5	76.5
Mean: 1-halogenonaphthalene	30.5	69.5
2-halogenonaphthalene	25	75

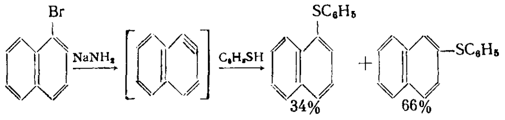
where X = F, Cl, Br, or I. Normal ratios were obtained with all halogens when the reaction was carried out in boiling piperidine (see Table 4).

From the isomer ratio it was possible to determine the course of the elimination of lithium halide from 1-lithium-2-halogeno- and 3-lithium-2-halogeno-naphthalenes, and of the addition of piperidinolithium to 1- and 2-dehydronaphthalenes. The results are:



Substitution is probably equal in the 2- and 3-positions of dehydronaphthalene-2,3, but as these positions are equivalent the products cannot be distinguished. These results were confirmed by Huisgen[94]. Similar results were also obtained with lithium diethylamide.

Bunnett[57] studied the addition of thiophenol to dehydronaphthalene.



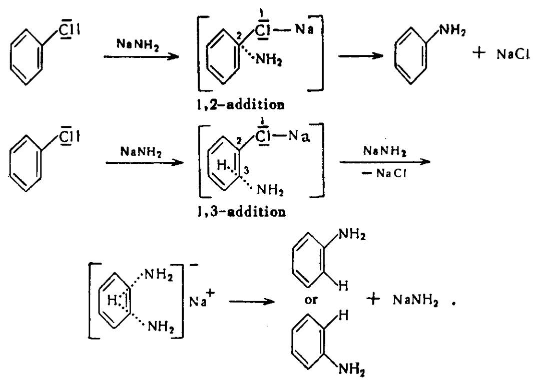
Two isomeric phenyl naphthyl sulphides were obtained in a ratio close to that established by Huisgen[93].

g) Other dehydro-systems. There is as yet no conclusive evidence for the formation of dehydro-compounds in the anthracene[95] and phenanthrene[50] systems. In the biphenyl[46,50], dibenzofuran, and dibenzothiophen systems[96,97] the substitution of halogens is accompanied by rearrangement. This indicates intermediate formation of dehydro-compounds.

The existence of dehydro-compounds may be regarded as fully established by the results described above. Three types of reactions of dehydro compounds are known at present: 1) polymerisation, to biphenylene and triphenylene, 2) addition (aromatic substitution followed by rearrangement is the best example), and 3) diene synthesis. Polymerisation is of no importance as evidence for dehydro-compounds, because it can be explained in terms of a Würtz-Fittig mechanism.

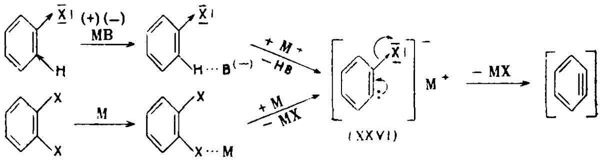
Nucleophilic substitution in the benzene ring can proceed by an S_N2 mechanism without rearrangement. If rearangement occurs, the reaction has an elimination-addition mechanism with dehydro-compounds as intermediates. This mechanism and the existence of dehydrobenzene were confirmed by Roberts using radioactive tracers. Addition to a dehydro-compound should yield isomers in a constant ratio, independent of the reagent concentrations. The deviations observed result from the reaction proceeding by both possible mechanisms.

Morton[98] suggested another mechnism for substitution with rearrangement. He regards the reaction as a 1,2- or 1,3-addition:



After the removal of NaCl, 1,3-addition yields a cyclic complex, which on decomposition may form either a normal or a rearranged product. Which mechanism the reaction follows is still unknown.

Diene synthesis provides further strong evidence for the existence of dehydrobenzene. Dehydro-compounds can be formed by the action of anions on halogen-containing compounds, by the action of metals on dihalogeno-compounds, or by thermal decomposition of organometallic compounds. The first two methods give the same intermediate *o*-halogeno-metallo compound (XXVI).

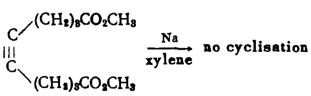


The substitution of a proton by a metal is possible owing to the electron-withdrawing properties of halogen atoms; the stronger this property is, the easier the substitution. The resulting *o*-halogenometallo-compound (XXVI) eliminates MX more easily, the more electropositive the metal. Wittig considers that the driving force of this elimination is high stability of the dehydro-compound resulting from partial overlapping of electron orbitals, although a triple bond is probably not actually formed. Thermal decomposition of organometallic compounds may yield the phenylene radical, which probably rearranges to dehydrobenzene.

The structure of dehydro-compounds will be discussed in the section on the stereochemistry of cyclic acetylenes.

3. CYCLIC ACETYLENES CONTAINING SEVERAL MULTIPLE BONDS

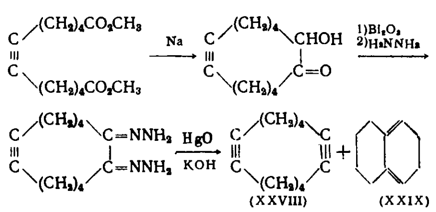
The first reports of the preparation of cyclic compounds containing several multiple bonds appeared in 1956. Cram's attempt to synthesise cyclodeca-1,5-diyne did not succeed because the ester (XXVII) fails to give the acyloin[99].



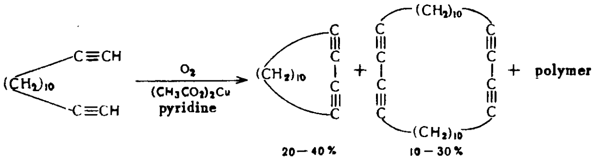
(XXVII)

Cyclisation occurred only after reduction of the triple bond to a *cis*-double bond.

In the synthesis of cyclododeca-1,7-diyne (XXVIII) the bicyclic byproduct (XXIX) was obtained.

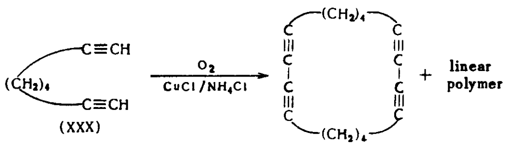


Eglington[100] obtained 1,3-diacetylenes by oxidising an α,ω-diacetylene with air in the presence of copper salts.

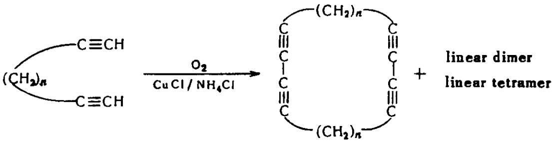


A mixture of cyclic and linear products was obtained. The yield of cyclic monomer depends on the concentration of the initial diacetylene. Cyclotetradeca-1,3-diyne absorbs oxygen from the air forming a C=O group.

Cyclisation of α,ω-diacetylenes has been thoroughly studied by Sondheimer and coworkers, who carried out first the cyclisation of octa-1,7-diyne (XXX).[101]



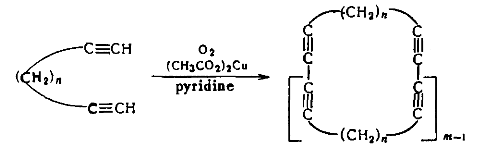
A number of other cyclic acetylenes were prepared by the same method[102].



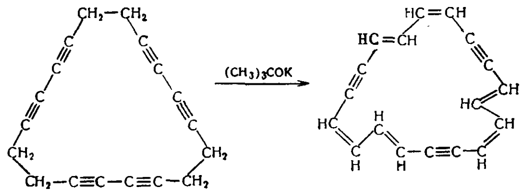
where n = 3, 4, or 5.

Cyclic products could not be obtained from hexa-1,5-diyne ($n = 2$) or deca-1,9-diyne ($n = 6$). In cyclotetradeca-1,3,8,10-tetrayne ($n = 3$) a shift of the ultra-violet absorption bands towards longer wavelenths was observed. The authors call this a "proximity effect"; its nature will be discussed in the section on the stereochemistry of cyclic acetylenes.

When Sondheimer and his coworkers used Eglington's method of oxidation[100], *viz.* very dilute pyridine solution with cupric acetate as catalyst, they isolated cyclic polymers containing several monomer units[103].

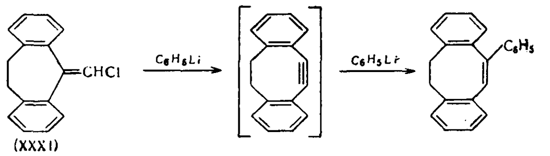


Cyclisation was also carried out with hexa-1,5-diyne-3-ol[104] and with the acetate of cyclohepta-1,6-diyne-4-ol[105]. The macrocyclic compounds cyclo-octadeca-1,3,7,9,13,15-hexayne (hexa-1,5-diyne trimer)[106], cyclotetracosa-1,3,7,9,13,15,19,21-octayne (hexa-1,5-diyne tetramer)[107,108], and cyclotriaconta-1,3,7,9,13,15,19,21,25,27-decayne (hexa-1,5-diyne pentamer)[108] underwent Favorskii isomerisation under the effect of potassium t-butoxide giving the corresponding conjugated polyenynes.



The authors are of the opinion that these compounds can have aromatic properties.

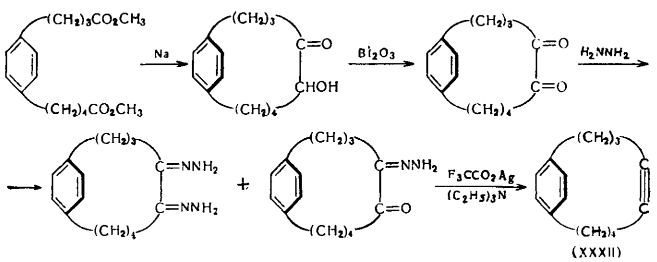
There are several papers devoted to the introduction of a triple bond into rings condensed with a benzene nucleus. Curtin[109] used the action of phenyl-lithium on 1-chloromethylene-2,3 : 6,7-dibenzocyclohepta-2,6-diene (XXXI). Rearrangement to dibenzocyclo-octyne occurred and this reacted with the phenyl-lithium.



(XXXI)

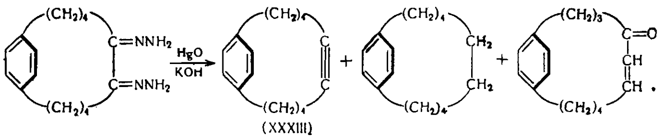
The free acetylene could not be isolated.

Cram and coworkers[110,111] studied the properties of paracyclophanes containing a triple bond; 4-[9]paracyclophyne (XXXII) was obtained from the corresponding dihydrazone:



(XXXII)

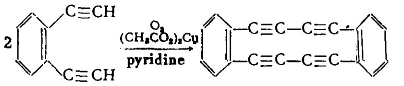
The reaction of the diketone with hydrazine gave a mixture of mono- and di-hydrazones, which could not be separated. This mixture did not react with mercuric oxide, but was decomposed by silver trifluoroacetate and triethylamine. This new method of oxidising dihydrazones was discovered by Newman. 5-[10]Paracyclophyne (XXXIII) was obtained by decomposing the dihydrazone with mercuric oxide and potassium hydroxide:



(XXXIII)

The authors think that the saturated hydrocarbon also obtained is formed by reduction of the dihydrazone according to the Wolff-Kishner method, and the unsaturated ketone by decomposition of the monohydrazone.

The compound that Eglington[112] obtained by the oxidative polymerisation of *o*-diethynylbenzene is of special note.



The structure of the cyclic compound obtained was determined by hydrogenation and from infra-red spectroscopy and X-ray analysis[113].

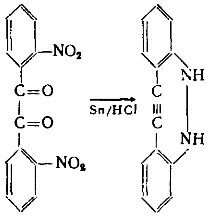
Oxidative condensation of α,ω-diacetylenes is one of the most important methods for the preparation of cyclic polyacetylenes. The mechanism of this reaction is probably identical with that which Klebanskii established for the coupling of linear acetylenes[114].

$$R{-}C{\equiv}CH \rightleftharpoons R{-}C{\equiv}C{:}^- + H^+$$
$$R{-}C{\equiv}C{:}^- + Cu^{2+} \xrightarrow{\text{rapid}} R{-}C{\equiv}C\cdot + Cu^+$$
$$2R{-}C{\equiv}C\cdot \xrightarrow{\text{rapid}} R{-}C{\equiv}C{-}C{\equiv}C{-}R$$
$$2Cu^+ + {}^1\!/_2O_2 + H_2O \longrightarrow 2Cu^{2+} + 2OH^-$$

This mechanism is supported by the fact that polymerisation proceeds the faster the more acidic the acetylene. Eglington[100] considers that biradicals $\cdot C{\equiv}C(CH_2)_nC{\equiv}C\cdot$ are formed, which, depending on the reaction conditions, yield a cyclic monomer or cyclic and linear polymers.

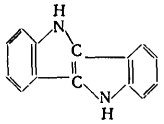
4. HETEROCYCLIC COMPOUNDS CONTAINING AN ACETYLENIC BOND

This group of compounds has received very little attention. Although Golubev obtained the first indications of the existence of these compounds as early as 1884, only a few heterocyclic acetylenes with precisely defined structure are known at present. Golubev[115] studied the reduction of *o,o'*-dinitrobenzil and obtained a compound of composition $C_{14}H_{10}N_2$, to which he ascribed the heterocyclic acetylene structure (XXXIV):



(XXXIV).

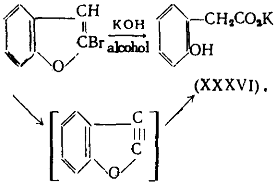
The structure (XXXIV) was not established with certainty. Kliegl[116] thinks that the compound has a completely different structure (XXXV), without the triple bond:



(XXXV).

The efforts of Ruggli[117] to obtain "Golubev's acetylene" by alkaline reduction of *o,o'*-dinitrobenzil failed.

Stoermer[118] observed cleavage of the furan ring in the action of alkali on 2-bromobenzo[*b*]furan:

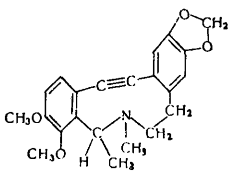


(XXXVI).

XXXVII

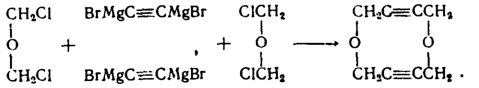
He assumed that dehydrobenzofuran (XXXVII) was formed as an intermediate product in the reaction, which subsequently yielded *o*-hydroxyphenylacetic acid (XXXVI).

Freund[119] reported the presence of a triple bond in the alkaloid des-*N*-methyldihydroberberine (XXXVIII):



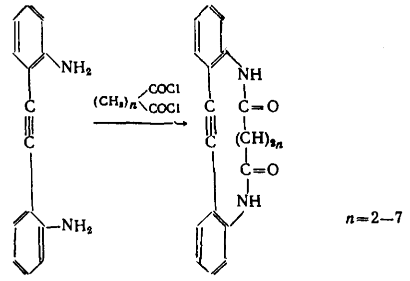
(XXXVIII).

Lespieau[120] obtained a cyclic acetylene in the reaction of dichlorodimethyl ether with ethynylene di(magnesium bromide):

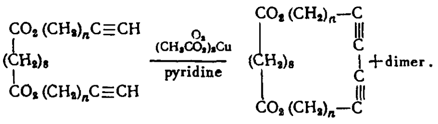


$$\begin{matrix}CH_2Cl\\ |\\ O\\ |\\ CH_2Cl\end{matrix} + \begin{matrix}BrMgC{\equiv}CMgBr\\ \\ \\ \\ BrMgC{\equiv}CMgBr\end{matrix}, + \begin{matrix}ClCH_2\\ |\\ O\\ |\\ ClCH_2\end{matrix} \longrightarrow \begin{matrix}CH_2C{\equiv}CCH_2\\ |\qquad\quad |\\ O\qquad\quad O\\ |\qquad\quad |\\ CH_2C{\equiv}CCH_2\end{matrix}.$$

The structure of the above-mentioned heterocyclic acetylenes has not been established with certainty. Ruggli[117,121] obtained the first heterocyclic acetylenes of definite structure by condensation of *o,o'*-diaminotolane with acyl chlorides of dicarboxylic acids.



Eglington[100] has recently obtained the heterocyclic acetylenes (XXXIX) by oxidative polymerisation of diacetylenes:



(XXXIX)

For *n* = 2 a cyclic monomer and dimer were obtained, but for *n* = 4, only the dimer.

5. STEREOCHEMISTRY OF CYCLIC ACETYLENES

As the present review shows, cyclic acetylenes can be divided into two large groups. The first — stable compounds, whose structure is established beyond doubt — at present includes very few members. They are of especial interest to theoretical organic chemistry, being suitable for the study of spatial configuration, strain, conjugation of multiple bonds, and the possible existence of large rings with aromatic properties.

The second group comprises unstable cyclic acetylenes, the seven-, six-, and five-membered rings containing a triple bond. The possibility of temporary formation of an acetylenic bond in a four-membered ring is hardly worth considering. The structure of these compounds is still not established beyond doubt, as they cannot be isolated in the free state. They are formed only for short periods, as intermediate products, which subsequently isomerise, polymerise or react with other compounds. From the reaction kinetics and resulting products their structure was assumed to be that of cyclic acetylenes. The importance to theoretical organic chemistry of their further study can hardly be overestimated. They are especially important for the theory of the chemical bond, strain theory and in the study of reaction mechanisms.

These unstable compounds are also of great importance in chemical technology. Dehydroaromatic systems, which arise as intermediates during the hydrolysis of aromatic halogen compounds, have a decisive effect on the products. The thorough study of the mechanisms of such reactions and of the properties of dehydro-compounds is therefore not only a means of understanding and of improving the reactions used in industry at present, but also of discovering and applying new processes. This is the main task of science.

Ruzicka[13] was the first to consider the spatial configuration of cyclic acetylenes, concluding that those with ten or more atoms in the ring should be stable. Wittig[122] also examined models of acetylenes and was of the opinion that ten-membered cyclic acetylenes should have no strain in the molecule. Nine- or eight-membered rings can contain a triple bond, but are not strainless.

Favorskii[3] and Domnin[14] studied the preparation of cyclic acetylenes and arrived at the following conclusions:

1) In five-, six-, and seven-membered rings the triple bond can exist for a very short time only. Such molecules are unstable, and rapidly isomerise or polymerise.

2) The acetylenic bond can exist in eight- or nine-membered rings, but it causes strain in the molecule.

3) Cyclic acetylenes with ten-membered or larger rings are strainless.

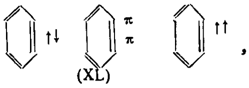
The existence of considerable strain in cyclo-octyne is indicated by the explosiveness of its reaction with azidobenzene[16]. Cyclononyne has not been studied. The infra-red spectra of both these compounds show the normal wavelength for vibration of the acetylenic bond (4.53 μ), identical with that of higher cyclic acetylenes.

Owing to the absence of data on their physical properties, the spatial configuration of cyclic acetylenes can be determined only from their chemical properties, consideration of models, and analogies with other compounds. Examination of models gave the following results. Higher cyclic acetylenes, starting with ten-membered ones, have non-planar rings, strainless or with slight strain caused by energetically unfavourable conformations of the methylene groups. Baeyer strain exists in the cyclononyne and cyclo-octyne molecules. In cyclo-octyne this is so great that it can alter the hybridisation of the atoms forming the triple bond, and cause the appearance of a dipole moment[123], *cf.* that reported by Allinger for *trans*-cyclo-octene[124]. Investigation of the structure of molecules containing a triple bond, such as dehydrobenzene, cycloheptyne, cyclohexyne and cyclopentyne is even more difficult than in the case of known strained molecules.

A good deal of attention has been given to the structure of dehydrobenzene. Bachman[26] suggested it was the phenylene radical. Roberts[33,45] accepted the existence of a triple bond in dehydrobenzene, considering that the orbitals of the second π-bond lie in the plane of the benzene ring and have no effect on the aromatic properties of the system, since they are perpendicular to the other p-orbitals (see Fig. 1). He suggested the name benzyne for dehydrobenzene.

Wittig[42] rejected this name because it implies that there is a triple bond in the molecule. He thinks that dehydrobenzene is a mesomeric molecule, with separate formulae for mesomeric states as given above (XVII), and prefers the name dehydrobenzene to benzyne because it does not presuppose the structure of the bond.

Huisgen[49] concluded that the structure of dehydrobenzene could best be represented by formula (XL):



(XL)

where π signifies partially paired electrons. This formula represents a state intermediate between the singlet and triplet states represented by the adjacent formulae.

The complexity of the problem of the structure of dehydrobenzene is shown by the fact that dehydrobenzene obtained from o-fluorophenyl-lithium reacts readily in diene synthesis, whereas dehydrobenzene formed by decomposition of o-phenylenebiscobalt chloride yields no adduct with furan, polymerising instead[43]. It is impossible to say as yet whether it is the structure of dehydrobenzene (polar or radical) or the reaction conditions which are responsible for this difference.

Some information regarding the structure of dehydro-compounds can be obtained from the work of Ingold *et al.*[125,126,127] on the excited states of acetylene. Ultra-violet spectra of photochemically excited acetylene were studied, the existence and structure of the first excited state in acetylene being established. The following results were obtained:

Stereochemical parameters

	C_2H_2 normal	C_2H_2 excited	C_6H_6 normal
C≡C bond length, Å$_o$	1.208	1.385	1.39
C–H bond length, Å	1.058	1.08	1.08
C≡C–H bond angle	180°	120.2°	120.0°
Force constants:			
C≡C stretching (dyne cm^{-1})	$15.8 \cdot 10^5$	$7.2 \cdot 10^5$	$7.6 \cdot 10^5$
C–H stretching (dyne cm^{-1})	$6.0 \cdot 10^5$	$5.1 \cdot 10^5$	$5.1 \cdot 10^5$
C≡C–H bending (dyne cm^{-1} radian^{-1})	$1.5 \cdot 10^{-12}$	$3.5 \cdot 10^{-12}$	$8.0 \cdot 10^{-12}$

The spatial and electronic structure of the excited molecule is shown in Fig. 2. The stereochemical parameters were obtained from moments of inertia. They show that the molecule is strictly planar and has a *trans*-configuration (centrosymmetrical). The force constants indicate that in the excited molecule it is more difficult to bend the C–H bond further than to stretch it; this leads to re-establishment of a linear molecule. These mechanical propertis are exactly opposite to those of the normal acetylene molecule.

The C–C bond is a three-electron bond $\{(2sp^2)\sigma\}\{2p\pi\}$, which is identical with the aromatic bond in benzene. The C–H bonds are normal two-electron bonds $\{(C2sp^2)(H1s)\sigma\}$, as in ethylene or benzene. The π-orbital of the triple bond is converted into two unpaired $2sp^2$ orbitals which have one free place and accept one excited electron from the other π-bond. This leads to a state in which three electrons are shared among two orbitals on two carbon atoms. Ingold describes the state of these electrons as follows: "They are mainly unpaired, although each carbon atom to a certain extent binds the free electrons of the neighbouring atom and to that extent completes its octet".

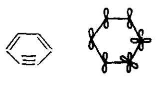


Fig. 1.

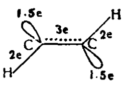


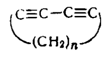
Fig. 2.

Ingold stresses the similarity in structure of the skeleton of the excited acetylene molecule to one third of a normal benzene molecule, which is supported by excellent agreement of bond lengths, valency angles and force constants. The one difference is the *trans*-arrangement of the atoms in the excited acetylene molecule. Other excited states of the acetylene molecule are also possible, but they have not yet been observed. Ingold thinks that one of those states is the *cis*-form of acetylene, which will be very similar to one third of a benzene molecule. This hypothesis is supported by the fact that acetylene forms a *cis*-transition state in the Diels–Alder reaction, just as the formation of a *trans*-transition state in addition reactions with acetylene supports the existence of the *trans*-form of the excited acetylene molecule.

Ingold considers the discovery of dehydrobenzene an additional argument in favour of the possible existence of the *cis*-form of the excited acetylene molecule, and conversely, that the structure of the triple bond in dehydrobenzene will be very similar to the *cis*-form. Arguments concerning the structure of the triple bond in the excited acetylene molecule can be applied to the molecule of dehydrobenzene. The excited triple bond has the character and spatial configuration of an aromatic bond. This is why its introduction into the benzene ring causes no appreciable change in the geometry of the molecule nor does it disturb the electronic structure and, hence, the aromatic properties. Such properties were predicted in dehydrobenzene by Roberts[33,45].

The properties of cyclo-octyne and the excited triple bond in acetylene considered above permit certain observations on the structure of the unstable cycloheptyne, cyclohexyne, and cyclopentyne. All these molecules are in a state of considerable strain, and therefore probably have a planar structure. In cyclo-octyne the strain is distributed among all the carbon atoms, changing their hybridisation and, both in the methylene groups and at the triple bond, the angles between the orbitals forming the bonds. Moreover, the strain causes accumulation of energy in the triple bond. As the number of atoms in the ring decreases, the strain becomes greater. Deformation of valency angles can no longer compensate for the shortage of ring members, so the strain on the triple bond becomes more and more pronounced, leading to the rupture of one of its component bonds, that is the triple bond becomes excited. It is difficult to say whether this is what really happens or whether dissociation of one of the simple bonds takes place earlier. Willstätter[2] observed such dissociation of a simple bond in the rupture of the four-membered ring in an attempt to prepare cyclobutyne. It follows that five-membered rings are the smallest in which a triple bond is able to exist, even for a short time. In its present form the strain theory cannot be used to predict the limiting strain tolerated for more protracted existence of a cyclic acetylene monomer. This can only be determined experimentally. Cyclic acetylenes are at present the only group of organic compounds in which the effect of strain on the structure of the molecule can be studied over a wide range of strain.

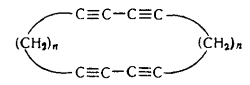
Eglington[100] made a study of models of cyclic diacetylenes with triple bonds in the 1,3-positions, concluding that twelve-membered rings of this kind (n = 8) should be relatively stable.



He did not attempt to prepare cyclododeca-1,3-diyne, but proved the existence of cyclic 1,3-diacetylenes by obtaining a fourteeen-membered ring.

The proximity effect was first observed and studied by Cram[99,110,111,128].

Sondheimer[102] observed a shift in the ultra-violet spectra of cyclic tetra-acetylenes. He showed that the long wavelength maximum for cyclotetradeca-1,3,8,10-tetrayne (n = 3) is shifted 9 mμ towards longer wavelength.



n = 3	226	238	263 mμ
n = 4 or 5	227	239	254 mμ

That this is a case of the proximity effect can be seen from the spatial structure of the tetra-acetylene molecules. A 1,3-diacetylenic group has a linear structure, and the cyclic tetra-acetylene molecule has two such "shafts" connected by methylene groups (Fig. 3).

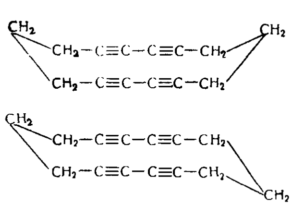


Fig. 3.

In tetradecatetrayne (n = 3) a considerable mutual approach of the triple bonds takes place, so that the shift in the ultra-violet spectra is understandable. There are two possible conformations of the ring — boat and chair. It has been shown by X-ray analysis that the molecule has a centre of symmetry and therefore exists in the chair conformation. Although the acetylenic bonds are drawn together to a considerable degree, the infra-red spectra showed triple bond absorption bands at normal frequencies. This is evidence of the absence of a transannular interaction, the possibility of which was discussed by Cram. In hexadecatetrayne (n = 4) the distance between the acetylenic groups is so great that their interaction is not observed. It should be stressed that cyclotetradeca-1,3,8,10-tetrayne (n = 3) is the first purely aliphatic compound to display the proximity effect.

Some problems of the stereochemistry of cyclic acetylenes which are still unsolved are listed below.

1. The study of the spatial structure and strain of those cyclic acetylenes known at present (especially the molecules of cyclononyne and cyclo-octyne).

2. The preparation of new cyclic acetylenes (that of cycloheptyne is especially challenging).
3. The synthesis of large rings containing several multiple bonds and the study of their aromatic properties.
4. Finally, the study of unstable cyclic acetylenes and of synthetic reactions based on them (the reactions of dehydrobenzene are of paramount importance since it is an intermediate product in certain industrial reactions, *e.g.* the manufacture of phenol from chlorobenzene under the action of alkali).

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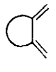
1, 2-DIMETHYLENECYCLOALKANES

Yu.A.Titov

1. INTRODUCTION

Conjugated dienes with double bonds fixed in a cisoid position are of great importance in the study of the properties of diene systems. Such a cisoid configuration occurs in cyclic dienes of type (I) and (II).

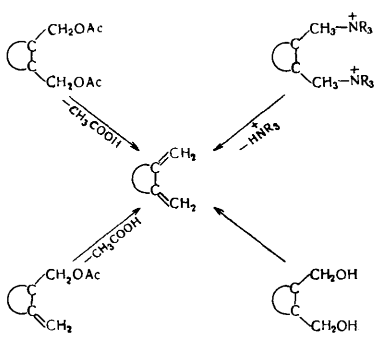

(I)


(II)

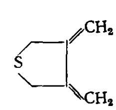
Dienes of type (I), for instance cyclopentadiene, have been known a long time and thoroughly investigated. Compounds of type (II), 1,2-dimethylenecycloalkanes, whose conjugated systems consist of semicyclic double bonds, have received much attention lately. More than fifty dienes of type (II) which are derived from saturated or unsaturated polymethylene rings, or aromatic (*e.g.* acenaphthene) and heterocyclic (*e.g.* dioxane) systems are already known.

2. SYNTHESIS

The development of efficient methods for the preparation of 1, 2-dimethylenecycloalkanes presents difficulties owing to the readiness of these compounds to polymerise, oxidise, and isomerise. Only recently have the experimental obstacles been overcome, and most publications on the synthesis of this group of compounds have appeared in the last 5 to 7 years. The two basic methods available at present for the preparation of 1, 2-dimethylenecycloalkanes are the pyrolysis of 1, 2-bis(acetoxymethyl)cycloalkanes[1–21] and the Hofmann elimination of 1, 2-bis(dimethylaminomethyl)cycloalkanes[18,22–30]. For the preparation of certain particular compounds several other methods are also available – cyclopolymerisation of allenes, dehydration, etc. These methods can be used for the preparation of dienes containing 4-,[22–24] 5-,[3,18,25] and 6-membered[1,5–9,21,26] rings, and condensed[14,15] and bridged rings[11–13,18,27]. It has been reported that the products of pyrolysis of 1, 2-bis(acetoxymethyl)cyclopropane contain 1, 2-dimethylenecyclopropane[31], which could not, however, be obtained pure.



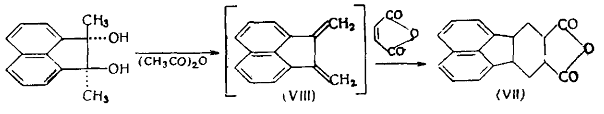
3, 4-Dimethylenethiophane(III) could not, however, be obtained by these methods[32,33].



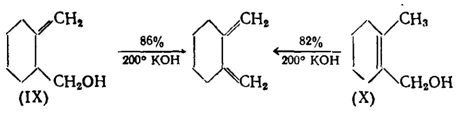
(III)

Some cases have been reported where different compounds were obtained instead of the expected 1, 2-dimethylenecyclohexanes[22,23,31–38].

A comparison of the two basic methods for the preparation of 1, 2-dimethylenecycloalkanes shows that the pyrolysis of acetates produces somewhat better yields, while the Hofmann elimination of diamines gives products of higher purity. The hydration of 1, 2-bis(hydroxymethyl)cycloalkanes over acid catalysts yields furans simultaneously, and is unsuitable for the synthesis of the corresponding dienes[39–40]. Nevertheless, on dehydration with acetic anhydride in the presence of maleic anhydride, *trans*-1, 2-dimethylacenaphthene-1, 2-diol produces good yields of the adduct (VII), corresponding to 1, 2-dimethyleneacenaphthene(VIII).[41]

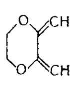


A paper has appeared recently[42] on the synthesis of 1, 2-dimethylenecyclohexane from alcohols (IX) and (X).

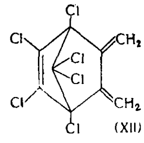


1,2-Dimethylene-3,3-dimethyl- and 1,2-dimethylene-3,3,4-trimethyl-cyclohexanes were prepared similarly[42].

Dimethylenecycloalkanes (XI)[43] and (XII)[42] were prepared by dehydrohalogenation of the corresponding dihalides in the presence of alkali. The same method was used for the synthesis of 1, 2-dimethylenecyclohexane[45], but the authors did not give either the details of the preparation, or the yield of the diene.

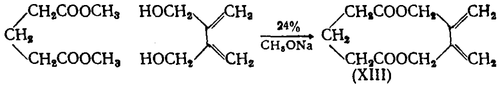


(XI)

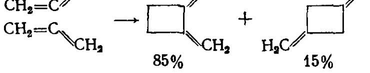


(XII)

The reaction of 2, 3-bis(hydroxymethyl)butadiene with the dimethyl ester of glutaric acid was used to synthesise a diene (XIII), which has an eleven-membered ring containing oxygen[46].

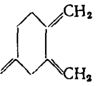


The thermal dimerisation of allene and its homologues yields 1, 2-dimethylenecycloalkanes with a four-membered ring[23,37,47–50].

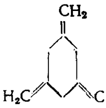


The homologues of allene containing alkyl and aryl substituents[39,47,51,52] and also tetrafluoro-[53] and tetrachloro-allene[54] react in the same way.

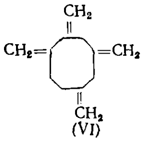
Cyclopolymerisation of allene[55] in the presence of the catalyst $Ni(CO)_2[P(C_6H_5)_3]_2$ gave trimers and tetramers of allene with the following structures:



(IV)



(V)



(VI)

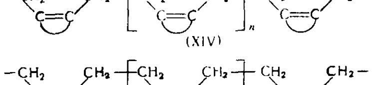
3. ULTRA-VIOLET AND INFRA-RED SPECTRA

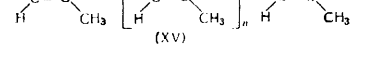
1, 2-Dimethylenecycloalkanes may be clearly divided according to their ultra-violet spectra into two groups: 1) dienes with a six-membered ring and 2) dienes with any other ring, including those containing bridges. Dienes of the first group have an absorption maximum at 213–221 mμ.[1,23,26,32,56,57], and those of the second group at 241–253 mμ[11–13,16,18,22,27,38,58]. The maximum calculated for 1,2-dimethylenecycloalkanes from the Woodward rule[59] is at 237 mμ; thus, for neither group of dienes do the absorption maxima agree with the calculated value†. The bathochromic shift of the absorption maximum in dienes of the second group apparently occurs as a result of strain in their cyclic systems. 1,2-Dimethylenecycloalkanes of the first group (six-membered rings) show a hypsochromic shift in λ_{max} of approximately 20 mμ from the calculated value. This is most probably explained by non-coplanarity of the exocyclic double bonds in such systems[6,11,16,26,56]. This view is confirmed by the observation of exactly the same hypsochromic shift (~ 20 mμ) after the loss of coplanarity for cisoid dienes with a different configuration, *i.e.* where the ring is closed in the 1,4-position of the diene system (cycloheptadiene, λ_{max} 248 mμ, and cyclo-octadiene, λ_{max} 228 mμ[60]). The molecular extinction coefficient ε is less than 10 000 in both groups of 1,2-dimethylenecycloalkanes. Variations in the intensity of absorption are connected primarily with the purity of the diene. The value ϵ_{max} = = 10 000 is evidently characteristic of the cisoid conformation of the diene system (the transoid conformation is characterised by ϵ_{max} of the order of 20 000).

The infra-red spectra of 1,2-dimethylenecycloalkanes display frequencies characteristic of conjugated double bonds, methylene groups, etc.[6,10,41,18,22,33,34,44,58,61]. However, owing to the diversity of the observations and in some cases to the insufficient purity of the substance, no general conclusions can be drawn from them, except to note that they do not show the anomalies characteristic of the spectra of acyclic dienes.

4. POLYMERISATION

The development of the chemistry of 1,2-dimethylenecycloalkanes is primarily connected with the problem of stereospecific polymerisation. Polymerisation of these dienes is important as it is expected to be certain to give *cis*-1,4-polymers (XIV), that is complete structural analogues of natural rubber (XV), which should display some of its invaluable properties:

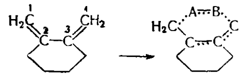

(XIV)


(XV)

The radical, ionic, and thermal polymerisation of 1,2-dimethylenecycloalkanes have so far been insufficiently studied.

As a rule, 1,2-dimethylenecycloalkanes polymerise more readily than the corresponding acyclic dienes. For instance, under the same conditions polymerisation of 1,2-dimethylenecyclobutane yields 96% polymer, whereas only 13% polymer is obtained from its open-chain analogue (2,3-dimethylbutadiene).[22] However, the ease of polymerisation depends essentially on the method used. Thus, 1,2-dimethylenecyclohexane polymerises well in various emulsion systems, or in the presence of BF_3 or $AlCl_3$ at -70°, but worse in the bulk in the presence of benzoyl peroxide, and not at all under Ziegler's conditions, *viz.* $TiCl_4$ + $Al(iso\text{-}C_4H_9)_3$, 50°, 24 h.[26,45,62] On the other hand, 1,2-dimethylenedecalin does not polymerise at all under the influence of peroxides, but in the presence of BF_3 it yields 47% polymer[15].

The connection between the reactivity of 1,2-dimethylenecycloalkane monomers and their spatial configuration is of particular interest. Blomquist and his coworkers[25,26] compared the polymerisation of 1,2-dimethylenecycloalkanes containing various numbers of carbon atoms in the ring. It was shown that the diene with a six-membered ring polymerises considerably more slowly than its analogues with four- and five-membered rings. This difference was related to the dissimilar spatial configurations of the exocyclic double bonds. In dienes with four- and five-membered rings the double bonds are rigidly fixed in the planar cisoid configuration, while in 1,2-dimethylenecyclohexane, if the cyclohexane ring has the thermodynamically favoured chair conformation[63], the double-bond system is not planar (the deviation from coplanarity can reach 60°). It was assumed that this was the reason for the reduced reactivity of the monomer to 1,4-addition. The transition state in 1,4-addition requires the formation of a double bond in the 2–3 position, and consequently bending the system of carbon atoms 1,2,3,4 into a coplanar or nearly coplanar position.



This is the reason for the greater energy required for the polymerisation of dienes with six-membered rings as compared with that needed for polymerisation of their four- and five-membered analogues where the diene system is coplanar[56]. It is impossible, at present, to tell whether this factor is completely responsible for the decreased reactivity of 1,2-dimethylenecyclohexane.

Another type of steric hindrance was observed in 3-methyl- and 3,6-dimethyl-1,2-dimethylenecyclohexane[7], which polymerise with difficulty, owing to the screening of the diene system by methyl groups; however, the copolymers of these dienes with 1,2-dimethylenecyclohexane were obtained relatively easily. The same type of steric hindrance was thought responsible for the failure of 1,2-dimethylenedecalin to polymerise with peroxide initiation[15].

As already mentioned, from their analogous structures the properties of poly-1,2-dimethylenecycloalkanes were expected to be similar to those of natural rubber. The first studies on this point, by Bailey and coworkers[56,62,64,65], gave completely unexpected results. Although infra-red spectra and X-ray analysis of the polymer of 1,2-dimethylenecyclohexane showed it to have similar structure to natural rubber, it did not possess rubber-like properties, and was found to be a solid crystalline compound with a sharp softening point (165°), soluble in benzene, decalin, and other organic solvents. Several similar polymers,

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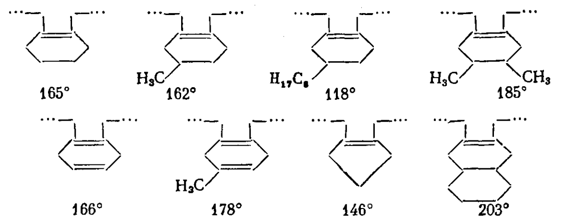
† It should be noted that the recently synthesised[43] 1,2-dimethylene-3,3-dimethylcyclohexane and 1,2-dimethylene-3,4,4-trimethylcyclohexane have absorption maxima close to the calculated value, at 233 and 230 mμ, respectively.

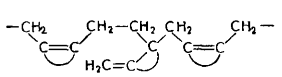
differing in degree of unsaturation, ring structure, molecular symmetry, softening point, etc. were obtained later:



Comparison of the softening points and solubilities of these polymers indicates that their properties are determined primarily by the general geometry of the molecule. Rubber-like polymers are obtained from the least symmetrical molecules. Ring substituents also play a part, although a minor one compared with the symmetry. Thus, changing from a methyl to an *n*-octyl substituent on the six-membered ring reduces the softening point of the resulting polymer by 44°.[56] The lack of elasticity in polymers of this type was accounted for by steric hindrance of the rings to internal rotation in the macromolecules‡.

The hydrogenation of poly-1, 2-dimethylenecycloalkanes lowers their softening points. Thus hydrogenation of poly-1, 2-dimethylenecyclohexane (softening point 165°) over a nickel-on-kieselguhr catalyst, in decalin solution, at 200° and 120 atm, gives a product which softens at 110°. The softening points of partially hydrogenated polymers lie between 110° and 165°.[67]

Some modification of Bailey's ideas resulted from the fact that the softening point of the polymer depends on the method of preparation[33]. For instance, on bulk polymerisation with SO_2, 1, 2-dimethylenecyclobutane yields a crystalline polymer, softening point 170°,[25] while on emulsion polymerisation with $K_2S_2O_8$ [25,26] or bulk polymerisation with benzoyl peroxide[68] it gives elastic rubber-like polymers. It was also found that in most cases the polymers are not exact structural analogues of natural rubber, but contain a certain number of 1, 2-links, the number apparently depending not only on the nature of the monomer, but also on the method of polymerisation. The structure of such polymers can be represented by formula (XVI):



(XVI)

A study has been made recently of the ability of 1, 2-dimethylenecycloalkanes to polymerise under various conditions, and their softening points and the relative amounts of 1, 4- and 1, 2-links in the polymer chain have been determined. The results are collected in the Table. This study did not include estimation of the mechanical properties of the polymers.

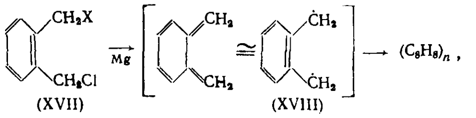
TABLE. Polymerisation of 1,2-dimethylenecycloalkanes.

Monomer	Method of polymerisation	Monomer conversion, %	Mol. weight of polymer*	*cis*-1, 4-links, %		Polymer properties	Ref.
				from IR spectra	from $C_6H_5CO_3H$ oxidation		
1,2-Dimethylene-cyclobutane	emulsion $K_2S_2O_8$			80	80	rubber-like	22,23
1,2-Dimethylene-cyclopentane	emulsion $K_2S_2O_8$,50°	100		100	94	rubber-like	18,25, 26
1,2-Dimethylene-3-methylcyclopentane	emulsion $K_2S_2O_8$,50°, 24 h	100		100	72	rubber-like	18,25, 26
1,2-Dimethylene-cyclobexane	emulsion or BF_3 at −70°	55	100 000	100		softg. pt. 164.5°–165°	62
1,2-Dimethylene-cyclohexane	emulsion $K_2S_2O_8$,50°, 60 h	100		100		softg. pt. 148°–152°	26
1,2-Dimethylene-4-neopentyl-cyclohexane	emulsion				66	rubber-like	57
1,2-Dimethylene-4-octylcyclohexane	emulsion with peroxide		30 000			softg. pt. 109°–118°	66
1,2-Dimethylenebicyclo[2,2,1]-heptane	emulsion with peroxide		50 000	70		softg. pt. 90°	12
1,2-Dimethylenebicyclo[2,2,2]-octane	emulsion with peroxide		40 000	85		softg. pt. 190°	12
1,2-Dimethylene-decalin	BF_3 at − 70°	57				softg. pt. 102°–112°	15

* Molecular weight of polymer estimated from viscosity data.

Copolymerisation of 1, 2-dimethylenecycloalkanes with other monomers, besides that of 1, 2-dimethylenecyclohexane with its methylated homologues[7] already mentioned, has been described in patents. 1, 2-Dimethylenecyclohexane has been copolymerised (in emulsion or with BF_3) with butadiene, chloroprene, styrene, various derivatives of acrylic and methacrylic acids, vinyl chloride and acetate, and methoxyethylene. The resulting oily or rubber-like products were suggested for use as plasticisers or siccative oils[45]. 1, 2, 4-Trimethylenecyclohexane was reported[67] to form a viscous rubber-like copolymer with butadiene under the action of lithium in cyclohexane at -70°.

A series of papers deals with the preparation of the solid poly-*o*-xylylene, the polymer of 1, 2-dimethylenecyclohexa-3, 5-diene [*o*-quinodimethane (XVIII)]. According to molecular orbital calculations[61,68], compound (XVIII) must have a biradical character (the free-valency index of the carbon atoms in the methylene groups is 0.96), and consequently should polymerise readily. In fact, efforts to synthesise *o*-quinodimethane by pyrolysis of the corresponding diacetate[69] or by the action of magnesium on compound (XVII) (where X = Cl, OCH_3, OC_6H_5)[70] resulted only in poly-*o*-xylylene:



(XVII) (XVIII)

Poly-*o*-xylylene also results from pyrolysis of *o*-xylene[69,71]. However, mass-spectrometer data indicate that at a high temperature (825°–1000°) and low pressure (10^{-3} mm) *o*-quinodimethane monomer is formed from *o*-xylene[72].

1, 2-Dimethylenecycloalkanes are distinguished by the ease of their thermal polymerisation. 1, 2-Dimethylene-3, 6-dioxane, after 24 h at 25°, yields quantitatively a white vitreous thermopolymer, m.p. 240°. There are reports of the polymerisation, on standing or heating, of 1, 2-dimethyleneacenaphthene[73,74], 1, 2-dimethylenecyclobutane[47,75], and 1, 2-dimethylene-3, 3, 4, 4-tetramethylcyclobutane[47], all giving solid thermopolymers without

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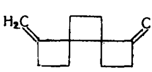
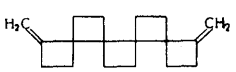
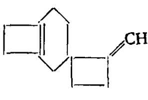
‡ In contrast to the polymers mentioned above, the chlorinated diene polymer (XII) obtained in the presence of peroxides, softens above 180°, and does not have a crystalline structure[44].

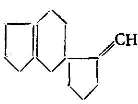
elastic properties. Only the structure of the 1, 2-dimethylenecyclobutane polymer, obtained at 200° (1.25 h) was investigated. It softens at 81° and melts at 162°–165°. Its degree of unsaturation, determined by bromination, corresponds to an average degree of polymerisation of 11.5, and its structure is that of the usual 1, 4-addition type (XIV).[47,75] Lebedev[47] also isolated thermopolymers formulated with a spiro structure (XIX) and (XX); this structure has, however, been questioned recently[53].

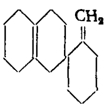

(XIX)


(XX)

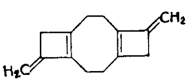
Thermal polymerisation of 1, 2-dimethylenecycloalkanes is almost always accompanied by, and sometimes results only in the formation of cyclic dimers. Lebedev[47], the first to study this phenomenon, isolated about 5% 1, 2-dimethylenecyclobutane dimer, to which he ascribed the structure (XXI), by heating allene in a sealed tube. Similar formulae were adopted for the dimers of 1, 2-dimethylenecyclopentane (XXII)[18] and 1, 2-dimethylenecyclohexane (XXIII)[76] on the basis of their infra-red spectra (and oxidation by $KMnO_4$).

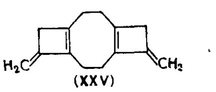

(XXI)


(XXII)

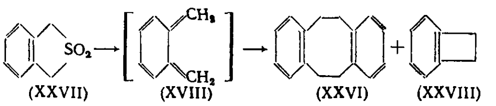

(XXIII)

Trimethylenecyclobutane dimerises at room temperature to a compound which, from its infra-red and ultra-violet spectra, is ascribed the eight-membered ring structure (XXIV) or (XXV)[37].


(XXIV)

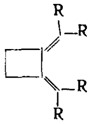

(XXV)

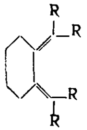
The eight-membered ring dimer, 1, 2: 5, 6-dibenzocycloocta-1, 5-diene (XXVI), is also formed from 1, 2-dimethylenecyclohexa-3, 5-diene (XVIII), which is an intermediate product in the pyrolysis of the sulphone (XXVII). The tetraene (XVIII) undergoes either intermolecular cyclisation, giving the dimer (XXVI), or intramolecular cyclisation forming benzocyclobutane (XXVIII). In the liquid phase pyrolysis of the sulphone (dissolved in diethyl phthalate at 300°) the product (XXIV) predominates, while the reaction in the vapour phase at 460°–770° yields mainly (XXVIII).[77] Other compounds containing an *ortho*-quinonoid system of double bonds cyclise in like manner[78,79].


(XXVII) (XVIII) (XXVI) (XXVIII)

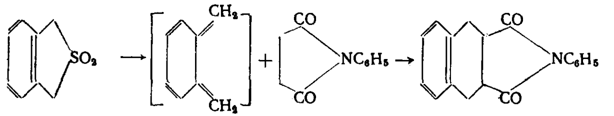
5. DIENE SYNTHESES

1, 2-Dimethylenecycloalkanes react readily not only with highly reactive dienophiles such as maleicanhydride and tetracyanoethylene[80], but also with ethylene[81]. The extra reactivity is expected because the transition state for diene synthesis requires the *cis*-configuration of the diene[82]. The reactivity of the dienes studied is not greatly affected by the ring size or the presence of alkyl substituents, although the introduction of a double bond or a carbon bridge into the ring considerably lowers the yield of adducts. Certain 1, 2-dimethylenecycloalkanes, for example the chlorinated diene (XII), are completely inactive in the diene synthesis, and this is explained by their diene system not being coplanar owing to the chlorine atoms in the bridge[44]. The ability to take part in diene condensation is also lost when the double bonds are screened by substituents, *e.g.* compounds of type (XXIX) and (XXX) ($R = CH_3$ or C_6H_5) do not react with maleic anhydride[39,83–85].

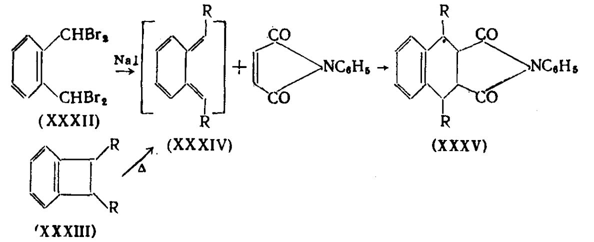

(XXIX)


(XXX)

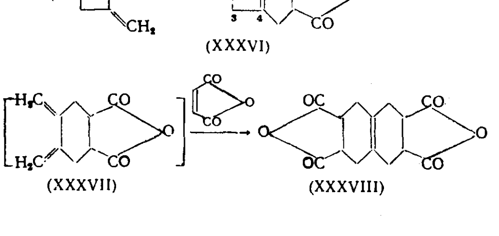
Many 1, 2-dimethylenecycloalkanes are very unstable in the free state, and condensations involving them must be carried out on the reaction mixture without their isolation. Examples are 1, 2-dimethyleneacenaphthene[41], 1, 2, 4-trimethylenecyclohexane[55], and the unisolatable *o*-quinodimethane (XVIII). Pyrolysis of the sulphone (XXVII) at 260° in the presence of *N*-phenylmaleic imide gives the adduct (XXXI) in 78% yield[77].


(XXVII) (XVIII) (XXXI)

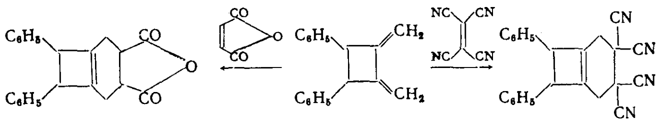
Similarly, tetrabromo-*o*-xylene (XXXII)[86] and 3, 4-di-idoor 3, 4-diphenyl-1, 2-benzocyclobutane (XXXIII) (R = I or C_6H_5),[87,88] yield as intermediate products the corresponding derivatives of *o*-quinodimethane (XXXIV), where R = Br, I or C_6H_5, which give the adducts (XXXV) with dienophiles. Unsubstituted 1, 2-benzocyclobutane does not react in this way[77].


(XXXII) (XXXIV) (XXXV) (XXXIII)

A cyclobutene ring formed in the diene synthesis is unstable. For instance, in the condensation of 1, 2-dimethylenecyclobutane with maleic anhydride[22,48,49] at room temperature or in boiling benzene, the monoadduct (XXXVI) is formed, but heating at 150° ruptures the 2, 3-bond of the cyclobutene ring; the intermediate (XXXVII) then gives the diadduct (XXXVIII).

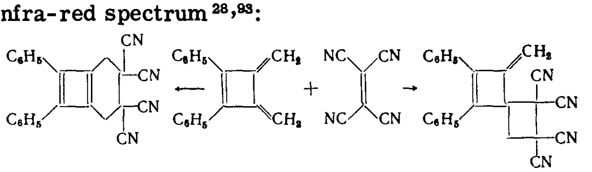

(XXXVI) (XXXVII) (XXXVIII)

Rupture of the cyclobutene ring in diene synthesis seems to be a general rule, and is the result of activation of the β-position by the presence of a double bond in the four-membered ring[89-92]. It is interesting that the reactions of 1, 2-dimethylene-3, 4-diphenylcyclobutane (XXXIX) with maleic anhydride and tetracyanoethylene are exceptions to this rule, yielding the normal monoadducts (XL) and (XLI), without rupture of the cyclobutene ring[28].



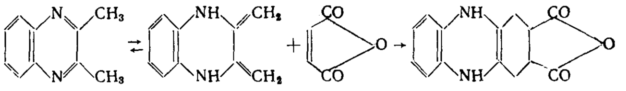
(XL) (XXXIX) (XLI)

The behaviour of the unsaturated hydrocarbon (XLII) is peculiar since with tetracyanoethylene it forms adduct (XLIV) instead of the substituted cyclobutadiene (XLIII). The spiro structure of (XLIV) was adopted on the basis of its infra-red spectrum[28,93]:



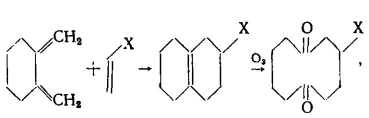
(XLIII) (XLII) (XLIV)

Dimethylene derivatives of heterocyclic compounds react with dienophiles according to the general scheme for diene synthesis[43]. For example, 2, 3-dimethylquinoxaline reacts in its tautomeric form (XLV) with dienophiles to give the normal adduct (XLVI)[94,95].



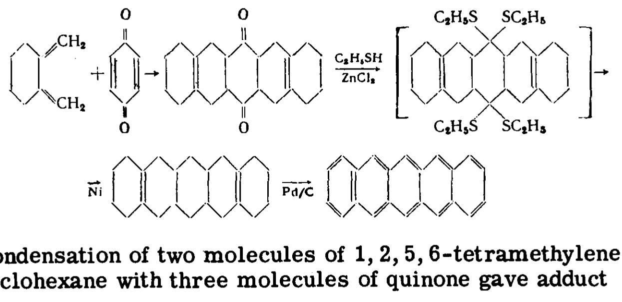
(XLV) (XLVI)

Adducts of 1, 2-dimethylenecycloalkanes with various dienophiles can be used for the synthesis of compounds otherwise difficult to obtain. For instance, ozonolysis of adducts of 1, 2-dimethylenecyclohexane gives cyclodecane derivatives in high yields[96]:

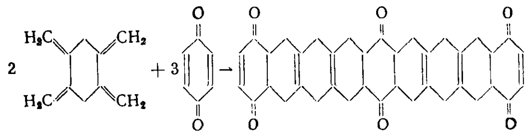


where $X = COOC_2H_5$, $COOCH_3$, NO_2.

Adducts of 1, 2-dimethylenecycloalkanes with quinones can be used to prepare linear fused aromatic hydrocarbons[5,97-100]. Pentacene, for example, has been synthesised in 30% yield as follows[98]:

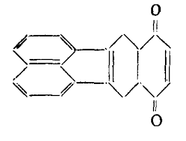


Condensation of two molecules of 1, 2, 5, 6-tetramethylenecyclohexane with three molecules of quinone gave adduct (XLVII), from which nonacene was obtained by the above method[21]:

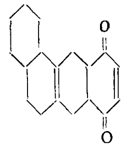


(XLVII)

Adducts of 1, 2-dimethyleneacenaphthene[41] and 1, 2-dimethylenedecalin[15] offer interesting possibilities for the synthesis of fused aromatic hydrocarbons. With quinone they give respectively adducts (XLVIII) (a derivative of 8, 9-benzofluoroanthene) and (XLIX) (derivative of 1, 2-benzanthracene).

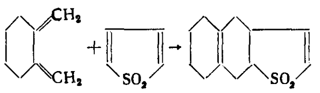


(XLVIII)



(XLIX)

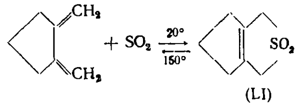
Finally, the reaction of 1, 2-dimethylenecycloalkanes with thiophene 1, 1-dioxide is used to prepare sulphur heterocycles of type (L):[101]



(L)

6. OTHER CHEMICAL PROPERTIES

1, 2-Dimethylenecycloalkanes react with sulphur dioxide to form cyclic sulphones. With SO_2 1, 2-dimethylenecyclopentane gives (two days, 20°) 60% yield of the sulphone (LI), which decomposes at 145° – 150° into the starting compounds[18].



(LI)

1, 2-Dimethylene-4-neopentylcyclohexane also forms a sulphone[57], while 1, 2-dimethylenecyclobutane gives with SO_2 a sulphur-free polymer and not the expected sulphone[22].

Oxidation and ozonolysis of 1, 2-dimethylenecycloalkanes have been used in structure determination. The C – C bond lying between the methylene groups ruptures during oxidation to yield the corresponding diacids[22-25]. On ozonolysis, 1, 2-dimethylenecyclohexane[6] gave adipic acid in 75% yield, and 1, 2-dimethylenebicycloheptane[11] gave 17% *cis*-cyclopentane-1, 3-dicarboxylic acid. Dicarboxylic acids are also obtained by the oxidation of 1, 2-dimethylenecycloalkanes with $KMnO_4$ [47,53] or $Na_2Cr_2O_7$.[73] The methylene groups are not then oxidised to formaldehyde, as in ozonolysis, but to formic acid.

Dimethylenecycloalkenes isomerise readily to form aromatic compounds on heating for a short time with palladium deposited on charcoal. In the conversion of dimethylenecyclohexene to a benzene derivative about 30 kcal mole^{-1} are liberated. 1, 2-Dimethylenecyclohex-4-ene isomerises to *o*-xylene in 97% yield[102]; its homologues react likewise[4,10]. Isomerisation of 1,2-dimethylene-3,6-dimethylcyclohex-4--ene[10] yielded only 40% 1,2,3,4-tetramethylbenzene, however. This was accounted for by repulsion of the methyl and methylene groups, hindering the aromatisation. Heating 1,2-dimethylenecycloalkenes with hydrochloric acid also causes their conversion to aromatic hydrocarbons, but in considerably smaller yield than with palladium[2,4,102]. 1,2,4-Trimethylenecyclohexane isomerises to trimethylbenzene in good yield on boiling with chloroform in the presence of *p*-toluenesulphonic acid[55]. Aromatisation is not complete if this triene is treated with t-butyl potassium.

Other reactions of 1,2-dimethylenecycloalkanes have not been studied to the same extent. Hydrogenation or bromination of these dienes is known to proceed normally, *viz.* by the addition of two molecules of hydrogen or bromine to one molecule of diene[1,23,29,44]. The addition of one molecule of halogen (Cl_2 or Br_2) to the triene (XII) takes place at the 1 and 4 positions of the diene system[44], but hydrogen chloride reacts with 1,2-dimethylenebicycloheptane at the 1 and 2 positions[17].

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A.A.Grinberg

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I. IMPORTANCE OF APPLICATIONS OF CO-ORDINATION CHEMISTRY

The name "co-ordination chemistry" shows that this branch of chemistry was based on Werner's co-ordination theory, but considerable development has taken place from the theory put forward in 1893 to co-ordination chemistry as it stands today. About forty years ago, at the time of Werner's death, co-ordination theory dealt with material which was regarded as part of inorganic chemistry and included a group of compounds whose compositions could not be explained satisfactorily by classical valency theory.

The chemistry of complex compounds was regarded as an extremely specialised branch of chemistry and many organic and physical chemists considered it unnecessary to become familiar with it. Gradually, however, it became apparent that co-ordination theory was of great importance for the development of adjacent fields of science, and as a result, co-ordination chemistry ceased to be merely a branch of inorganic chemistry and became a field of interest to inorganic, organic, analytical, and physical chemists, biochemists, chemical crystallographers, and technologists in different fields. It first became clear that complex compounds were extremely important for developing analytical chemistry, and an important part was played by Chugaev, whose work on dioximes[1] laid the foundation for the systematic application of co-ordination complexes in qualitative and quantitative analysis. Dimethylglyoxime, dicyandiamidine[2], cupferron[3], and α-nitroso-β-naphthol, proposed for the determination of cobalt[4] as early as 1885, were the first successful examples of the use of organic reagents in chemical analysis.

It would be difficult now to list briefly the reagents proposed for qualitative detection or quantitative determination of individual elements. The methods of applying the reagents have also become extremely varied, and extend beyond their use for precipitation and colour reactions. Of particular importance is the use of complex-forming ligands in combination with extraction and ion-exchange methods. These processes are finding ever-increasing application for the separation and purification of lanthanides and actinides. Also we have the sequestering agents, which make it possible to bind complex-forming metals as very stable soluble complexes and so eliminate the catalytic influence of their ions on processes of technological or biochemical interest[5]. It is well known that the technology of the platinum group metals is entirely based on the use of complex compounds, and that the principal process for extracting gold from its ores (cyanide process) is also based on complex formation.

It has recently become clear that complex compounds are of considerable importance as catalysts or intermediate products in a variety of organic syntheses[6]. The change in the reactivity of organic ligands accompanying complex formation with a metal is particularly important. It is also important that the product formed by the organic molecules or ions with the complex-forming metal should be sufficiently labile to allow the process to occur again. Some examples of processes of practical importance where complexes act as catalysts are: (a) catalytic oxidation of

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These examples show the importance of complexes in organic synthesis. They must also be exceptionally important in processes taking place in animal and vegetable tissues. The part played in biology by such typical complex compounds as haemoglobin and chlorophyll is well known. When we consider that insulin is a zinc complex, vitamin B_{12} one of cobalt, the phenoloxidase enzymes complexes of copper, and the catalases and peroxidases complexes of iron, it becomes clear that complex formation is closely related to important vital processes. We could also quote illustrations of the importance of co-ordination chemistry in the development of crystal chemistry and radiochemistry, but the above examples suffice to emphasise that the *applications* of modern co-ordination chemistry are increasing rapidly and continuously. The combined theoretical and practical importance of co-ordination chemistry apparently explains the great interest shown in this branch of chemistry by young students.

II. IMPORTANCE OF QUANTITATIVE PARAMETERS IN CO-ORDINATION CHEMISTRY

A second characteristic of modern co-ordination chemistry is its gradual transformation to a strictly quantitative science. Hein has stated[7] that Werner's theory was the last great purely-chemical theory. The theory itself contains no calculation, apart from the enumeration of the isomers to be expected from octahedral or planar models of complex ions. For the solid state, X-ray structure analysis has not only confirmed the correctness of Werner's models but has also made them more definite by giving the values of the interatomic distances and bond angles. In the case of solutions, it is interesting that even as early as the end of the nineteenth century Abegg and Bodländer had introduced the concept of instability constants and pointed out several approaches to a quantitative estimation of the stability of various complexes. This pioneer work, however, remained obscure for a long time.

In the first decade of the present century, the concept of instability (or stability) constants was used systematically by a few workers, including Niels Bjerrum. The energy effects accompanying the manifestation of secondary valency were at first characterised quantitatively by thermochemical and tensimetric measurements; the vapour pressures of ammines of various metals were measured at different temperatures by Isambert, Ephraim, and more particularly, W.Biltz.

A quantitative theory of stepwise complex formation in solutions was given by J. Bjerrum in his classic paper of 1941.[8] He developed this theory and also an experimental procedure applied to the formation of ammines and amine complexes in aqueous solution. Systematic studies on the determination of stepwise constants in solutions of acido-complexes were carried out at about the same time by Babko[9]. The work of Bjerrum and Babko was the starting point for a vast number of determinations and methods of calculation of instability constants in aqueous solutions of complexes of a number of metals. They marked a new stage in the development of co-ordination chemistry. In addition to Bjerrum's method for finding stepwise constants of complex formation in solution, methods were put forward by Leden[10] and Fronaeus[11]. All these methods are applicable to stepwise complex formation provided that only mononuclear complexes are present in the solution. Sullivan and Hindman[12] have made a comparison and critical analysis of Bjerrum, Leden, and Fronaeus' methods for finding stepwise constants.

The experimental data necessary for calculating the constants can be obtained by potentiometric, conductometric, spectrophotometric, distribution, or ion exchange methods. Certain other methods can also be used, including polarography, developed in Czechoslovakia. Each method has special features which must be taken into account and the reliability of the results is naturally higher if they are confirmed by independent methods. A fairly large amount of data on stepwise formation constants for complexes of many metals with various ligands has now been accumulated.

In a few cases measurements have been made at different temperatures, making it possible to characterise the separate stages of complex formation by the thermodynamic quantities ΔG, ΔH, and ΔS. The accumulation of these data is exceptionally important, since it makes possible a complete thermodynamic characterisation of the tendency for a central ion to form complexes with ligands of very different chemical character. This should lead to a detailed analysis of the relation between the position of an element in the Periodic Table and its tendency to form complexes. As a first approximation, this relation has been established using a statistical approach[13]. On the other hand, these quantitative data on the stability of complexes raise new and extremely interesting problems concerning, for example, the factors determining the relative magnitudes of the stepwise constants of complex formation and the relation of these factors to the electronic structures of the complex-forming metal and ligand and hence to the nature of the bond in the complex.

In dealing with polybasic acids, each subsequent proton is, as a rule, more difficult to remove than the preceding one. However, within the limits of this effect, understandable in terms of electrostatics, individual acids show very large differences in the values of the successive constants. In the case of complexes consisting of a charged central ion and neutral ligands, the stepwise dissociation of the ligands is not accompanied by a change in the charge on the complex ion, so that there is no apparent electrostatic factor which might hinder the removal of ligands after the first. Examination of the available data on the stepwise dissociation of complexes of this type shows that in many cases the ratio of the successive constants is fairly close to that required by the statistical effect. Sometimes, however (for example with mercury(II) ammines), there is a very marked difference in the values of K_4 and K_3 on the one hand, and K_2 and K_1 on the other. In some cases (silver ammines), the first stability constant K_1 is found to be even smaller than K_2, that is, the attachment of a second ammonia molecule to the $AgNH_3^+$ ion leads to a marked increase in the stability of the co-ordination compound[8].

The case of silver ammines is not unique, and it is clear that the ratios of the successive constants and the factors on which they depend require further study. These relations should reveal a functional dependence on the nature of the co-ordinate bond in the individual cases, and should probably be analysed using the molecular orbital and ligand field theories. In the author's opinion, the crystal field theory and even the simpler electrostatic and polarisation theories still have a part to play in the chemistry of complex compounds. It is of course true that the molecular orbital theory is more rigorous and probably closer to reality, but the difficulties associated with its application to actual systems will, for some time, make it necessary to resort to crystal field theory, particularly in its improved form (ligand field theory)[6,14,15] and even to the less refined polarisation theories. Any theories based on the unmodified picture of an isolated central atom and isolated ligands can of course only approximately reflect the actual relationships.

The theory of stepwise complex formation was developed for the analysis of systems containing mononuclear complexes. Much work on methods for their synthesis and determination of their structures was done by Werner himself[16]. In extending the ideas of Bjerrum, Leden, Fronaeus, and others, the Swedish chemist Sillen[17] evolved an experimental procedure for the study of hydrolytic and polymerisation equilibria in solution leading to the formation of polynuclear complexes. The procedure of Sillen and co-workers establishes unambiguously the existence of polymerisation equilibria and makes it possible, without isolating the products from solution, to determine their composition and the constants for the separate stages of the dissociation.

Sillen's procedure is essentially a form of physicochemical analysis and this work introduces substantial changes in current theories of the nature of the hydrolysis products of salts of a number of metals and is of great importance in examining the complex nature of equilibria in solutions of borates, vanadates, chromates, etc. The successive and overall instability constants in solutions of platinum complexes are being systematically studied in our laboratory[18-19].

All this shows that the thermodynamics of complex formation is being extensively developed and will continue to be for many years. In the USSR it is being systematically studied by Babko, Komar', Yatsimirskii, and others. For several years the author has held the view that our ideas on the chemical behaviour of complex compounds will be complete only when we have enough information on both the thermodynamics and kinetics of complex formation. This is particularly true of the most typical and characteristic complex-forming species, for which the reactions of substitution and exchange in the co-ordination sphere take place relatively slowly.

The kinetics and mechanism of complex formation are now being studied in a number of laboratories. In England, Ingold's school, which has done much work on the mechanism of organic reactions and introduced the concepts of the S_N1 and S_N2 reactions, has taken up the study of exchange and substitution in cobalt(III) derivatives. Systematic studies of the kinetics of substitution in cobalt(III) derivatives are being made in the USA by Basolo and Pearson, who have developed the theory of the so-called S_N1CB mechanism, and also by Adamson and his pupils. The conclusions reached by English and American workers regarding the mechanism of these reactions show some disagreement.

Important kinetic studies on the trans effect in Pt^{II}, Pt^{IV}, and Rh^{III} derivatives have been made by Gel'man[20] and Zvyagintsev and Karandasheva-Shubochkina[21], and the kinetics and mechanism of exchange and substitution reactions in platinum derivatives are being systematically studied in our laboratory[22]. Some work on this topic has been done in the USA by Banerjea, Basolo, and Pearson[23] and by Elleman and Martin[24,25]. Interesting work on the kinetics and mechanism of redox reactions involving complex ions has been done in the USA by Taube, who has also attempted to classify complex ions as "labile" and "inert". One of his most interesting results is the discovery of the intermediate formation of bridged complexes of the type $(NH_3)_5Co^{III}Cl...Cr^{II}(H_2O)_5$. In these reactions the oxidation is accompanied by migration of a co-ordinated anion from the oxidising agent to the reducing agent[26]. Interesting work by Jezowska-Trzebiatowska's school[27] in Wrocław (Breslau) has shown that an increase in the rate of reduction of permanganates and ferrates by hydroxyl ions takes place on the addition of alkali metal cations, which apparently act as bridges, facilitating the approach of ions with charges of the same sign.

Work by the present author, Gil'dengershel' and In'kova has shown that some substitution reaction in the co-ordination sphere of Pt^{IV} derivatives involves intermediate redox processes[28,29], and additional data confirming these results were obtained in work with Kukushkin[30]. A general conclusion from our studies of the kinetics of exchange and substitution in Pt^{II} derivatives is that the lability or inertness of complexes is determined not only by the nature of the central atom and the co-ordination type of the complex, but also by the nature of the ligand and the solvent in which the reaction takes place. Studies by Taube[31] and Dreyer[32] indicate that another factor is the presence of catalysts, which can accelerate or retard isotopic exchange.

A second general conclusion is that the kinetics of isotopic exchange and substitution in Pt^{II} derivatives are not always determined by their thermodynamic characteristics. On the contrary, more stable complexes often undergo exchange and substitution reactions much more rapidly than those less stable[33,34]. This applies not only to platinum derivatives. Brown, Fallab, and Erlenmeyer[35] found that when α,α'-bipyridyl reacts with iron(II) and copper(II) salts, the less stable iron(II) complex is formed first and is converted to the more stable copper complex only after several hours. In the case of platinum derivatives, these characteristic relationships can be explained by the mutual influence of the co-ordinated groups.

III. MUTUAL INFLUENCE OF CO-ORDINATED GROUPS

Chernyaev's discovery[36] in 1926 of the trans effect was an exceptionally important addition to co-ordination theory. As he himself said of the trans effect, "it introduces the elements of dynamics into the pure geometry of Werner's theory".[37] The co-ordination theory, which made it possible to predict the number of isomers for any complex ion composition, did not indicate methods for the synthesis of these theoretically-possible iosmers. Chernyaev's rule gave chemists a means of predicting the direction of reactions in the co-ordination sphere and of synthesising compounds with a required structure. The theoretical essentials of the trans effect have not yet been revealed completely.

Recent experimental results have made it possible to characterise the trans effect quantitatively as a kinetic effect[21], but there are also data indicating that it has a thermodynamic aspect[38-45]. The recent attempts by Chatt[46], Cardwell[47], and Orgel[48] to explain the trans effect are essentially applicable only to the kinetic effect in Pt^{II} derivatives, but the trans effect is also shown in octahedral complexes of atoms other than Pt^{II}.

Of all the attempts which have been made to explain the trans effect, the most general is perhaps the suggestion that it is due to a redox interaction between the central ion and the ligand[49]. This interaction leads to an increase in the electron density between the central ion and the trans-active ligand. The interaction between the central ion and the group in the *trans*-position to the active ligand is changed and as a result the properties of this group approach those of a group in the unco-ordinated state. The old Nekrasov–Grinberg polarisation model is a particular case of this general theory.

It is possible that in Pt^{II} derivatives the presence of an electron pair capable of forming a dative bond is another factor intensifying the trans effect. In any case the study of the mutual influence of groups in the co-ordination sphere of various central ions is one of the most important problems in modern co-ordination chemistry. This importance is further emphasised by the fact that, as shown in our laboratory, co-ordinated groups may also influence kinetics and thermodynamic properties when present in the *cis*-position (the cis effect)[22]. Moreover, different workers hold different views on the relative magnitude of the trans effect shown by ligands attached to Co^{III}.[6,50-52]

IV. DIRECTIONS OF DEVELOPMENT OF CLASSICAL CO-ORDINATION THEORY WHICH ARE STILL IMPORTANT

For a long time after the co-ordination theory was put forward, attention was mainly directed to the stereochemistry of complexes with co-ordination numbers six and four. We have at present data on the stereochemistry of many elements in different oxidation states. The stereochemistry of Pt^{IV} was developed to an exceptional extent by Chernyaev's school[53-55]. Bailar's school made the first attempt to apply conformational analysis to the stereochemistry of complex compounds[56].

Of particular interest is the stereochemistry of those elements for which different degrees of oxidation correspond to different co-ordination numbers, and also of elements for which the spatial distribution of the co-ordinated groups depends on the chemical nature of the ligands. The stereochemistry of large ions, which can have a co-ordination number greater than six, is also interesting. In this connection attention should be directed to systematic studies of the stereochemistry of the lanthanides, actinides, and alkaline earth elements; such work has already begun in the Radium Institute and the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences. In its further development purely chemical studies will have to be combined with physical methods for determining structures. The work of Debye and Scherrer, Dickinson, Cox, Belov, Bokii, Porai-Koshits, Hanic, Rasmussen, Rundle, and others has already shown the important part played by direct X-ray diffraction methods in the determination of the structure of complexes.

If we do not restrict stereochemistry to stereostatics, the range of problems is extremely wide and should include all phenomena associated with the relation between chemical and physical properties of complex compounds and their spatial configuration.

In addition to stereochemistry, another very important problem of classical co-ordination chemistry is that of the acid–base and redox properties of complex compounds. Studies carried out over a number of years in our laboratory show that the features observed in the manifestation of acid–base properties by geometrical isomers may vary, depending on the mobility of the proton in the co-ordinated ligand and on the mutual influence of the co-ordinated groups. The fact that the acidity of U^{IV} derivatives is greater than that of Th^{IV} derivatives is of considerable interest. The importance of studies of the redox properties of complexes has already been mentioned: many years ago in our laboratory it was found that complexes of the platinum metals, in addition to stepwise secondary dissociation with the removal of co-ordinated ions or molecules, showed another characteristic property of complex ions, *viz.*, redox interaction between the central ion and the ligands leading to reduction of the central ion and removal of the oxidised form of the ligand[57,58]. Thus for the PtX_6^{2-} ion, for example, dissociation according to the scheme $Pt^{IV}X_6^{2-} \rightleftharpoons Pt^{IV}X_5^- + X^-$ is accompanied by dissociation according to the scheme $Pt^{IV}X_6^{2-} \rightleftharpoons Pt^{III}X_5^{2-} + X^0$. Measurement of the redox potentials of systems composed of PtX_6^{2-} and PtX_4^{2-} ions, together with a knowledge of the normal potentials of the $Pt^{4+} + 2e \rightleftharpoons Pt^{2+}$ and $X_2 + 2e \rightleftharpoons 2X^-$ systems, enables a quantitative relationship between these types of secondary dissociation of the complex to be established. Systematic studies on the influence of complex formation on the redox potentials of systems formed by a central ion and ligand are being made in the USSR by Fridman[59,60].

An extremely important direction of study in modern co-ordination chemistry is the synthesis and properties of such complex compounds as the carbonyls, the nitrosyls, compounds containing unsaturated olefinic or acetylenic ligands, the complexes, synthesised by Chatt and coworkers, containing co-ordinated hydrogen atoms[61], complex hydrides, and complex organometallic compounds of various types. Many of these types of compound are of considerable practical importance. We would merely refer to special new ligands like 1,8-bis(salicylideneamino)-3,6-dithiaoctane, first synthesised by Dwyer and Lions[62] (the co-ordination capacity of these ligands is six), and a number of new complexes prepared by Schwarzenbach's school and by Czechoslovak chemists. Particular mention may be made of the work of Majer, Dvořak, and Strugar[63], who prepared racemic and meso-forms corresponding to 2,3-diaminobutanetetra-acetic acid and stilbenediaminetetra-acetic acid.

The further study and application of these complexes, together with the use of optically-active ion exchangers, may be of wide theoretical and practical interest, and we may conclude, with Syrkin[64], that the synthesis of new types of complex may be extremely important in the further development of the theory of the chemical bond.

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SORPTION AND ION EXCHANGE ON AMPHOTERIC OXIDES AND HYDROXIDES

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CONTENTS

1. APPLICATIONS OF AMPHOTERIC OXIDES AND HYDROXIDES AS INORGANIC ION EXCHANGERS AND SORBENTS

The study of the sorption of electrolytes on oxides and hydroxides is of considerable importance in various fields of science: ion exchange, radiochemistry, chromatography, catalysis, inorganic chemistry, geochemistry, and soil science. The majority of amphoteric oxides and hydroxides are amphoteric ion exchangers (ampholytes) exhibiting both cation- and anion-exchange properties. The oxides and hydroxides of aluminium, iron, zirconium, tin, uranium, and other metals have been extensively used as ion exchangers and sorbents.

Considerable interest has recently been shown in the problems of sorption on amphoteric oxides and hydroxides in connection with study of the behaviour of fission fragments[1], isolation of radioactive isotopes[2], deactivation of effluents from radiochemical plants[3-6], studies in radiochromatography[7-8], and concentration of microquantities of radioelements[9].

Inorganic ion exchangers have a number of advantages over synthetic resins. In most cases the latter are decomposed in solution at temperatures over 150° and their capacity, selectivity, and rate of exchange are affected by high doses of ionising radiation (over 10^8 r [10-12]), whereas inorganic ion exchangers, particularly amphoteric oxides and hydroxides, are in most cases stable to high temperatures and ionising radiations[13].

Synthesis of inorganic ion exchangers of the amphoteric oxide and hydroxide type is extremely simple[14-16] and the cost per unit of capacity is in most cases much lower than that for organic resins. When inorganic ion exchangers are used to purify and deactivate various industrial solutions and effluents, regeneration of the ion exchanger is often unnecessary and it is effective when used once only. Some inorganic ion exchangers, such as zirconium and uranium hydroxides and zirconium phosphate, have high selectivity[7] and make possible a sharp separation of elements in the same group of the Periodic System on a column only a few centimetres long.

In addition to ion-exchange sorption, amphoteric oxides and hydroxides can be used for chemical[17-19] and molecular[20] sorption. The properties of ampholytes are also shown by some oxides and hydroxides which normally do not exhibit amphoteric properties, for example nickel oxide[21].

The chief disadvantage of these ion exchangers is that in most cases their capacity is lower than that of synthetic resins. Also, many amphoteric oxides and hydroxides dissolve in concentrated solutions of acid or alkali, making it impossible to use them when there is a marked change in hydrogen ion concentration. If, however, the ion exchanger is a polymer with a network structure, it is practically stable over any pH range[22].

Other possible uses of the sorptive and ion-exchange properties of amphoteric oxides and hydroxides should be mentioned. The ion-exchange sorption of cations and anions and also chemisorption on amphoteric oxides and hydroxides can be used as methods for changing the microchemical composition of the surface of oxide catalysts and for controlling catalytic properties. Zhabrova, Vladimirova, and Egorov[23] established that Na^+ and Cl^- ions introduced into zinc oxide by ion exchange increased the activity of the zinc oxide catalyst in the dehydrogenation of isopropyl alcohol. The sorption of zinc sulphate on zinc oxide, however, considerably decreased the rate of dehydrogenation and increased the rate of dehydration of the alcohol. Boreskov, Dzis'ko, and Borisova[24] found a decrease in the rate of dehydration of ethyl alcohol on aluminium oxide after sorption of sodium hydroxide. This is attributed to displacement, by sodium ions, of hydrogen atoms of the hydroxide groups on the catalyst surface.

The influence of sodium ions sorbed by the surface of oxide catalysts of more complex composition has been considered by many workers, but we shall refer to only a few examples. Bitepazh[25] showed that the aluminosilicate catalyst used for cracking is poisoned by sodium and other alkali metal ions sorbed by cation exchange on the catalyst surface. Topchieva[26] showed that it is possible to alter the activity of aluminosilicate catalysts (for various reactions) by means of sodium ions, introduced either from sodium chloride or acetate solutions or from sodium hydroxide solution.

The use of ion exchange to prepare sorbents with different sorptive properties, for example silica gels in which the exchanger hydroxide ions are replaced by fluoride ions[27], has also been proposed. It appears that by the rational use of the anion- and cation-exchange properties of oxides and hydroxides from which catalysts and sorbents are prepared, it is possible to introduce controlled quantities of impurities on to the surface; this is of considerable importance for controlling catalytic activity and sorptive properties. The irreversible chemisorption of electrolytes can be used as an effective method for controlling the microchemical composition of the surface of many amphoteric hydroxides used for the preparation of catalysts and sorbents.

2. SORPTIVE PROPERTIES OF VARIOUS OXIDES AND HYDROXIDES

A. Aluminium Oxide and Hydroxide

Aluminium oxide and hydroxide have been studied by many workers[28-32]. Nikol'skii[33] showed that the hydroxide ions or protons of aluminium hydroxide are replaced by anions or cations from the solution. This exchange is due to dissociation of $Al(OH)_3$ in two ways:

$$Al(OH)_3 \rightleftharpoons Al(OH)_2^+ + OH^-,$$
$$Al(OH)_3 \rightleftharpoons Al(OH)_2O^- + H^+.$$

Thus aluminium hydroxide may be either a cation exchanger (in alkaline medium) or an anion exchanger (in acid medium), and within a certain pH range can act as an amphoteric ion exchanger.

Various chromatographic processes on aluminium oxide have been studied[34-39], and cations and anions have been arranged[40-41] in order of their sorbability on aluminium oxide standardised by Brokmann's method[42]. The same has been done by Gapon and Shuvaeva[43]. The authors regard exchange on aluminate aluminium oxide as one of cations with Na^+ and exchange on acidic aluminium oxide as one of anions with NO_3^-. In aluminium oxide cation-exchanger the functional groups are the Na^+ groups in $(Al_2O_3)_x.AlO_2^-.Na^+$; when the aluminium oxide cation-exchanger is washed with nitric acid the product is aluminium oxide anion-exchanger whose exchange groups are the NO_3^- groups in $(Al_2O_3)_x.AlO^+.NO_3^-$.

The interesting phenomenon of the combined sorption of anions with highly-charged cations and of cations with highly-charged anions, established by Schwab[28-29], was attributed by Gapon and Shuvaeva[43] to a change in the sign of the surface charge. The sorption of anions with singly-charged cations and of cations with singly-charged anions was not observed by the authors.

Fischer[44] and Umland[45] classified the sorption of electrolytes on aluminium oxide as equivalent or nonequivalent†.

In the first case more cations than anions are sorbed (from $CuCl_2$ solution) and the solution becomes acidic. Equivalent quantities of cations and anions are readily washed off with water but an excess of sorbed cations cannot be washed off. This excess was attributed to exchange with aluminium ions or sodium ions present as an impurity in the Al_2O_3, being equivalent to the quantity of Na^+ or Al^{3+} passing into solution. The replacement of Al^{3+} by H^+ in the surface layer by treating the Al_2O_3 with 0.1*N* hydrochloric acid solution decreases the sorption and makes it equivalent. This phenomenon is related to the order of the cations in Schwab's series. In the second case more anions than cations are sorbed; this is attributed to exchange of anions with NO_3^- or OH^- ions, and has been observed for $NiCl_2$ and KCl. Excess sorption of anions or cations is attributed to a relatively strong bond (the sorbability) between cation or anion and the ion exchanger. Umland[45] and Hayek *et al.*[46] point out, however, that in many cases the separation of ions cannot be due entirely to processes of ion exchange or molecular sorption. The observed deviations from equivalence and the non-reproducibility of the series may be due to precipitation of sparingly soluble bases and basic salts.

Fischer[44] and Umland[45] observed sorption of anions and cations on pure aluminium oxide although Gapon[43] considers that it does not exhibit ion-exchange properties. Sorption was attributed to production on the surface of the oxide of H^+ and OH^- groups capable of exchange.

Voznesenskii *et al.*[18], using radioactive caesium, strontium, cerium, and ruthenium, showed that sorption of cerium and ruthenium takes place at a positively charged aluminium oxide surface by exchange with the potential-determining aluminium ions in the primary layer, while sorption of strontium takes place at a negatively charged surface as a result of the formation of aluminate at high pH values (Fig. 1). Almost no caesium is sorbed.

The structure and sorptive properties of aluminium oxide and hydroxide are greatly influenced by the conditions of their preparation. At the moment of formation aluminium hydroxide consists of amorphous particles and is an extremely active sorbent. During aging the gel becomes more compact and crystallises, with a decrease in active surface area and sorptive capacity[47-50]. By varying the conditions of preparation it is possible to obtain aluminium oxide with cation- or anion-exchange and also amphoteric ion-exchange properties[14, 15, 42, 43].

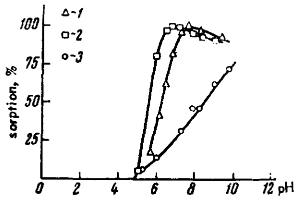

Fig. 1. Sorption isotherms for strontium, ruthenium, and cerium on aluminium hydroxide[18]: 1) Ce; 2) Ru; 3) Sr.

B. Ferric Oxide and Hydroxide

Much has been done on the sorption of ions on ferric oxide and hydroxide, and the work of Kurbatov and coworkers[51-61] must be mentioned first. From their results, they attempt a quantitative estimation of the sorption of doubly-charged cations. They consider that ferric hydroxide acts as a chemisorbent towards strontium, calcium, and barium, and assume that the process is reversible and obeys the law of mass action, but the regular features they observed can hardly express the general rules of sorption on hydroxides[62].

Ratner[63, 64] established that the sorption of cobalt, zinc, and radium on ferric hydroxide exhibits the characteristics of secondary exchange (ion exchange in the outer layer of the electrical double layer). Sorption is negligible at low pH values but increases sharply at pH 7.

According to the data of Voznesenskii *et al.*[3], the nature and mechanism of the sorption of highly-charged ions on ferric hydroxide differ from those for alkali and alkaline-earth metal ions. Sorption of highly-charged cations (yttrium, cerium, promethium and ruthenium) takes place to a considerable extent throughout the whole volume of the precipitate (internal sorption), whereas alkali and alkaline-earth metal ions (strontium and calcium) are sorbed only on the surface of the precipitate (adsorption). Desorption of alkaline-earth elements from ferric hydroxide is comparatively easy, but desorption of polyvalent elements is difficult. Highly-charged cations can

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† The term "nonequivalent sorption" denotes sorption of the cations and anions from an electrolyte solution in nonequivalent quantities. Electrical neutrality of the solution and sorbent is maintained by sorption or desorption of foreign ions.

be regarded as sorbed in the internal micro-cracks and micro-capillaries[65], or it is possible that solid solutions are formed. It is difficult to establish the nature and type of sorption on ferric hydroxide, however, since the structure of the sorbent itself is still disputed. The conditions of its precipitation and preparation have a decisive influence on its structure and sorptive capacity[47, 66-69]. According to Krause[70], the ferric hydroxide particles initially have the structure

$$Fe(OH)_2-O-Fe(OH)-O-Fe(OH)-Fe=O.$$

Polymerisation of these molecules yields complexes containing 40–50 iron atoms. These amorphous spherical particles of ferric hydroxide subsequently pack together and crystallise[47].

Pushkarev[19], in a study of the sorption of radioactive caesium, strontium, cerium, and ruthenium on ferric hydroxide, showed that the sorption of ruthenium and cerium is maximal at pH 3–6.5 and takes place at a positively charged surface by exchange with the potential-determining iron ions in the primary layer. The sorption of strontium takes place at fairly high pH values on a negatively charged surface with the formation of ferrites. Almost no cerium is sorbed. The shape of the sorption isotherms is similar to that for aluminium hydroxide (Fig. 1). Although this mechanism of the sorption of ruthenium and cerium (exchange with the potential-determining iron ions) is probably correct, there are some experimental data which made Pushkarev's conclusions doubtful. A negative charge may appear[71] on ferric hydroxide at pH > 3 and sorption of ruthenium and cerium as potential-determining ions becomes improbable. It is also necessary to take account of the state (ionic or colloidal) of the microquantities of radioelements which were used in the work[72]. Moreover, the nature of the potential-determining ions in ferric hydroxide is still disputed; different authors have assumed them to be Fe^{3+}, FeO^+ [73-75], or hydrogen ions[76,77].

Kargin *et al.*[76,78] studied the processes taking place when an Fe_2O_3 sol is treated with electrolytes and established that they involve complete or partial replacement of the peptising acid (HCl) by the acid (H_2SO_4) formed in the reaction between HCl and the added salt (Na_2SO_4). It was also found that the sorbed acids do not react with Fe_2O_3 to form iron salts down to pH 3. At low initial HCl concentration, the sorption of SO_4^{2-} and the displacement of Cl^- are approximately equivalent. With increase in the concentration of one or other of the acids, deviation from equivalent exchange takes place. The deviation is greater, the lower the equilibrium pH values.

Others have studied the sorption of cations on ferric hydroxide[79-82]. The results show that ferric oxide and hydroxide may exhibit either cation- or anion-exchange properties, depending on the presence of various impurities, the concentration of electrolyte, and the pH of the solution.

C. Titanium Dioxide

Titanium dioxide has been shown to exhibit amphoteric ion-exchange properties. According to Amphlett *et al.*[83], titanium dioxide exhibits anion-exchange properties in acid and neutral solutions, and cation-exchange properties in alkaline solutions. Amphlett attributes the amphoteric ion-exchange properties of titanium dioxide to hydrolysis of the oxide with formation of a surface layer of hydroxide and dissociation of the latter in two ways to form H^+ and OH^- functional groups capable of exchange, *i.e.*, the mechanism proposed by Nikol'skii for aluminium oxide[33].

Kargin[84] regards colloidal titanium dioxide as a sorbent capable of molecular sorption of salts and acids, and points out that sorption of neutral salts is negligible compared with the sorption of acids. It was found that with a mixture of sulphuric and hydrochloric acids, sorption of sulphuric acid predominates. At a fairly high equilibrium concentration of Na_2SO_4 (sulphuric acid is formed by reaction between HCl in the sol and the Na_2SO_4 added), the relation between sorption of SO_4^{2-} ions and solution pH is linear. Sorption of SO_4^{2-} stops almost completely at pH 6.5–7.

According to Maidanovskaya[85], titanium dioxide exhibits cation-exchange properties. It hydrolyses in water according to

$$TiO_2 + 2H_2O \rightleftharpoons TiO_2(OH)_2^{2-} + 2H^+.$$

The H^+ ions are functional groups capable of cation exchange.

D. Zirconium Oxide and Hydroxide and Derived Ion Exchangers

Ion exchangers based on zirconium are of particular interest. They have a high capacity, of the order of one milligramme-equivalent per gramme, corresponding to two milligramme-equivalents per cubic centimetre of dry material. They exhibit exceptional selective sorption, which makes it possible to separate elements in the same group of the Periodic System on a column only a few centimetres long. These ion exchangers have a three-dimensional polymeric network structure and are in most cases stable to acids, alkalies, high temperatures, and radiation. Much work has been done on them recently.

Zirconium oxide and hydroxide dissociate, in aqueous solution, as a weak base or weak acid[83]. The H^+ and OH^- functional groups produced on dissociation are capable of exchanging with cations and anions of the solution. In neutral and acid media, pure zirconium hydroxide acts chiefly as an anion exchanger. In alkaline solution, zirconium oxide and hydroxide are capable of exhibiting cation exchange[86]. Typical ion-exchange curves for zirconium hydroxide are given in Fig. 2

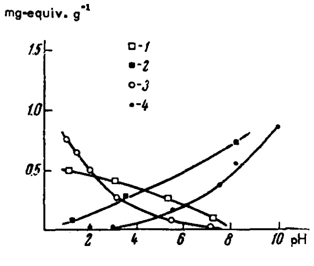
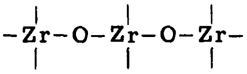


Fig. 2. Dependence of ion-exchange capacity of zirconium and stannic hydroxides on hydrogen ion concentration in solution[7, 86]:
1) and 2) $Zr(OH)_4$; 3) and 4) $SnO_2 . 2H_2O$.

The cation-exchange capacity of zirconium hydroxide is increased when the sorbent is treated with phosphoric acid[13,87,88]. This is shown in Fig. 3, which also gives the dependence of the cation-exchange sorption by zirconyl chromate on the pH of the solution[89]. Zirconium phosphate possesses a strongly acidic ionogenic group. The ion-exchange properties of the sorbent remain unchanged at 200° and it is extremely selective towards singly-charged ions. For example, rubidium and caesium ions are readily separated using zirconium phosphate.

Polymeric chains of the type



$$-\overset{|}{\underset{|}{Zr}}-O-\overset{|}{\underset{|}{Zr}}-O-\overset{|}{\underset{|}{Zr}}-$$

have been shown to exist in zirconyl perchlorate solutions. When such a solution is treated with a polybasic acid or its salt, the polymeric chains are linked by acid anionic bridges, and part of the acid or salt, by attaching itself to the free valencies, forms functional groups capable of exchange[89]. If the acid is strong, the products are strong ion exchangers; if the acid is weakly dissociated, titration of zirconium ion exchangers containing this acid as functional group shows that the ion-exchange sorption is very dependent on the pH of the solution. This dependence is similar to that for weakly acidic carboxylic or phenolic organic ion exchangers.

There are two viewpoints on the nature of ion exchange on zirconium exchangers. Bresler[89] considers that it takes place throughout the whole volume of the ion exchanger and is, within limits, independent of the particle size. The capacity of the ion exchanger will thus be directly proportional to its weight, but in contrast to a synthetic resin, the swelling is negligible. On the other hand, Kraus[7,90,91] suggests that exchange on zirconium ion exchangers takes place at the surface of the sorbent and the exceptional selectivity is attributed to differences in accessibility of the pores of the sorbent to different ions. Increase in the temperature of drying and ignition leads to partial sintering of the pores and to a decrease in the working surface and ion-exchange capacity of the sorbents.

Two possible mechanism of ion exchange on pure zirconium oxide and hydroxide may be put forward. According to the first, exchange is due to dissociation of zirconium hydroxide as an acid or base[83]. According to the second, reaction takes place in acid medium between the acid and the hydroxide[7], leading to formation of water from the proton of the acid and the hydroxide ion. According to Kraus and coworkers, this water remains fixed in the lattice or on its surface. The zirconium hydroxide lattice is positively charged, and the anion of the acid is attracted to it, so that both sorbent and solution attain electrical neutrality. If the anion of the acid does not diffuse into the depth of the lattice but remains on the surface, it can exchange with other ions of the solution and thus determine the ion-exchange capacity of the zirconium hydroxide. A similar phenomenon is shown in alkaline solution, but then the lattice is negatively charged and cations sorbed on the surface are responsible for the cation-exchange capacity. These schemes can be represented as follows:

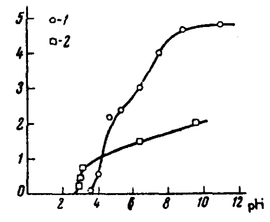


Fig. 3. Dependence of cation-exchange capacity of zirconium ion-exchangers on hydrogen ion concentration in solution[13,89].
1) zirconyl phosphate; 2) zirconyl chromate.

$$Zr(OH)_4 + HCl \rightleftharpoons [Zr(OH)_3H_2O]^+\ Cl^-$$
$$Zr(OH)_4 + NaOH \rightleftharpoons [Zr(OH)_3(O)H_2O]^-\ Na^+.$$

With lower pH, there is a higher positive charge on the lattice and greater anion-exchange capacity; with higher pH, higher negative charge on the lattice and greater cation-exchange capacity. Within a certain range of hydrogen ion concentration, both reactions are possible.

The frontal method has been used with zirconium ion exchangers to separate cations, and fairly high enrichment coefficients have been obtained[89]; the elution method has been used to separate alkali and alkaline-earth elements and to carry out separations within each group of the Periodic System. Zirconium oxide, hydroxide, tungstate, molybdate, and phosphate have been used for this purpose[13].

E. Zinc Oxide and Hydroxide

Less work has been done on ion exchange and sorption on zinc oxide and hydroxide than on typical inorganic sorbents and ion exchangers such as the hydroxides of iron, aluminium, zirconium. This is due firstly to the low ion-exchange capacity of zinc oxide and hydroxide and secondly to the solubility of zinc oxide sorbents in both acid and alkali solutions. Maidanovskaya[85] has shown that zinc oxide sorbs potassium and barium cations from neutral, weakly acidic, and weakly alkaline solutions, the sorption being of the electrochemical type. Sorption of anions from solution was not observed.

Tewari[92] studied sorption of hydroxide ions and protons on zinc hydroxide. The zinc hydroxide was prepared by reaction of a zinc salt ($ZnCl_2$) with alkali (NaOH), and its sorptive properties were found to depend on the presence of excess of one or other of these components. When prepared with excess NaOH it sorbed H^+ ions most strongly, and with excess zinc salt OH^- ions most strongly. Zhabrova and coworkers[17,23] established that zinc oxide is an amphoteric ion exchanger with functional groups of the weak acid type in alkaline solution and of the weak base type in acid solution (Fig. 4). In the neutral range, zinc oxide may exhibit both cation- and anion-exchange properties. Ion exchange on zinc oxide is limited to the narrow pH range 6.5–9.5. At pH ≥9.5 various zincates are formed, and in the acid range (pH ≤ 6.5) basic salts of varying composition may exist. Molecular sorption from fairly concentrated solutions of neutral salts, for example zinc sulphate[23], has been observed.

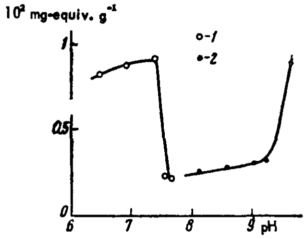


Fig. 4. Dependence of cation- and anion-exchange capacities of zinc oxide on hydrogen ion concentration in solution:
1) anionic exchange (Cl^-); 2) cationic exchange (Na^+).[17, 23]

F. Stannic Hydroxide; Oxides and Hydroxides of Some Other Metals

According to Merz, stannic hydroxide exhibits anion-exchange properties in acid media[86]. Stannic hydroxide contains mobile hydroxide ions which are replaced by an equivalent quantity of anions from the solution. At pH > 7, stannic hydroxide exhibits chiefly cation-exchange properties (Fig. 2). Kraus *et al.*[7] consider that stannic hydroxide starts to operate as a cation exchanger at pH > 3 (Fig. 2). The ion-exchange properties of uranium oxide and hydroxide, thorium and tungsten oxides, and various other oxides and hydroxides have also been described[7, 83].

3. SOME FEATURES OF THE MECHANISM OF ION EXCHANGE ON OXIDES AND HYDROXIDES

The ion-exchange properties of amphoteric oxides and hydroxides are as a rule determined by two factors. Firstly, they depend on the composition and structure of the sorbent. The presence of impurities may produce a sharp change in the capacity and selectivity of the ion exchanger. The structure of the sorbent may also have a marked influence on the selectivity of sorption. Thus crystalline sorbents are more selective than amorphous sorbents. Secondly, the ion-exchange properties of amphoteric oxides and hydroxides depend on the solution conditions, especially the hydrogen ion concentration. Since most of the ion exchangers we have considered are weak bases and weak acids, this dependence is particularly marked.

The regular features of ion exchange on hydroxides and oxides can be explained qualitatively in terms of two possible ion exchange mechanisms. According to the first, the functional groups capable of exchange are H^+ and OH^- groups on the surface or in the bulk of the oxide and hydroxide[17, 33, 83]. As a rule, the exchange sorption is markedly dependent on the pH of the solution. Whether dissociation is acidic or basic, with transfer of protons or hydroxide ions to the outer layer of the electrical double layer, is determined primarily by the pH.

The second mechanism of ion exchange is applicable to oxides and hydroxides with a high capacity for impurities[43-45], which may be introduced beforehand or on contact between the sorbent and solution. The amphoteric oxide or hydroxide acts as a rigid insoluble or sparingly soluble skeleton (often a three-dimensional polymeric network) on which functional groups capable of exchange are situated. These sorbents may be weak or strong ion exchangers, depending on the nature of the functional groups. In a number of cases these ion exchangers have a capacity greater than that of the pure oxides and hydroxides. When the functional groups are highly dissociated, the quantity of sorbed ions depends only to a slight extent on the pH of the solution.

Although the theory of ion exchange on oxides and hydroxides satisfactorily explains and confirms the experimental results qualitatively, there is as yet no clear quantitative theory of ion exchange on these sorbents. The isolated attempts to develop such a theory for individual sorbents can hardly reflect the general relationship[62].

The lack of a theory of ion exchange on oxides and hydroxides is due chiefly to the difficulty of systematising the experimental material and separating ion exchange distinctly from other sorption processes (this is not always possible). Molecular and chemical sorption may take place on these sorbents in addition to ion-exchange processes.

The results obtained by different authors for the same oxides and hydroxides and the same range of pH and electrolyte concentration often differ considerably. This is evidently due to differences in the conditions of preparation of the sorbents, uptake of impurities, etc. Data for ion exchange on stannic hydroxide and the hydroxides of zirconium, zinc, and other metals are given in the Table.

TABLE. Cation- and anion-exchange capacities of amphoteric oxides and hydroxides.

Sorbent	Cation exchange (capacity in mg-equiv. g^{-1})							Anion exchange (capacity in mg-equiv. g^{-1})							Reference
	pH 1	pH 3	pH 5	pH 7	pH 9	pH 11	pH 13	pH 1	pH 3	pH 5	pH 7	pH 9	pH 11	pH 13	
$Zr(OH)_4$	0	0.25	0.4	0.6	0.9	—	—	1	0.9	0.8	0.6	0	0	0	86
$Zr(OH)_4$	0	0	0.03	0.1	0.25	0.5	—	1	0.8	0.4	0.1	0	0	0	7
ZrO_2	—	—	—	—	—	—	—	1.15	0.8	0.6	0.4	0.2	0.1	0	88
$SnO_2 \cdot 2H_2O$	0	0	0.15	0.3	0.65	—	—	0.8	0.25	0.1	0.05	0	0	0	7
$SnO_2 \cdot 2H_2O$	0.05	0.35	0.5	0.7	0.8	—	—	0.5	0.4	0.3	0.2	0	0	0	86
ThO_2	—	—	—	—	—	—	—	—	1	0.75	0.5	0.15	0	0	88
$Fe(OH)_3$	—	—	—	—	—	—	—	—	—	0.07	0.13	pH 9.4 0.077	—	—	93
$Zn(OH)_2$	0	0	0	pH 8 $2.5 \cdot 10^{-3}$	pH 9.55 $2.7 \cdot 10^{-3}$	—	—	—	—	—	$8 \cdot 10^{-3}$	pH 7.75 $2 \cdot 10^{-3}$	0	0	17

For a quantitative consideration of ion exchange on amphoteric oxides and hydroxides, the following points must be noted. The ion-exchange capacity of the pure sorbent is determined chiefly by the degree of its acidic or basic dissociation. Let us assume that α_1 and α_2 are the degrees of acidic or basic dissociation of the hydroxide at the hydroxide – solution boundary. The functional H^+ or OH^- groups responsible for the ion-exchange properties lie in the outer layer of the electrical double layer. The degree of dissociation α_1 or α_2 is a function of the solution pH, concentration of ions, the ionic strength, nature of the solvent, temperature, etc. If exchange takes place only at the surface of the sorbent, the total ion-exchange capacity under a given set of conditions (pH, concentration of ions, temperature, etc.) will be

$$\Gamma = \alpha NS \qquad (1)$$

where Γ is the exchange capacity of 1 g of sorbent, α the degree of dissociation, N the number of hydroxide molecules per unit surface area, and S the specific surface of the sorbent.

If exchange takes place throughout the whole volume of the sorbent, Eqn. (1) becomes

$$\Gamma = \alpha MV \qquad (2)$$

where M is the number of hydroxide molecules in unit volume and V the specific volume of the sorbent.

When dealing with Eqns. (1) and (2) it is assumed that the volume of sorbent, the number of molecules of hydroxide per unit volume or specific surface, and the actual specific surface and specific volume are constant quantities independent of the pH of the solution, concentration of ions, ionic strength, temperature, etc. The variable α in Eqns. (1) and (2) which is a function of many parameters cannot at present be calculated.

It appears possible to determine the degree of dissociation experimentally by measuring the capacity of the electrical double layer under various initial conditions. Although the capacity of the double layer and the degree of dissociation are not related unambiguously to one another, to a first approximation this method may give useful results for moderate values of electrolyte concentration and pH close to 7.

Ion exchange on amphoteric oxides and hydroxides exhibits the features of a heterogeneous chemical reaction at the boundary of the electrical double layer, and Nikol'skii, on the basis of the law of mass action, put forward an equation for the exchange of two ions of equal valency[94, 95]

$$\frac{f'^{1/z_1}_{M_1} \cdot g^{1/z_1}_{M_1}}{f'^{1/z_2}_{M_2} \cdot g^{1/z_2}_{M_2}} = K \frac{f^{1/z}_{M_1} \cdot c^{1/z_1}_{M_1}}{f^{1/z_2}_{M_2} \cdot c^{1/z_2}_{M_2}}, \qquad (3)$$

where g is the concentration of the ion in the solid phase, c the concentration of the ion in solution, f' the activity coefficient of the ion in the solid phase, f the activity coefficient of the ion in solution, z the valency of the ion, M its index, and K the ion-exchange constant. Experiment has shown[96] that K is constant over a wide range of concentration of the sorbed ions.

Determination of the activity coefficients of ions in the solid phase is not at present possible. For ion exchangers such as pure oxides and hydroxides, however, the concentration of ions in the solid phase is generally small and the activity coefficients can, to a first approximation, be taken as unity.

The participation of H^+ and OH^- ions in an ion-exchange process often makes it difficult to treat the experimental results by means of any ion-exchange equation. The energy of the bond formed by a proton and a hydroxide ion with the sorbent is very much greater than that of bonds formed by other ions. The proton and hydroxide ion penetrate into the depth of the sorbent and may be held very strongly[97]. Moreover, when a proton or hydroxide ion takes part in ion exchange, there is a change in the pH of the solution before and after exchange, leading to a change in the constant in ion-exchange equations [for example K in Eqn. (3)].

Published data indicate that the following sorption processes are possible on amphoteric oxides and hydroxides: (1) ion exchange in the primary layer with potential-determining ions (cationic in acid, anionic in alkaline medium); (2) ion exchange in the outer (secondary) layer (anionic in acid, cationic in alkaline medium); (3) combined anionic and cationic exchange in the outer layer (close to the isoelectric point); (4) chemical sorption in acid medium with formation of basic salts and other surface compounds; (5) chemical sorption in alkaline medium with formation of aluminates, ferrites, zincates, and other compounds; (6) molecular sorption at high electrolyte concentrations and pH close to 7; (7) exchange between cations and anions in molecules sorbed by molecular sorption and cations and anions in solution; (8) combined sorption of anions with polyvalent cations and of cations with polyvalent anions, associated with a change in the sign of the surface charge.

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THE WITTIG REACTION

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CONTENTS

1. INTRODUCTION

As early as 1919 Staudinger and Meyer[1] discovered the formation of olefines in the reaction of phosphoranes of the type $Ar_3\overset{+}{P}-\overset{-}{C}R'R''$ with carbonyl compounds of the phenylisocyanate type:

$$Ar_3\overset{+}{P}-\overset{-}{C}R'R'' + O=C=NAr \rightarrow ArN=C=CR'R'' + Ar_3PO.$$

However, it was not till 1953 that Wittig and his collaborators[2] established that methylenetriphenylphosphorane, obtained by the reaction of phenyllithium with methyltriphenylphosphonium iodide, reacts with benzophenone to form 1,1-diphenylethylene (84%) and triphenylphosphine oxide (80%). They subsequently[3-6] generalised and developed this reaction into a method for transforming a C=O group into C=C:

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}HR + OC\langle \rightarrow \rangle C=CHR + (C_6H_5)_3PO.$$

This reaction has become very important in organic chemistry. It proceeds as a rule in one direction only, and gives high yields of a single product with the double bond in a definite position. For this reason it has a wide field of application in complex organic syntheses. In the synthesis of natural products and their analogues in particular, it has facilitated the solution of some basic problems. Its importance in the chemistry of natural products is brought out by the fact that about 80 out of 100 cases of its application were devoted to the synthesis of natural products and their analogues.

Several reviews on the Wittig reaction have already appeared in foreign periodicals[5-10]. The Soviet literature, however, has not yet dealt with it, apart from a translation of the review by Wittig[5] which appeared in November 1955, and was devoted to the initial stages of the development of this reaction.

In the present review we deal with the applications of the Wittig reaction in the synthesis of natural products (polyacetylenes, terpenes, carotenoids, vitamin A, steroids, vitamin D_2) and their analogues, *i.e.* the field where it has made the most important contributions.

2. ALKYLIDENEPHOSPHORANES

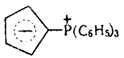
Until recently it was believed that only alkylidenetriphenylphosphoranes(I), where R = C_6H_5, are capable of undergoing the normal Wittig reaction. The view that alkylidenetriphenylphosphoranes are specific reagents in the Wittig reaction was based on theoretical considerations implied by the reaction mechanism put forward by Wittig[2-5]. For example, in 1949 Wittig and Rieber[11] prepared methylenetrimethylphosphorane, treated it with benzophenone, and after neutralising the reaction mixture with acid and adding potassium iodide they obtained a small yield of (β,β-diphenyl-β-hydroxyethyl)trimethylphosphonium iodide. In his systematic study of the Wittig reaction, Johnson[12-15] concluded that fluorenylidenetriphenylphosphorane and fluorenylidenetrimethylphosphorane do not give different reactions with carbonyl compounds, but are distinguished only in their stability and reactivity. This was later confirmed by Trippett and Walker[16], who showed that phosphoranes of type $(CH_3)_n(C_6H_5)_{3-n}\overset{+}{P}-\overset{-}{C}HCOCH_3$, $(CH_3)_n(C_6H_5)_{3-n}\overset{+}{P}-\overset{-}{C}HC_6H_5$ (where n = 0, 1, 2, 3), and $(CH_3)_2(C_6H_5)\overset{+}{P}-\overset{-}{C}HCOOC_2H_5$ react readily with carbonyl compounds, and form normal Wittig reaction products in high yields. These authors also succeeded in causing methylenetrimethylphosphorane to react with benzophenone and, in contrast to the results of Wittig and Rieber[11] (see above), obtained about 40% of 1,1-diphenylethylene, *viz.* the normal reaction product. The Wittig reaction is thus general to alkylidenephosphoranes and is only limited by their stability and reactivity.

The structure of alkylidenephosphoranes (including alkylidenetriphenylphosphoranes) can be expressed by formula (Ia) or (Ib):

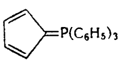
$$\underset{\text{(Ia)}}{R'R''\bar{C}-\overset{+}{P}(R)_3},\quad \underset{\text{(Ib)}}{R'R''C=P(R)_3},$$

viz. ionic or covalent.

The stability and reactivity towards carbonyl compounds is determined primarily by the distribution of the negative charge in the alkylidenephosphorane molecule, which in turn depends on the nature of substituents R′ and R″ in the alkylidene radical and of substituent R bound to phosphorus. It should be noted that increased stability of a phosphorane lowers its reactivity. The strong carbanion properties of alkylidenephosphorane (Ia) evidently assist its nucleophilic reaction with carbonyl compounds. If for any reason the carbanion character of alkylidenephosphorane decreases, reactivity is reduced. For example, cyclopentadienylidenephosphorane, whose structure is close to the covalent one (IIb), does not react with carbonyl compounds[17,18]:

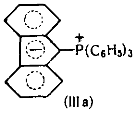


(IIa)

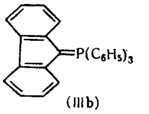


(IIb)

Fluorenylidenetriphenylphosphorane[13] whose structure is intermediate between ionic (IIIa) and covalent (IIIb), has a markedly low reactivity:



(IIIa)



(IIIb)

Methylenetriphenylphosphorane, where R′ = R″ = H, and no electronic influences lower the carbanion character of the molecule, has a pronounced reactivity[3,4,9]. Accordingly, methylenetriphenylphosphorane is the most unstable of all alkylidenetriphenylphosphoranes. It can be assumed that the substituents R′ and R″ in the carbanion lower the reactivity of alkylidenephosphorane in proportion to their electron-withdrawing capacity.

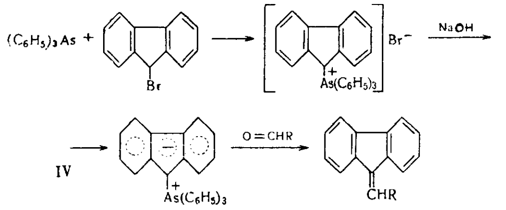
Very relevant to the stability and reactivity of alkylidenephosphoranes is the interaction between the carbanion and the phosphorus atom. The phosphorus atom can expand its octet to a decet, *viz.* form a fifth covalent bond, at the expense of its vacant *d* orbital. This property plays an important role in the chemistry of phosphoranes. In extreme cases the phosphorus atom accepts an electron pair from the *p* orbital of carbon into its *d* orbital, and this results in the establishment of a double bond between phosphorus and carbon (Ib) involving the *d* orbital. The possibility of the formation of multiple bonds was disputed by Jaffe[19-21], who concluded that such bonds are only possible if the central atom is positively charged. Thus, the degree to which the *d* orbital is involved in the reaction with the carbanion depends primarily on the magnitude of the formal positive charge carried by phosphorus. But what determines this charge?

Jaffe[20,21] and Rao[22], with their collaborators, showed in their study of the ultra-violet spectra of the polyphenyl derivatives of tri- and penta-valent phosphorus (in particular of triphenylphosphine and triphenylphosphine oxide) that there is no interaction between benzene rings and the tetracovalent phosphorus atom. However, although there may not be any electronic interaction, the substituents R attached to phosphorus can affect the magnitude of its positive charge by induction. As a result it could be expected that the higher the inductive electron-withdrawing effect (*I*-effect) of the substituent R the more probable is the participation of the *d* orbital in phosphorus in the reaction. This hypothesis is supported by the following data in the literature. Chatt *et al.*[23] studied the ultra-violet and visible spectra of a series of planar complexes of the type *trans*-[*L*, piperidine $PtCl_2$], where the ligands *L* were aliphatic amines, phosphines, etc., and found that the extent of the participation of the phosphorus *d* orbital in the reaction with the metal atom increased in the order $L = P(n\text{-}C_3H_7)_3 < L = P(OCH_3)_3$, which could only be explained by the larger *I*-effect of the methoxy group. Earlier, Chatt and Williams[24] in their study of the "trans effect" of ligands in complexes of trivalent phosphorus established that the π-bonding ability of trivalent phosphorus decreases in the order $PF_3 > PCl_3 > P(OCH_3)_3 > P(n\text{-}C_3H_7)_3$, *viz.* in the same order as the *I*-effect of the substituent. Finally, on the basis of studies of the infra-red spectra of nickelcarbonyldiphosphines[25] and of the compound[26] $L_3Mo(CO)_3$, where $L = PCl_3$, $P(C_6H_5)_3$, etc., it was concluded that the participation of the *d* orbital of phosphorus in the reaction with metal decreases in the order $PCl_3 > P(OC_2H_5)_3 > P(C_6H_5)_3 > P(C_4H_9)_3$, *viz.* in accordance with the *I*-effect.

Thus, alkylidenetrialkylphosphoranes in which the formal positive charge of the phosphorus atom is reduced by the *I*-effect of alkyl substituents should, other conditions being equal, be more reactive than alkylidenetriphenylphosphoranes in which the formal positive charge of the phosphorus atom is increased by the *I*-effect of phenyl rings. This can be illustrated by Johnson's experimental data[15].

Carbonyl compound	% yield of olefine, referred to phosphorane, under similar reaction conditions	
	fluorenylidenetriphenylphosphorane	fluorenylidenetri-*n*-butylphosphorane
CH_3CHO	90	93
$p\text{-}O_2NC_6H_4CHO$	96	99
$p\text{-}ClC_6H_4CHO$	93	96
C_6H_5CHO	84	96
$p\text{-}CH_3OC_6H_4CHO$	37	94
$p\text{-}(CH_3)_2NC_6H_4CHO$	0	94
$p\text{-}O_2WC_6H_4COC_6H_4NO_2\text{-}p$	0	93

Finally, it should be added that the ability to react with carbonyl functions to olefines is not confined to phosphoranes only. Wittig and Henry[27] found that methylenetriphenylarsane reacts with benzophenone to form, among other products, 1,1-diphenylethylene, the normal product of the Wittig reaction. More recently Johnson[14,15] made a thorough study of the reactions of fluorenylidenetriphenylarsane(IV) readily obtained by treating fluorenyltriphenylarsonium bromide with aqueous sodium hydroxide. On boiling with carbonyl compounds in chloroform solution fluorenylidenetriphenylarsane gives high yields of the corresponding olefines:



IV

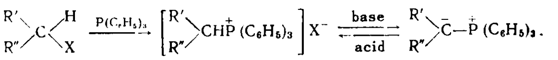
The yields obtained were: R = C_6H_5 (74%); p-$O_2NC_6H_4$ (92%); p-ClC_6H_4 (98%); p-$CH_3OC_6H_4$ (89%); p-$(CH_3)_2NC_6H_4$ (97%); CH_3 (91%).

Fluorenylidenetriphenylarsane is a stable, light-yellow compound which on long boiling with aqueous alcoholic sodium hydroxide yields triphenylarsine oxide. In its stability it is similar to the corresponding phosphorane.

To compare the reactivity of various reagents in the Wittig reaction, Johnson[15] determined the acid pK_a values of some fluorenylidenephosphoranes and obtained: for the triphenylphosphorane 7.5; the triphenylarsane 7.8; the tri-n-butylphosphorane 8.0. The pK_a of the fluorenylidene derivatives therefore decreases in the order triphenylphosphorane> triphenylarsane> tri-n-butylphosphorane, *viz.* in the inverse order of reactivity. Measurements of pK_a can therefore be used to determine the reactivity of the Wittig reagents.

According to their stability and reactivity, Wittig reagents can be divided into three groups. The first and largest group comprises the alkylidenetriphenylphosphoranes, which are characterised by considerable instability and high reactivity. The second group is relatively small, and includes stable yet reactive compounds. Finally, the third group includes a few alkylidenetriphenylphosphoranes having high stability and low reactivity.

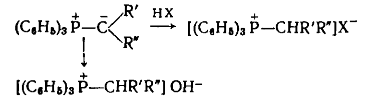
Alkylidenetriphenylphosphoranes are prepared from the easily obtained quaternary phosphonium salts according to the scheme



$$\overset{R'}{\underset{R''}{}}\!\!>C<\!\!\overset{H}{\underset{X}{}} \xrightarrow{P(C_6H_5)_3} \left[\overset{R'}{\underset{R''}{}}\!\!>CH\overset{+}{P}(C_6H_5)_3\right]X^- \underset{\text{acid}}{\overset{\text{base}}{\rightleftharpoons}} \overset{R'}{\underset{R''}{}}\!\!>\overset{-}{C}-\overset{+}{P}(C_6H_5)_3.$$

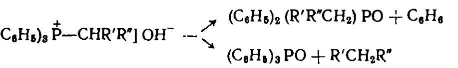
The method for the isolation of phosphoranes from phosphonium salts is chosen according to the group to which a particular phosphorane belongs.

The first group covers mainly phosphoranes containing hydrocarbon radicals in the alkylidene group, which have little or no effect on the carbanion character of the molecule. For example, the following are unstable and reactive triphenylphosphoranes: methylene-, ethylidene-, benzylidene-, cinnamylidene-, etc. These Wittig reagents have a strongly pronounced nucleophilic character and as a result react readily, often in the cold, with carbonyl and other polar groups. The action of hydrogen halides upon these alkylidenetriphenylphosphoranes results in the formation of the initial phosphonium salts, whereas the reaction with water yields hydroxides:



$$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}<^{R'}_{R''} \xrightarrow{HX} [(C_6H_5)_3\overset{+}{P}-CHR'R'']X^-$$
$$\downarrow$$
$$[(C_6H_5)_3\overset{+}{P}-CHR'R'']\,OH^-$$

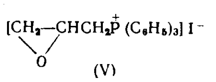
Hydroxides of this type are extremely unstable and decompose irreversibly into diphenylalkylphosphine oxide and benzene or triphenylphosphine oxide and alkane:



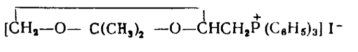
$$[(C_6H_5)_3\overset{+}{P}-CHR'R'']\,OH^- \to \begin{cases}(C_6H_5)_2(R'R''CH_2)PO + C_6H_6\\ (C_6H_5)_3PO + R'CH_2R''\end{cases}$$

For this reason the alkylidenetriphenylphosphoranes of the first group are highly sensitive to moisture and usually cannot be prepared from phosphonium salts using alkali hydroxides.

In rare cases the Wittig reagents of the first group are so reactive that during preparation they undergo secondary reactions. For instance, Bohlmann and Herbst[28] could not obtain phosphoranes from phosphonium salts of type (V) and (VI) owing to the extreme instability of the products formed



(V)



(VI)

The second group of Wittig reagents comprises compounds which contain, in the alkylidene radical, atoms or groups with electron-withdrawing properties, for instance acyl or ethoxycarbonyl groups. These do not, however, appreciably affect the carbanion character of the molecule, nor consequently, its reactivity. Acetylmethylene-[29] and ethoxycarbonylmethylene-triphenylphosphoranes[3], for instance, are colourless crystalline compounds which can be kept for a long time without change. The Wittig reagents of the second group react relatively readily with a number of carbonyl compounds. In contrast to the reagents of the first group, however, they do not react with ketones, as was observed, for example, in the reaction of ethoxycarbonylmethylenetriphenylphosphorane with the diethyl acetal of acetoacetic aldehyde[30]. Nor do alkylidenetriphenylphosphoranes of this type react with water, so that no precautions to exclude moisture are needed.

A typical representative of the third group is cyclopentadienylidenetriphenylphosphorane, which is a yellow crystalline substance, m.p. 229°–231°, which does not react with benzophenone, fluorenone, cyclohexanone, and other ketones on boiling in ether, chloroform, alcohol, or tetrahydrofuran for 120 h.[17,18] Although it apparently reacts with benzaldehyde[17], no pure reaction product could be isolated.

The unusual stability of this phosphorane, as already pointed out, is a result of the formation of a covalent bond between phosphorus and carbon with the participation of the vacant *d* orbital in phosphorus.

Fluorenylidenetriphenylphosphorane[13] is an interesting example of a compound similar in structure to cyclopentadienylidenetriphenylphosphorane, but in which the tendency for the formation of such a bond is considerably lower. It is nearly as stable as cyclopentadienylidenetriphenylphosphorane, and like this compound it does not react with acetone, cyclohexanone, fluorenone, and *p*-dimethylaminobenzaldehyde. Nevertheless, it reacts with benzaldehyde, *p*-methoxybenzaldehyde, *p*-nitrobenzaldehyde, and 2,4,7-trinitrofluorenone, giving the corresponding 9-arylmethylenefluorenes in 84–100% yield. Compounds of this group do not hydrolyse even on prolonged boiling in water.

It follows, therefore, that the use of the Wittig reaction in organic synthesis for the introduction of alkylidene groups is confined to reagents of the first and second (occasionally of the third) group. The application of the method is also limited by the reactivity of the reagents towards carbonyl functions.

Mention may be made of a recent new method[31] for the synthesis of alkylidenetriphenylphosphoranes, *viz*. formylalkylidenephosphoranes of the type $(C_6H_5)_3\overset{+}{P}-\overset{-}{C}(R)CHO$, by the reaction of methylenetriphenylphosphorane with an excess of ethyl formate:

$$R\overset{-}{C}H-\overset{+}{P}(C_6H_5)_3 + HCOOC_2H_5 \rightarrow (C_6H_5)_3\overset{+}{P}-\overset{-}{C}(R)CHO + C_2H_5OH,$$

where $R = H, C_2H_5$.

Formylalkylidenetriphenylphosphoranes belong to the second group of Wittig reagents and react normally with aldehydes on boiling in benzene solution. For example:

$$RCHO + (C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCHO \rightarrow (C_6H_5)_3PO + RCH{=}CHCHO,$$

where $R = C_6H_5$, yield 60%, $R = n\text{-}C_7H_{15}$, yield 81%.

It should be noted, however, that like ethoxycarbonylmethylenetriphenylphosphorane, formylmethylenetriphenylphosphorane does not react with ketones.

Methods of preparing quaternary phosphonium salts and, hence, alkylidenetriphenylphosphoranes, are given below.

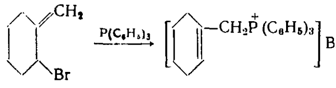
Phosphonium salts are prepared, according to the nature of the organic halide, by one of the following three methods:

1. heating triphenylphosphine with excess halide[32,33];
2. dissolving triphenylphosphine with an equimolar quantity of halide[33,34];
3. reacting equimolar quantities of triphenylphosphine and halide at or above room temperature in a suitable solvent[1,33].

The first two methods are rarely used, and then mainly for the preparation of phosphonium salts which are difficult to obtain. For instance, by heating triphenylphosphine with excess of 1,2-dibromoethane, 1,3-dibromopropane, or 1,4-dibromobutane at 150°–180° Wittig *et al.*[32] obtained bis-phosphonium salts of the type $[(C_6H_5)_3\overset{+}{P}(CH_2)\overset{+}{P}(C_6H_5)_3]2Br^-$ in 80 to 90% yields. Mondon[34] obtained the bis-phosphonium salt $[(C_6H_5)_3\overset{+}{P}(CH_2)_4\overset{+}{P}(C_6H_5)_3]2Br^-$ in 80% yield by melting at 250° the monophosphonium salt $[(C_6H_5)_3\overset{+}{P}(CH_2)_3.CH_2Br]Br^-$ with triphenylphosphine.

The third method, which is most widely used, is simple, convenient, and flexible. Ether and benzene[3] are most often used as solvents, toluene and xylene[33,35] and chloroform[33] less so. For phosphonium salts which are difficult to obtain, the use of highly polar solvents is recommended (nitromethane, nitrobenzene, and especially dimethylformamide[10,33]). For instance, boiling triphenylphosphine with 1,4-dichloro-2-butene or ω,ω′-dibromo-*m*-xylene in ether solution gives a mixture of mono- and bis-phosphonium salts; in chloroform, only the bis-phosphonium salts are obtained, in low yield; using nitrobenzene or dimethylformamide enables almost quantitative yields of bis-phosphonium salts to be obtained[33].

It should be noted that the formation of phosphonium salts from allyl halides is sometimes complicated by allylic rearrangement[36]:



Triphenylphosphine can react with various primary and secondary mono- and di-halogen derivatives: aliphatic saturated halides (methyl chloride, methyl bromide, or methyl iodide[2,3], isoamyl bromide[37] or iodide[38], n-dodecyl bromide[39], 1,2-dibromoethane[32], etc.), aliphatic-aromatic halides (benzyl chloride[40] or bromide[3], ω,ω′-dichloro-*p*-xylene[41], etc.), halides of the type of 9-bromofluorene[14], and various unsaturated halides (allyl bromide[3,42], cinnamyl bromide[40], 1-bromo-2,8-decadiene-4,6-diyne[42], geranyl bromide[43], cyclogeranyl bromide[43]). A most important feature of phosphonium salts is that they are capable of being formed from various halogen derivatives containing functional groups, *e.g.* haloketones (bromoacetone[29], ω-bromoacetophenone[29]), esters of halogen-substituted carboxylic acids (ethyl α-bromoacetate[3], methyl 4-bromocrotonate[44], etc.), and halogen-substituted ethers (α-chlorodimethyl ether[45]). The reaction rate decreases in the order iodide > bromide > chloride. The bromides are more commonly used, as they are easier to obtain.

In certain cases the success of the Wittig reaction depends on the kind of phosphonium salt (iodide, bromide, or chloride) used for the preparation of phosphorane. For example, Collins and Hammond[46] were unable to obtain methylenecyclopentane using the Wittig reagent prepared from methyltriphenylphosphonium iodide.

The most important stage in the development of the Wittig reaction was the preparation of alkylidenetriphenylphosphoranes from phosphonium salts. We discussed above the structure, stability, and reactivity of Wittig reagents. Methods for preparing alkylidenetriphenylphosphoranes from phosphonium salts depend entirely on the nature of the resulting phosphorane. The unstable alkylidenetriphenylphosphoranes, which belong to the first group, must be prepared in an anhydrous medium by reactions involving organometallic compounds, which serve as proton-acceptors. Most frequently a suspension of phosphonium salt in ether, tetrahydrofuran, or some other suitable solvent is treated with an ether solution of an equimolar amount of phenyl- or butyl-lithium, in a dry nitrogen atmosphere[3,4]. The reaction usually proceeds in the cold, and the formation of alkylidenetriphenylphosphorane can be observed from the appearance of an orange or cherry coloration. The carbonyl compound is subsequently introduced and the mixture is heated, if necessary, whereupon the colour gradually disappears. A variation of this procedure is the preparation of alkylidenetriphenylphosphorane by treating a suspension of phosphonium salt in liquid ammonia with sodamide and subsequently replacing the ammonia by ether or tetrahydrofuran. The preparation of phosphoranes by the action of alkali acetylides on a solution of phosphonium salt in dimethylformamide has also been described[47,48]. Since many phosphonium salts are conveniently prepared in dimethylformamide (see above), this variant of the Wittig reaction reduces to one stage only, without isolation of the quaternary salt.

In another method for the preparation of alkylidenetriphenylphosphoranes from phosphonium salts, sodium, potassium, or lithium ethoxide, or methoxide is used as proton-acceptor[3,10,40]. This method can be used for the preparation of stable phosphoranes of the second and third groups, as well as for some of the more stable phosphoranes of the first group, *e.g.* from bis-phosphonium salts. Mondon[34] used this method for the preparation of $(C_6H_5)_3\overset{+}{P}-\overset{-}{C}H(CH_2)_2\overset{-}{C}H-\overset{+}{P}(C_6H_5)_3$ from the appropriate bis-phosphonium salts, and Campbell and McDonald[41] for the preparation of bis-phosphorane from *p*-xylylene-bis-(triphenylphosphonium chloride). The reaction with unstable phosphoranes is carried out by adding an alcoholic solution of the equivalent amount of an alkali metal alkoxide to the mixture of the phosphonium salt and the carbonyl compound in alcohol, dimethylformamide, alcohol–methylene chloride, or alcohol–dimethylformamide[10].

Finally, the most suitable method for the preparation of stable phosphoranes of the second and third groups is the reaction of aqueous solutions of the phosphonium salt and alkali[49]. The resulting phosphorane forms a crystalline precipitate which after drying in the air can immediately be used in the reaction. The condensation of a stable phosphorane with carbonyl compounds is usually carried out in boiling benzene, tetrahydrofuran, chloroform, or other solvents.

One possible complication in the preparation of bis-phosphoranes from bis-phosphonium salts is the splitting off of triphenylphosphine. For instance, this was observed during the treatment of bis-phosphonium salt obtained from 1,2-dibromoethane and triphenylphosphine with an ether solution of phenyllithium[10]:

$$[(C_6H_5)_3\overset{+}{P}CH_2CH_2\overset{+}{P}(C_6H_5)_3]\,2Br^- \xrightarrow{C_6H_5Li} [(C_6H_5)_3\overset{+}{P}-CH=CH_2]\,Br^- + (C_6H_5)_3P.$$

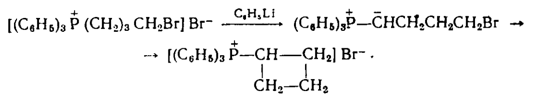
The resulting compound was vinyltriphenylphosphonium bromide.

A similar phenomenon was observed during the reaction of an ether solution of phenyllithium with the quaternary salt obtained from 1,4-dibromo-2-butene:[10]

$$[(C_6H_5)_3\overset{+}{P}CH_2CH=CHCH_2\overset{+}{P}(C_6H_5)_3]\,2Br^- \xrightarrow{C_6H_5Li} [(C_6H_5)_3\overset{+}{P}CH=CHCH=CH_2]\,Br^- + (C_6H_5)_3P.$$

These cases illustrate the need to use alkali metal alkoxides in the preparation of bis-phosphoranes.

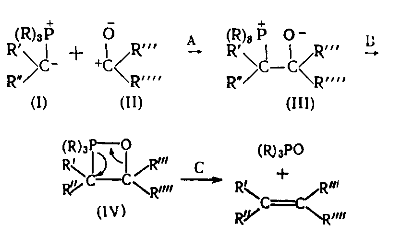
An interesting case is the decomposition of alkylidenetriphenylphosphorane to form a cyclic product[34]:



$$[(C_6H_5)_3\overset{+}{P}(CH_2)_3CH_2Br]\,Br^- \xrightarrow{C_6H_5Li} (C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCH_2CH_2CH_2Br \rightarrow [(C_6H_5)_3\overset{+}{P}-\underset{CH_2-CH_2}{\underline{CH-CH_2}}]\,Br^-.$$

3. MECHANISM AND STEREOCHEMISTRY OF THE WITTIG REACTION

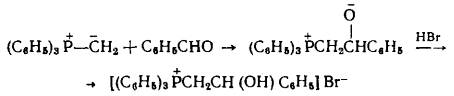
According to Wittig and Schöllkopf[3] the formation of olefines in the reaction of alkylidenetriphenylphosphoranes with carbonyl functions proceeds as follows:



In the first place the alkylidenetriphenylphosphorane (I) (where R = C_6H_5) reacts with the polarised carbonyl group in a carbonyl compound (II) forming a betaine (III). If the phosphorus atom shows a tendency to expand its external electron shell to a decet, and if the steric factors allow it, an electron pair from the oxygen will attach itself to the phosphorus atom. A four-membered ring is formed (IV) and subsequently decomposes into triphenylphosphine oxide and olefine, either spontaneously or on heating.

The success of the Wittig reaction depends on the success of the three reaction stages (A, B, and C). Stage A is made easier by the presence of a highly polarised carbonyl group, or, with less strongly polar carbonyl compounds, by the high reactivity of phosphorane.

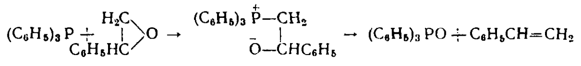
The formation of betaine (III) in the first stage of the reaction has been proved by the isolation of a stable betaine in the reaction of methylenetriphenylphosphorane with benzaldehyde:



$$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}H_2 + C_6H_5CHO \rightarrow (C_6H_5)_3\overset{+}{P}CH_2\overset{\overset{\bar{O}}{|}}{C}HC_6H_5 \xrightarrow{HBr} [(C_6H_5)_3\overset{+}{P}CH_2CH(OH)C_6H_5]\,Br^-$$

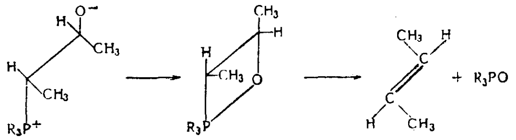
Betaine is characterised as its crystalline hydrobromide, which is converted back into betaine by the action of RLi. An ether suspension of the betaine, heated at 60°–65° for several hours, decomposes into triphenylphosphine oxide (91%) and styrene (67%).

The formation of the same betaine was postulated by Wittig and Haag[4] for the reaction of styrene oxide with triphenylphosphine, which, carried out at 165°, yields styrene (50%) and triphenylphosphine oxide:



$$(C_6H_5)_3P + \underset{C_6H_5HC}{\overset{H_2C}{|}}\!\!>O \rightarrow \underset{\bar{O}-CHC_6H_5}{(C_6H_5)_3\overset{+}{P}-CH_2} \rightarrow (C_6H_5)_3PO + C_6H_5CH=CH_2$$

Boskin and Denney[50] made a study of this reaction with the oxides of *trans*-2-butene and *cis*-2-butene, using tributylphosphine. They showed that the *trans*-oxide yielded a mixture of 72% *cis*-2-butene and 28% *trans*-2-butene, whereas the *cis*-oxide yielded a mixture of 81% *trans*-2-butene and 19% *cis*-2-butene. Under their reaction conditions (150°) the spontaneous isomerisation of the olefines amounted to less than 2%. Their work therefore confirmed the reaction mechanism previously suggested by Wittig:



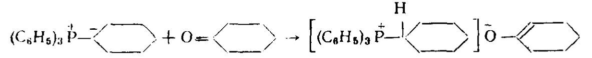
While the decomposition of betaine yields the primary product in the reaction mixture, the mechanism of the formation of the second product is still not clear.

It should be noted that the first stage (A) of the Wittig reaction is reversible, which is confirmed by the increased yield of olefine on raising the amount of alkylidenetriphenylphosphorane above the theoretical.

The mechanism of the third stage (C) is not clear, since the kinetic aspects of the Wittig reaction have not yet been studied.

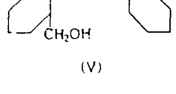
Wittig[3,5,6] considered that the overall success of the reaction is determined by stage B, namely by the transformation of the betaine (III) into the four-membered ring (IV). He thought that the reaction would stop at the betaine stage if, through steric or electronic factors, the ring (IV) could not be formed. Hence he argued that alkylidenetrialkylphosphoranes are unable to react with carbonyl compounds to give olefines because the cyclisation of betaine (III) (where R = alkyl) into the intermediate ring (IV) is made impossible by the inductive effect of alkyl groups, which prevent any attack of oxygen on phosphorus. In the light of the most recent work by Johnson[13-15] and Trippet[16], however, these arguments appear irrelevant, since there is no inductive effect of alkyl groups and no suppression of the attack by oxygen on phosphorus, and alkylphosphoranes undergo Wittig reaction with the same ease as alkylidenetriphenylphosphoranes. Johnson[15] considers stage A to be the most important, and stage B to be affected by steric factors only.

In the reaction with enolisable ketones, alkylidenetriphenylphosphoranes (especially those with sterically hindered molecules) may form enolates instead of addition products with the carbonyl group. This side-reaction is sometimes the principal one. For instance[10]:

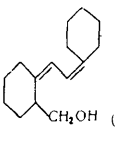


Unsymmetrical alkylidenetriphenylphosphoranes and carbonyl compounds generally yield mixtures of *cis*- and *trans*-isomers. For instance, a suspension of vinylmethylenetriphenylphosphorane in ether and benzaldehyde, heated at 65°, gives 58% 1-phenyl-1,3-butadiene[2] as a 1 : 1 mixture of *cis*- and *trans*-isomers. In a number of cases, however, *trans*-isomers are the predominant or the exclusive products. The reaction of benzylidenetriphenylphosphorane with benzaldehyde gave 82% stilbene, which consisted of 70% *trans*- and 30% *cis*-isomer. Most frequently, only *trans*-isomers are formed in the synthesis of natural products (lycopene, β-carotene, etc.). Cases with *cis*-isomer predominating in the reaction mixture (up to 80%) have also been reported[39].

No systematic study of the stereochemistry of the Wittig reaction has yet been made, nor has the effect of changes in reaction conditions upon the ratio of *cis*- and *trans*-isomers been elucidated, although such an effect is recognised. Indeed, the reaction of (o-hydroxymethylcyclohexylidene)ethylidenetriphenylphosphorane with cyclohexanone in tetrahydrofuran solution at -25° yields almost entirely the *cis*-diene (V), while at room temperature the reaction mixture contains a considerable amount of the *trans*-isomer (VI).[51]

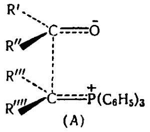


(V)

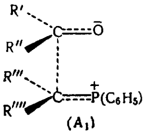


(VI)

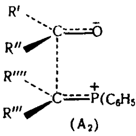
Levisalles[9] attempted in a number of cases to explain the stereospecificity of the reaction. He considers that the steric structure of the resulting olefine R′R″C =CR‴R⁗ depends on the transition state which precedes the formation of betaine. According to Levisalles, the transition state (A), where the dipoles $\overset{+}{C}-\bar{O}$ and $\bar{C}-\overset{+}{P}$ are arranged so that the electrostatic interaction between them is at a minimum, is the most probable. This state is subjected to two mutually opposing forces: 1) the transfer of electrons from oxygen to phosphorus (O → P), resulting in the formation of the four-membered ring, and 2) the tendency to rotation about the C–C axis, which is a result of the mutual repulsion of the uncombined carbon atoms. Since the transfer of electrons proceeds faster than that of atoms, the steric structure of the four-membered ring and of the resulting olefine is determined by the transition state (A). Depending on the volume of the substituents R′, R″, R‴, and R⁗ and on their polarity, the preferred transition state (A_1 or A_2) is the one in which the interaction between the uncombined atoms is smallest, and the bulkiest groups in the intermediate four-membered ring take up position in which they are farthest apart:



(A)



(A_1)



(A_2)

Therefore, the largest groups in the resulting olefine are placed in *trans*-position. The exclusive formation of *trans*-isomers in a number of cases may be attributed to the unfavourable steric relations in the *cis*-position of the transition state, which increases the energy barrier of the reaction or causes the dissociation of A into the starting components.

4. SYNTHESIS OF NATURAL POLYACETYLENIC COMPOUNDS

It has recently been shown that compounds containing triple bonds are widely distributed in plants. A systematic study of such compounds revealed that in a number of cases they have remarkable biological properties (antibiotic activity at high dilution, strong toxic properties, etc.). This stimulated a number of research workers to work out methods for the synthesis of polyacetylenes similar to, or identical with the natural ones, with a view to a thorough investigation of their physiological activity.

The most difficult task in the synthesis of any highly unsaturated chain of carbon atoms is the introduction of the double bond of a definite configuration in a strictly fixed position. Most of the earlier methods for the introduction of the double bond resulted in a mixture of geometrical or steric isomers. That is why Wittig reaction, which facilitates the introduction of the double bond in a predetermined position (as a rule, in a stereospecific manner), and which is at the same time a powerful means for lengthening the carbon chain by a group of desired structure, has aroused great interest among those working on polyacetylenes.

It was shown in a number of papers by Bohlmann and his collaborators [28,40,42,44,52-61] that the Wittig reaction can be widely and successfully used in the synthesis of polyenynes. The most interesting examples of the application of this reaction in the synthesis of natural polyacetylenic compounds are the syntheses of oenanthetol[52,60], isolated from *Oenanthe crocata*, of cicutol[53] from *Cicuta virosa*, of anacycline[56], the natural insecticide from the roots of *Anacyclus pyrethrum*, and of aethusanol B[61] from *Aethusa cynapium* L.

The Wittig reaction was used in the synthesis of oenanthetol for the preparation of 3,5-dodecadien-1-yne (I). The oxidative condensation of (I) with 3-penten-1-yn-5-ol (II) in the presence of cuprous chloride gave 14.1% oenanthetol. To prepare (I), the phosphonium salt (III) obtained in 44% yield from 1-bromo-2-nonene and triphenylphosphine, was treated with the solution of n-butyllithium in oil, and to the resulting solution of 2-nonenylidenetriphenylphosphorane, propargyl alcohol was added. The yield of the final enyne (I) was 43%.

$$\mathrm{BrCH_2CH{=}CHC_6H_{13}\text{-}}n+\mathrm{(C_6H_5)_3P} \rightarrow \underset{\text{(III)}}{[\mathrm{(C_6H_5)_3\overset{+}{P}CH_2CH{=}CHC_6H_{13}]\overset{-}{Br}}} \xrightarrow{\mathrm{C_4H_9Li}}$$

$$\rightarrow \mathrm{(C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}HCH{=}CHC_6H_{13}\text{-}}n \xrightarrow{\mathrm{HC{\equiv}CCHO}}$$

$$\rightarrow \underset{\text{(I)}}{\mathrm{HC{\equiv}C(CH_2{=}CH)_2C_6H_{13}\text{-}}n} \xrightarrow{\mathrm{HC{\equiv}CCH{=}CHCH_2OH}\ \text{(II)}}$$

$$\rightarrow \underset{\text{oenanthetol}}{n\text{-}\mathrm{C_6H_{13}(CH{=}CH)_2(C{\equiv}C)_2CH{-}CHCH_2OH}} .$$

A similar reaction scheme was used to obtain cicutol:

$$n\text{-}\mathrm{C_4H_9CH{=}CHCH_2Br+(C_6H_5)_3P} \xrightarrow{70\%} [\mathrm{(C_6H_5)_3\overset{+}{P}CH_2CH{=}CHC_4H_9\text{-}}n]\mathrm{Br^-} \rightarrow$$

$$\xrightarrow{\mathrm{C_4H_9Li}} \mathrm{(C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}HCH{=}CHC_4H_9\text{-}}n \xrightarrow{\mathrm{HC{\equiv}CCH{=}CHCHO}}$$

$$\rightarrow n\text{-}\mathrm{C_4H_9(CH{=}CH)_3C{\equiv}CH} \xrightarrow[8.3\%]{\mathrm{HC{\equiv}CCH_2CH_2CH_2OH}}$$

$$\rightarrow \underset{\text{cicutol}}{n\text{-}\mathrm{C_4H_9(CH{=}CH)_3\ (C{\equiv}C)_2CH_2CH_2CH_2OH}} .$$

For the synthesis of anacycline, the phosphonium salt obtained in 90% yield from decadiynyl bromide (IV) was converted to the phosphorane (V) by butyllithium. This reacted with the methyl ester of 2-buten-1-al-4-oic acid (VI) to give 47% of the key methyl ester of 2,4-tetradecadiene-8,10-diyn-1-oic acid (VII); (VII) was saponified and converted to the acid chloride by thionyl chloride. Treatment of the acid chlorides with isobutyl amine gave anacycline, *viz*. the isobutylamide of 2,4-tetradecadiene-8,10-diyn-1-oic acid.

$$\underset{\text{(IV)}}{n\text{-}\mathrm{C_3H_7(C{\equiv}C)_2(CH_2)_2CH_2Br}}+\mathrm{(C_6H_5)_3P} \xrightarrow{90\%} [\mathrm{C_3H_7(C{\equiv}C)_2(CH_2)_3\overset{+}{P}(C_6H_5)_3]Br^-} \rightarrow$$

$$\xrightarrow{\mathrm{C_4H_9Li}} \underset{\text{(V)}}{\mathrm{C_3H_7(C{\equiv}C)_2CH_2CH_2\overset{-}{C}H{-}\overset{+}{P}(C_6H_5)_3}} \xrightarrow[47\%]{\mathrm{H_3COOCCH{=}CHCHO}\ \text{(VI)}}$$

$$\rightarrow \underset{\text{(VII)}}{\mathrm{C_3H_7(C{\equiv}C)_2(CH_2)_2(CH{=}CH)_2COOCH_3}} \xrightarrow[\text{3. }\mathrm{(CH_3)_2CHCH_2NH_2}]{\text{1. KOH; 2. }\mathrm{SOCl_2}}$$

$$\rightarrow \underset{\text{anacycline}}{\mathrm{C_3H_7(C{\equiv}C)_2CH_2CH_2(CH{=}CH)_2CONHCH_2CH(CH_3)_2}} .$$

The Wittig reaction was also used for the preparation of polyenynes required in the synthesis of natural polyacetylenes isolated from various species of *Corlopsis*, *Artemisia vulgaris*, *Centaurea ruthenica*, etc. They include 3,5-hexadien-1-yne[55] (from propargyl aldehyde and vinylmethylenetriphenylphosphorane); 3,5,11-dodecatrien-1-yne[58] (from propargyl aldehyde and 1,7-nonadienylidenetriphenylphosphorane, in 53% yield), 1,3,5,11-tridecatetraene-7,9-diyne[42] (from 2,8-dodecadiene-4,6-diyn-1-al and vinylmethylenetriphenylphosphorane in 50% yield), 8,10,16-heptadecatriene-2,4,6-triyne,[51] 2,2,15,15-tetramethyl-7,9-hexadecadiene-3,5,11,13-tetrayne,[57] etc.

By using appropriate aldehydes and alkylidenetriphenylphosphoranes, the Wittig reaction can thus be used for preparing a great variety of substituted polyenynes, the limiting factor being only the availability of the starting compounds.

In the majority of cases the yields of the required substances are satisfactory (40–60%). However, polyenynes are sometimes formed in very low yields. For instance, the condensation of acrolein with 2,8-decadiene-4,6-diynylidenetriphenylphosphorane[42] gave only 5% 1,3,5,11-tridecatetraene-7,9-diyne (as a mixture of *cis*- and *trans*-isomers), and 1-phenyl-7-nonaene-1,3,5-triyne-9-al with ethylidenetriphenylphosphorane gave a low yield of 1-phenyl-7,9-undecadiene-1,3,5-triyne.

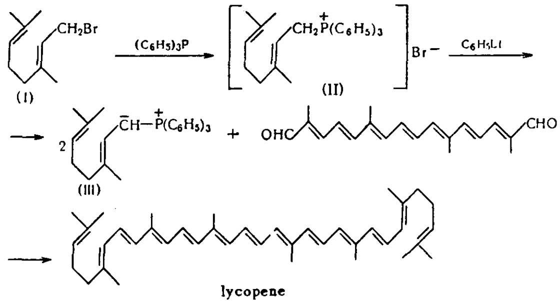
The Wittig reaction is an invaluable method for the synthesis of polyynes and polyenynes. Its potentialities have by no means been fully exploited in the field of natural polyacetylenes: in many cases no attempt was made to increase the yield by varying the experimental conditions.

5. SYNTHESIS OF TERPENES, CAROTENOIDS, AND VITAMIN A

In the field of terpenes, carotenoids, and vitamin A, whose synthetic preparation has till recently been very laborious and complicated, the Wittig reaction has opened new horizons. Its importance in the synthesis of carotenoids and vitamin A was first noted by Wittig himself[5] in 1954. Since then the Wittig reaction has acquired practical importance in isoprenoid chemistry, as is borne out by the ever-increasing number of patents issued for its application to the synthesis of useful substances such as vitamin A, β-carotene, vitamin A acid, etc.

The Wittig reaction made possible the simple synthesis of symmetrical carotenoid hydrocarbons from isoprenoid bromides, which are easy to obtain, and the relatively accessible dialdehydes.

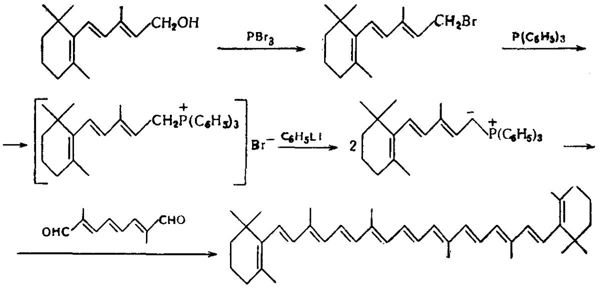
Isler and collaborators[62,63] used the Wittig reaction in the simplest synthesis of lycopene (the natural pigment in tomatoes) yet available. They reacted phosphorus tribromide with linalool (linalool is now produced on an industrial scale) and obtained geranyl bromide (I), which reacted even in the cold with triphenylphosphine forming a crystalline phosphonium salt (II) in high yield. By treatment of (II) with phenyllithium a red solution of geranylidenetriphenylphosphorane (III) was obtained, which reacted readily with crocetindialdehyde to give lycopene, identical with the natural pigment, in about 70% yield.



lycopene

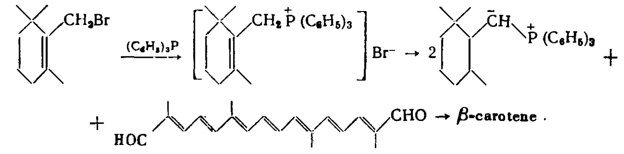
Likewise, 2,2'3,3'-tetrahydrolycopene[63,64] was obtained from 6,7-dihydrogeranylidenetriphenylphosphorane and crocetinaldehyde, and 15,15'-dehydrolycopene from geranylidenetriphenylphosphorane and 8,8'-dehydrocrocetindialdehyde[62-65].

A very interesting and convenient method for the preparation of β-carotene (the widely distributed plant pigment, which is pro-vitamin A) was developed by Wittig and Pommer[47] using the readily available β-ionylideneethanol, *via* the corresponding bromide and phosphorane. Their synthesis differs from the earlier ones by the small number of stages involved, and certainly has possibilities for the industrial preparation of β-carotene.



β-carotene

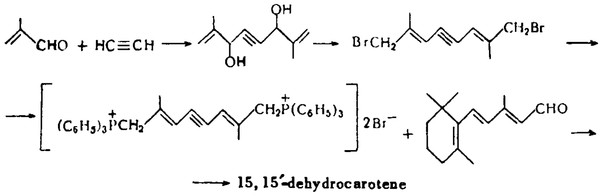
An even simpler scheme was described in a patent[66].



It should be noted that 2,6,11,15-tetramethyl-2,4,6,8,10,12,14-hexadecaheptaene-1,16-dial, which is used in this synthesis, is readily available.

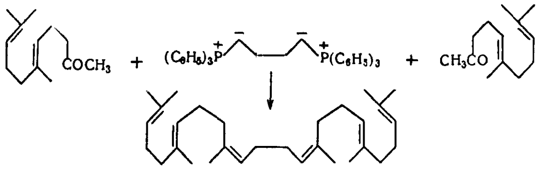
15,15'-Dehydro-β-carotene was obtained similarly by the condensation of β-ionylideneethylidenetriphenylphosphorane with 2,7-dimethyl-2,6-octadien-4-yne-1,8-dial,[47] or of β-cyclogeranylidenetriphenylphosphorane with 8,8'-dehydrocrocetindialdehyde[62].

Surmatis and Ofner[67] carried out an interesting variation of the synthesis of 15,15'-dehydro-β-carotene:



These authors used the same scheme for the synthesis of β-carotene itself and of decapreno-β-carotene.

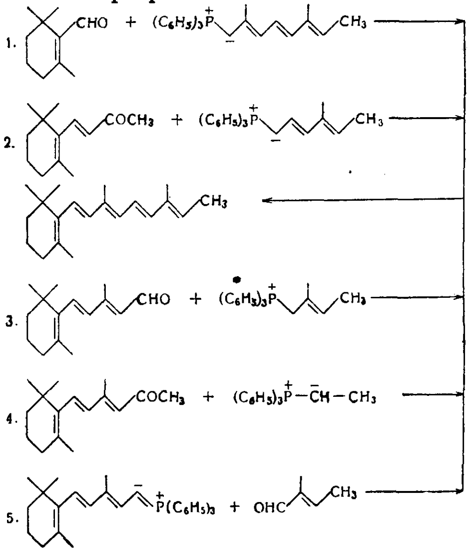
The best example of the successful use of the Wittig reaction in the synthesis of symmetrical isoprenoid hydrocarbons is the synthesis of squalene, the aliphatic triterpenic hydrocarbon constituent of living organisms and the precursor of steroids. A somewhat different principle from the one used in the synthesis of β-carotene was used in the case of squalene. Whereas the synthesis of β-carotene was carried out by the condensation of phosphorane with the symmetrical dialdehyde of appropriate structure, in the synthesis of squalene the symmetrical diphosphorane, prepared from 1,4-dibromobutane, was condensed with geranylacetone[34,68-70]. Squalene was isolated from the reaction mixture in 26% yield. This was the first synthetic squalene identical with the natural one. The methods used previously gave complex mixtures, from which it was possible to isolate pure squalene. The above synthesis of squalene is, like that of β-carotene, very simple and practicable.



squalene

Squalene labelled with ^{14}C in positions 11 and 14, which is very important in the study of steroid biosynthesis in the living organisms, has been synthesised[71] similarly, from 1,4-dibromo[2,3-^{14}C]butane. This method was also used in the synthesis of 3,8-dimethyl-3,5,7-decatriene-1,9-diyne,[72] an important intermediate in the synthesis of many carotenoids.

The Wittig reaction was also used in the preparation of unsymmetrical isoprenoid hydrocarbons, in particular axerophthene, the hydrocarbon with a vitamin A skeleton[73-75]. This example illustrates the flexibility of the Wittig reaction, which can use the most varied starting compounds for the preparation of the same product. Axerophthene was prepared as follows:



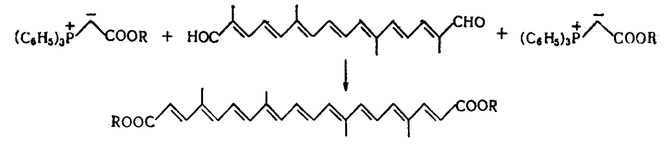
During his study of the stereochemistry of phytol, geraniol, and nerol, Burrell[76] treated *DL*-6, *D'*-10,14-trimethylpentadecan-2-one with methylenetriphenylphosphorane and obtained the corresponding hydrocarbon.

The application of the Wittig reaction to isoprenoid chemistry is not limited to hydrocarbons. Using phosphoranes prepared from the halogen derivatives of acids, a convenient and simple method has been devised for introducing the carboxyl group into the polyene chain, thus providing an easy path to the carotenoid and other polyenic acids.

The introduction of the methyleneethoxycarbonyl group has been widely applied. It proceeds by the general scheme:

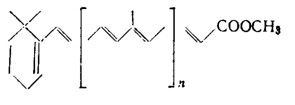
$$\mathrm{RCHO} + (\mathrm{C_6H_5})_3\overset{+}{\mathrm{P}}\text{—}\overset{-}{\mathrm{C}}\mathrm{HCOOC_2H_5} \rightarrow \mathrm{RCH{=}CHCOOC_2H_5}.$$

Isler and collaborators[49] used this reaction scheme in the condensation of crocetindialdehyde with alkoxycarbonylmethylenetriphenylphosphoranes and prepared a number of bixin esters:



bixin (where R = H)

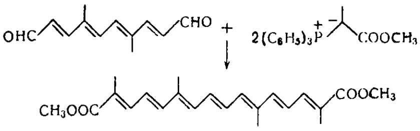
The condensation of methoxycarbonyltriphenylphosphorane with 15,15'-dehydro-β-apo-12'-carotenal (C_{25}) and its vinylogues up to 15,15'-dehydro-β-apo-2'-carotenal (C_{37}) was used [77-80] in the first reported preparations of the methyl ester of 15,15'-dehydro-β-apo-10'-carotenic acid (C_{27}) and its vinylogues up to the methyl ester of 15,15'-dehydro-β-apo-2-carotenic acid (C_{37}). Partial hydrogenation of the latter gave the corresponding methyl esters of β-apo-carotenic acids



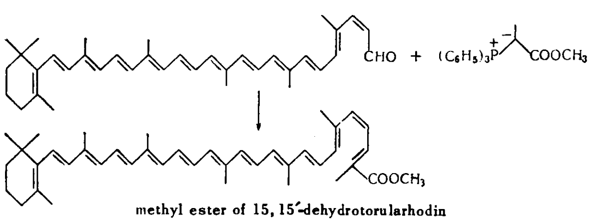
where n = 3,4,5.

The previously available methods for the introduction of a carboxyl group were not well suited to the synthesis of such highly unsaturated acids.

By using α-alkoxycarbonylethylidenetriphenylphosphoranes obtained from the esters of β-bromopropionic acid it is possible to introduce not only a methylenecarboxyl group, but also a side methyl group. Isler and collaborators[49,77-80] made use of this possibility in their synthesis of the dimethyl ester of crocetin, methyl ester of 15,15'-dehydrotorularhodin and its vinylogues according to the scheme:



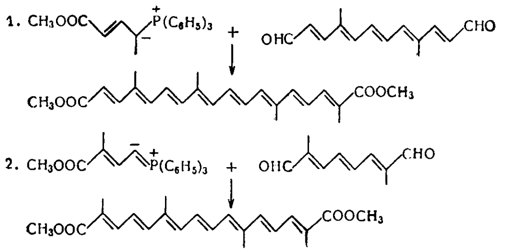
dimethyl ester of crocetin



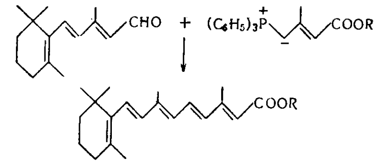
methyl ester of 15, 15'-dehydrotorularhodin

Partial hydrogenation, isomerisation, and saponification of the methyl ester of 15,15'-dehydrotorularhodin gave the carotenoid torularhodin, identical with the natural material isolated from *Rhodotorula mucilaginosa*. Its structure was thus confirmed by synthesis. This was one of the great successes of the Wittig reaction.

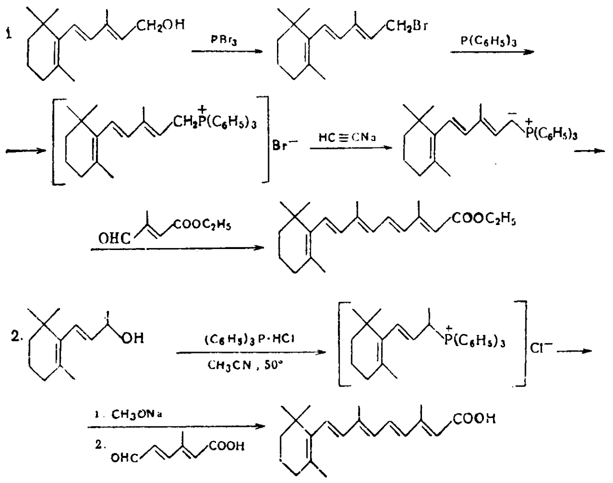
Buchta and Andree's[81-84] recent preparation of isoprenoid and other unsaturated acids from phosphoranes obtained from ω-haloacids offers several interesting possibilities. These workers suggested new methods for the synthesis of dimethyl ester of bixin and crocetin, and of dimethyl ester of 4,4'-desmethylbixin by the condensation of phosphoranes prepared from the methyl esters of γ-bromocrotonic or γ-bromotiglic acids with the appropriate dialdehydes according to the scheme:



Analogous methods for the preparation of the esters of vitamin A acid were patented[73,85-87]. For instance:



For the Wittig synthesis of the esters of vitamin A acid, the condensation of phosphoranes with aldehydic acids is preferable[88-93]. For instance, condensation of the phosphorane prepared from β-ionylideneethanol, *via* the corresponding chloride or bromide, with the ethyl ester of 3-methyl-2-buten-4-al-1-oic acid gave vitamin A acid ethyl ester[90-92]:



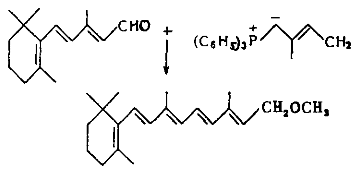
Vitamin A acid methyl ester was also prepared by the reaction of the phosphorane prepared from β-ionyl chloride with 3-methyl-2,4-hexadien-6-al-1-oic acid[92,93], followed by esterification. This condensation was carried out in dimethylformamide, and sodium acetylide or methoxide was used for the preparation of phosphorane. High yields of the final products were obtained.

An interesting new method has been suggested for the preparation of β-ionyltriphenylphosphonium chloride from β-ionol and triphenyl phosphine hydrochloride. The halide stage was thus by-passed. This method may also find application in the preparation of other phosphonium salts directly from alcohols.

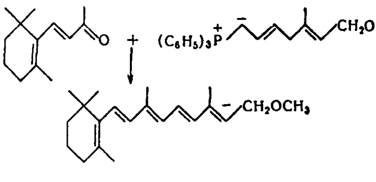
As already mentioned[30], ethoxycarbonylmethylenetriphenylphosphorane does not react with ketones. All efforts to condense ethoxycarbonylmethylenetriphenylphosphorane with nopinone have failed[94]. This factor limits somewhat the use of the Wittig reaction for the introduction of alkylideneethoxycarbonyl group.

The value of the Wittig reaction in isoprenoid chemistry is its wide applicability in the synthesis of various polyenyne hydrocarbons and acids otherwise difficult to obtain, and also because, by the selection of appropriate components, it can be used for the synthesis of their derivatives containing functional groups: alcohols, ethers, aldehydes, and ketones. These potentialities of the Wittig reaction have by no means been fully exploited yet, but they can be adequately assessed on the basis of available data.

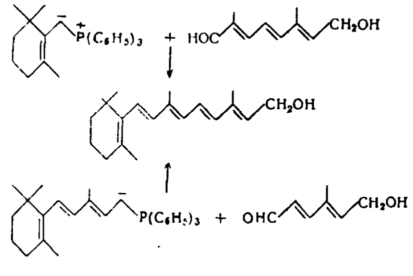
A number of patents[95-99] deals with simple new methods for the synthesis of vitamin A, its ethers, and 11,12-dehydrovitamin A. In one of these[85,95], the easily obtained β-ionylideneacetic aldehyde is condensed with 2-methyl-4-methoxy-2-butenylidenetriphenylphosphorane directly to give the methyl ether of vitamin A:



In another method[96,98] the vitamin A methyl ether is prepared by the reaction of β-ionone with 1-methoxy-3-methyl-2,4-hexadienylidenetriphenylphosphorane:



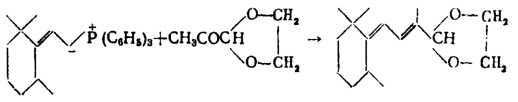
Vitamin A itself was obtained by the condensation of β-cyclogeranylidenetriphenylphosphorane[97] with 8-hydroxy-2,6-dimethyl-2,4,6-octatrien-1-al, or of β-ionylideneethylidenetriphenylphosphorane[88,89] with 6-hydroxy-4-methyl-2,4-hexadien-1-al:



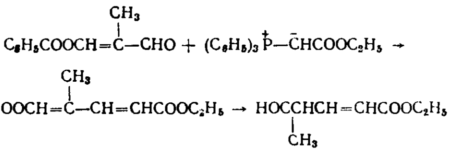
In the foregoing reactions, hydrocarbon phosphoranes and hydroxyaldehydes were used. The application of alkoxyaldehydes or acetoxyaldehydes leads in this case to the formation of ethers or the acetate derived from vitamin A.

The above methods compete with the one at present used for the industrial manufacture of vitamin A.

The introduction of an aldehyde group using the Wittig reaction has not yet been sufficiently developed. One of the patents by Isler and collaborators[100] describes the interesting condensation of 2-(2′,6′,6′-trimethylcyclohexylidene)ethylidenetriphenylphosphorane with 2-oxopropanal-1-ethyleneacetal, which yields the ethyleneacetal of the corresponding aldehyde:



The introduction of an aldehyde group by means of the Wittig reaction can also be carried out by using enolic esters of dialdehydes. For example, it was reported[30] that ethoxycarbonylmethylenetriphenylphosphorane reacts with methylmalonic dialdehyde benzoate to form the corresponding enolic ester of an aldehydic carboxylic acid, which after saponification yields the corresponding aldehydic acid.

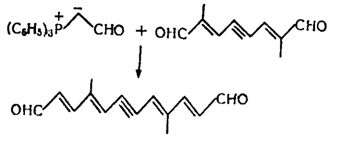


$$C_6H_5COOCH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CHO + (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}HCOOC_2H_5 \rightarrow$$

$$\rightarrow C_6H_5COOCH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH{=}CHCOOC_2H_5 \rightarrow HOC\underset{\underset{\displaystyle CH_3}{|}}{C}HCH{=}CHCOOC_2H_5$$

This is a simple and convenient method for the preparation of difunctional derivatives.

Trippett and Walker[31] (see section 2) have recently suggested the use of formylmethylenetriphenylphosphorane for the introduction of aldehyde groups. This phosphorane reacts with 2,7-dimethyl-2,6-octadien-4-yne-1,8-dial forming 4,9-dimethyl-2,4,8,10-dodecatetraen-6-yne-1,12-dial, a valuable intermediate in the synthesis of carotenoids:



The yield of the final dialdehyde was 50% according to spectral data, but owing to difficulties involved in its separation from the large quantity of triphenylphosphine, it was isolated in only 15% yield.

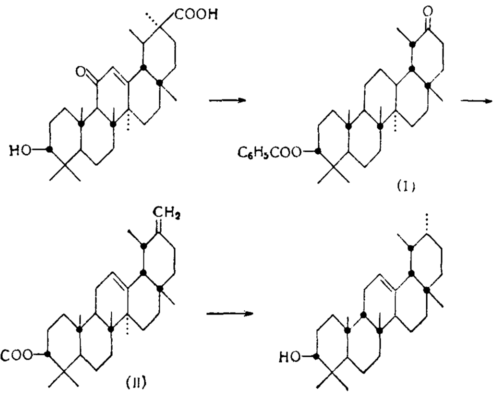
In the next section we shall discuss in detail another possible method of introducing an aldehyde group by means of methoxymethylenephosphorane[45].

The introduction of a keto group using the Wittig reaction can be carried out with acetylmethylenephosphorane, as was first reported by Ramirez[29]. This method, however, has hardly been used. An interesting new method[35] for the synthesis of γ-bromoacids has appeared recently:

$$CH_3CHBrCHO + (C_6H_5)_3\,P{-}CHCCOC_2H_5 \rightarrow CH_3CHBrCH{=}CHCOOC_2H_5\,.$$

We conclude this section by mentioning the work by Corey and Cantrall[101] on the stereochemical relationships in the triterpenic series. They treated glycyrrhetic acid (a β-amyrin derivative of known configuration) with a

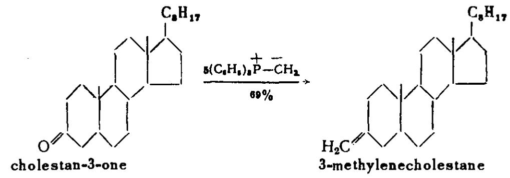
Wittig reagent and obtained, *via* ketone (I), an olefine (II), whose selective reduction by lithium in diethylamine gave α-amyrin.

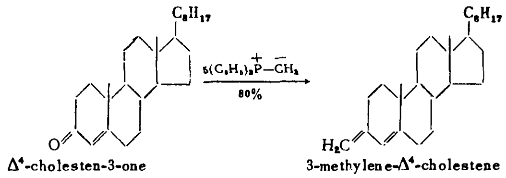


6. SYNTHESIS OF STEROIDS AND VITAMIN D_2

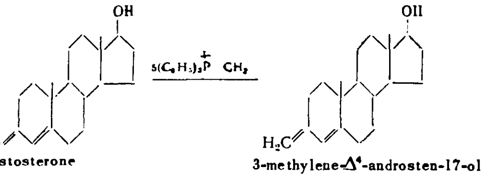
Barton *et al.*[102] were the first to use the Wittig reaction in the steroid series, in their synthesis of 3-methylcholestan-3-one. Since 1957 this reaction has been widely applied to the steroid series, and its importance in that field is likely to increase. So far, it has only been used for the introduction of a methylene group.

Sondheimer and Mechoulam[103,104] made a thorough study of the introduction of a methylene group by means of the Wittig reaction. They became interested in this reaction while searching for a method for synthesising the side-chain in 17- and 20-ketosteroids. On boiling in tetrahydrofuran both saturated (cholestan-3-one) and unsaturated (Δ^4-cholesten-3-one) steroid ketones react readily with methylenetriphenylphosphorane forming the corresponding methylenesteroids of high purity, which are otherwise difficult to obtain.





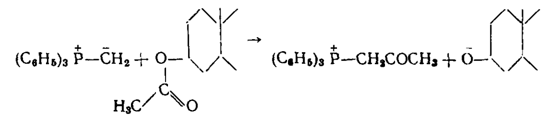
Steroid hydroxyketones react in the same way, and no screening of the hydroxyl group is necessary. For instance, testosterone reacts readily with methylenetriphenylphosphorane forming 3-methylene-Δ^4-androsten-17-ol in 75% yield.



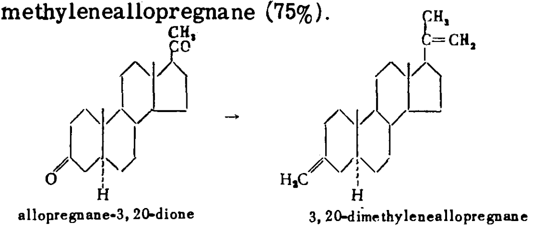
The reversibility of the first stage of the Wittig reaction (see section 3) is pronounced in the steroid series. A considerable excess of methylenetriphenylphosphorane should therefore be used in order to achieve maximum yields of methylenesteroids. For instance, the reaction of androstan-3β-ol-17-one[103] with three equivalents of methylenetriphenylphosphorane yields 32% of 17-methyleneandrostan-3β-ol, whereas by using five equivalents of the Wittig reagent a 58% yield is obtained. This also applies to the introduction of a methylene group into androstan-17β-ol-3-one, Δ^3-pregnen-3β-ol-20-one,[103] and allopregnan-3β-ol-20-one.[104]

Although protection of the hydroxyl group during the reaction is not strictly necessary, it does as a rule lead to higher yields. For instance, the introduction by the Wittig reaction of a methylene group into Δ^5-androsten-3β-ol-17-one yields 36% 17-methylene-Δ^5-androsten-3β-ol, while by using the corresponding tetrahydropyranyl ether the yield of the final product (after saponification) reaches 44%.[103]

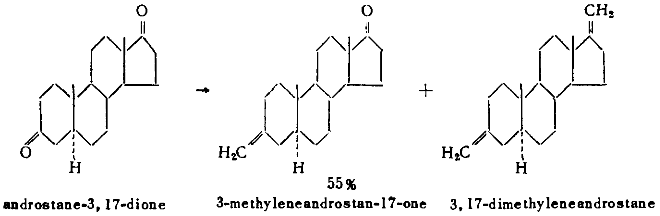
21-Nor-20-ketocholesterol and $\Delta^{5,16}$-pregnadien-3β-ol-20-one acetates, and androstan-3β,17β-diol-7-one and Δ^5-androsten-3β,17β-diol-7-one diacetates react with methylenetriphenylphosphorane without elimination of the acetate group[103,104]. In some cases, however, as in the reaction of hecogenin[102] or 7-ketocholesterol acetate[103], an acetyl group is eliminated, yielding 12-methylenetigogenin and 7-methylenecholesterol, respectively. The cleavage proceeds by the following general scheme:



Depending on their nature, steroid diketones may react once or twice. For instance, the reaction of methylenetriphenylphosphorane with allopregnan-3,20-dione[104] in ether solution at room temperature yields immediately 3,20-dimethyleneallopregnane (75%).



Under the same conditions androstan-3,17-dione[104] forms 3-methyleneandrostan-17-one as main product, and 3,17-dimethyleneandrostane as side-product.



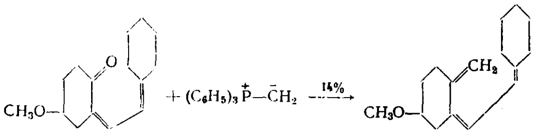
Under identical conditions 3-methyleneandrostan-17-one gave 3,17-dimethyleneandrostane in 76% yield.

In addition to the above reactions, the introduction of the methylene group by Wittig's method has been used for the synthesis of 24-methylenecholesterol[105,106] (contained in certain molluscs) and 25-dehydrocholesterol[107]. The condensation of 3β-acetoxy-5-cholenaldehyde with isopropylidenetriphenylphosphorane gave 24-dehydrocholesterol[108] identical with desmosterol, isolated from chick embryo.

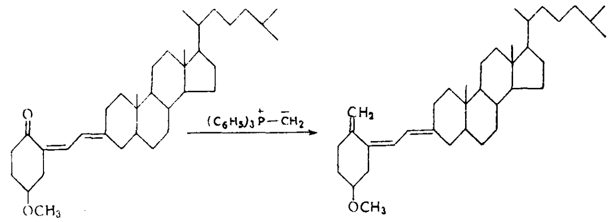
The fact that in the steroid series the Wittig reaction has been used almost exclusively for the introduction of methylene groups into ketosteroids is of no small significance since other methods are far less convenient, efficient or practicable.

The Wittig reaction can also be used for introducing groups other than methylene into steroids. For example, Levine[45] reacted tigogenone (5*α*,22*β*,25*D*-spirostan-3-one) with methoxymethylenetriphenylphosphorane and obtained 85% 3-methoxymethylene-5*α*,22*β*,25*D*-spirostane, which after extraction with ether saturated with 72% perchloric acid formed quantitatively 3-formyl-5*α*,22*β*,25*D*-spirostane. This method of introducing an aldehyde group, which was simultaneously suggested by Wittig[109], is undoubtedly very promising.

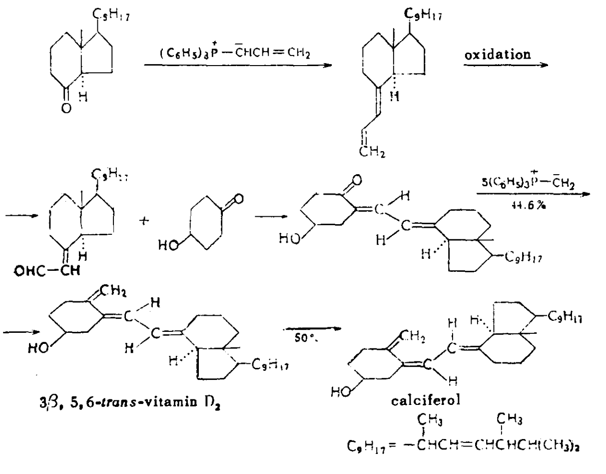
The possible contribution of the Wittig reaction to the synthesis of vitamin D_2 is of great importance. The classical experiments of Milas and collaborators[110,111] indicated the possibility of synthesising a system of double bonds typical of calciferol:



1-Cholestanylidene-2-(5′-methoxy-2′-methylenecyclohexylidene)ethane, the biologically active homologue of vitamin D_2, was synthesised according to that scheme[112].

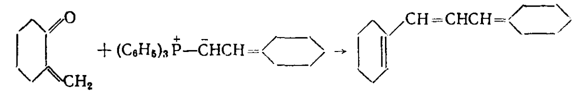


Finally, as a result of a systematic study, Inhoffen and collaborators[36,113-121] synthesised completely 3β-5,6-*trans*-vitamin D_2,[119-121] photoisomerisation of which yielded vitamin D_2 (calciferol):



This synthesis would have been impossible had the Wittig reaction not enabled the key-step, *viz*. the introduction of a methylene group in position 10. Harrison and Lythgoe[51,122-125], simultaneously and independently developed a method for the synthesis of calciferol using the Wittig reaction.

It was noticed, in the course of investigations of the methods for the synthesis of vitamin D_2, that certain unsaturated ketones are able to react with phosphoranes in 1,4-addition. For instance:



The above are examples of the successful uses of the Wittig reaction in the chemistry of natural products.

7. PROSPECTS FOR FUTURE USES OF THE WITTIG REACTION IN THE SYNTHETIC FIELD

In this section we shall briefly consider several contributions of the Wittig reaction other than the ones already discussed, and the prospects of its future development.

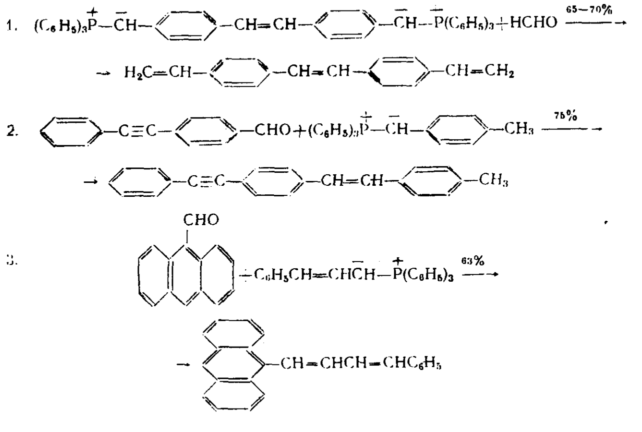
The Wittig reaction can of course be used not only in the synthesis of complex natural products, but also for numerous other materials. For the preparation of simple compounds, however, there is usually a wide choice of simpler methods, and the use of the Wittig reaction in such cases is unprofitable (*e.g.* the preparation of styrene from benzaldehyde and methylenetriphenylphosphorane, of 1-phenylbutadiene from cinnamic aldehyde and methylenetriphenylphosphorane, etc.). That is why the application of the Wittig reaction in organic synthesis is limited to complex natural compounds and related materials.

We shall now discuss the most interesting and promising applications of this reaction in organic synthesis.

Synthesis of hydrocarbons. The Wittig reaction can be used for the synthesis of a number of aliphatic and cyclic hydrocarbons which are difficult to prepare by the normal methods. For instance, the following synthesis of 3-pentadecen-1-yne[126] is attractive:

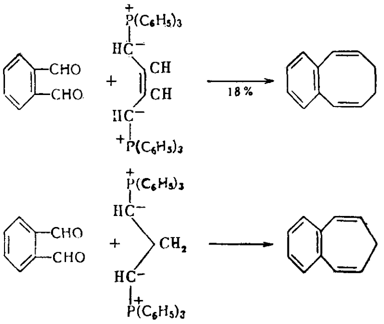
$$n\text{-}C_{11}H_{23}\overset{-}{C}H-\overset{+}{P}(C_6H_5)_3+OHCC\equiv CH\rightarrow n\text{-}C_{11}H_{23}CH=CHC\equiv CH\,.$$

Drefahl and collaborators[127-129] used the Wittig reaction to prepare vinyl derivatives of stilbene, tolan, and arylbutadienes which are otherwise difficult to obtain. For instance:



Wittig and Pommer[130] have patented the preparation of various arylpolyene hydrocarbons.

Most interesting is the synthesis of 1,2-benzo-1,3,7-cyclooctatriene and 1,2-benzo-1,3,6-cycloheptatriene according to the following scheme[10,32]:



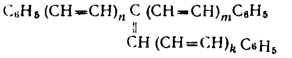
The synthesis of *o*-divinylbenzene[32] from *o*-phthalic dialdehyde and methylenetriphenylphosphorane in 75% yield may also have preparative importance, as may the synthesis of 9-vinylanthracene from 9-anthranyl aldehyde and methylenetriphenylphosphorane[131]. The Wittig reaction also proved useful in the preparation of 2-methoxy-3-methylstilbene[132].

As applied to aromatic ketones this reaction has significance only in special cases, for instance, in the synthesis of *o,o′*-distyrylbiphenyl[133], which cannot be prepared by the dehydration of the glycol obtained by the Grignard reaction of *o,o′*-dibenzoylbiphenyl and methylmagnesium bromide, since all attempts at dehydration result in cyclisation.

The reaction of alkylidenetriphenylphosphoranes with unsaturated ketones often consists in 1,4-addition. For instance, the synthesis of cross-conjugated hydrocarbons by the following scheme[40]:

$$C_6H_5(CH{=}CH)_nCO(CH{=}CH)_mC_6H_5 + (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}H(CH{=}CH)_kC_6H_5$$

$n = 1 \quad m = 0 \quad k = 0.1$
$n = 2 \quad m = 1$
$n = 2 \quad m = 1$
$n = 2 \quad m = 2$
$n = 2 \quad m = 0$



$$C_6H_5(CH{=}CH)_n\underset{\underset{\displaystyle CH(CH{=}CH)_kC_6H_5}{\|}}{C}(CH{=}CH)_mC_6H_5$$

In cases where $n = 0$, $m = 2$, and $k = 1$, in addition to normal reaction products, the product of 1,4-addition, *viz.* 1,6-diphenyl-1,3,5-hexatriene was also obtained. In other cases normal reaction products were obtained in high yields.

Synthesis of alkenyl halides. Another interesting extension of the Wittig reaction was discovered recently: the reaction of chlorocarbene with triphenylphosphine forming chloromethylenetriphenylphosphorane[134], which reacts with carbonyl compounds in the usual way:

$$(C_6H_5)_3P + :CHCl \rightarrow (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}HCl \xrightarrow[31\%]{(C_6H_5)_2CO}$$
$$\rightarrow (C_6H_5)_2C{=}CHCl + (C_6H_5)_3PO.$$

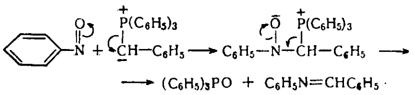
The reaction with dichlorocarbene proceeds likewise[135]:

$$(C_6H_5)_3P + :CCl_2 \rightarrow (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}Cl_2 \xrightarrow[46\%]{(C_6H_5)_2CO}$$
$$\rightarrow (C_6H_5)_2C{=}CCl_2 + (C_6H_5)_3PO.$$

These are the new methods for the preparation of 1-mono- and 1,1-di-haloolefines.

Synthesis of acids. According to Bohlmann[44] the preparation of methyl esters of 5-arylsorbic acids by the reaction of substituted benzaldehydes with methoxycarbonylvinylmethylenetriphenylphosphorane, in the case of nitro-, chloro-, and hydroxy-benzaldehydes, is preferred to the Reformatski reaction between substituted benzaldehydes and the methyl ester of γ-bromocrotonic acid.

Reaction with nitroso compounds. It was established[10,136] that nitroso compounds, where the nitroso group, like the carbonyl group, has an electrophilic character, can combine with alkylidenetriphenylphosphoranes to form Schiff's bases:



Since Schiff's bases readily hydrolyse to carbonyl compounds, this reaction is a new method for the preparation of aldehydes and ketones. For instance, the reaction of geranylidenetriphenylphosphorane with nitrosobenzene gave good yield of citrylidene anil, which on hydrolysis yielded citral[10]. Similarly, fluorenylidenetriphenylphosphorane and nitrobenzene gave fluorenylidene anil[136].

Reaction with isocyanates. Staudinger and Meyer[1] described the reaction of diphenylmethylenetriphenylphosphorane with phenylisocyanate to form diphenylketene phenylimine:

$$(C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}(C_6H_5)_2 + O{=}C{=}N{-}C_6H_5 \rightarrow (C_6H_5)_2C{=}C{=}NC_6H_5.$$

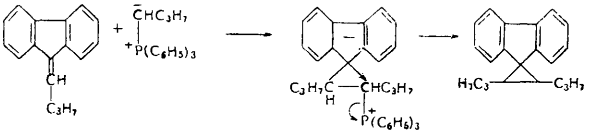
Reaction with ketens. According to Lüscher (see Meyer[137,138]) diphenylmethylenetriphenylphosphorane reacts with diphenylketen according to the scheme:

$$(C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}(C_6H_5)_2 + O{=}C{=}C(C_6H_5)_2 \xrightarrow{140°}$$
$$\rightarrow (C_6H_5)_2C{=}C{=}C(C_6H_5)_2 + (C_6H_5)_3PO.$$

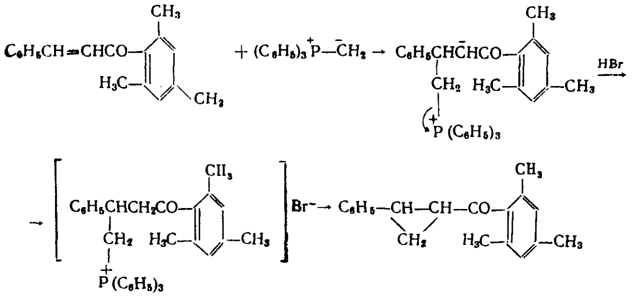
Reaction with thiocarbonyl compounds. Thiobenzophenone and Michler thioketone react with methylenetriphenylphosphorane like ordinary ketones[10]:

$$R_2CS + H_2\overset{-}{C}{-}\overset{+}{P}(C_6H_5)_3 \rightarrow (C_6H_5)_3PS + R_2C{=}CH_2$$
where $R = C_6H_5$, or $p\text{-}(CH_3)_2NC_6H_4$.

Addition of alkylidenephosphoranes to a double bond. Alkylidenetriphenylphosphoranes react with readily polarisable C–C bonds. For example, propylmethylenetriphenylphosphorane reacts with 9-n-butylidenefluorene according to the scheme[139]:



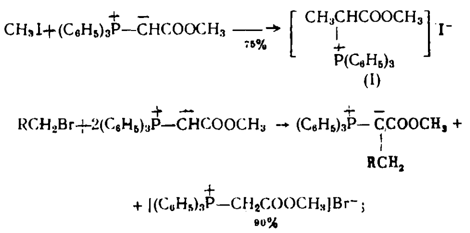
Alkylidenetriphenylphosphoranes can thus be used for the synthesis of the cyclopropane ring. Freeman[140] showed that methylenetriphenylphosphorane unites with the double bond of mesityl styryl ketone forming a product which with hydrogen bromide yields an insoluble, unstable phosphonium salt:



Heating this salt in xylene solution for four hours results in the formation of 2-phenylcyclopropyl mesityl ketone in 52% yield.

The formation of tribenzoylcyclopropane (in but 7% yield) was recently observed in the reaction of benzoylmethylenetriphenylphosphorane with phenacyl bromide[141].

Bestman[142,143] described recently a very promising addition reaction of alkylidenetriphenylphosphoranes. He showed that in boiling ethyl acetate solution methyl iodide as well as α-bromoacids react with the double bond in methoxycarbonylmethylenetriphenylphosphorane according to the scheme:

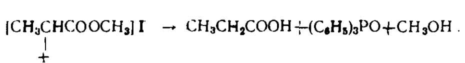


$$CH_3I+(C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCOOCH_3 \xrightarrow[75\%]{} \left[\begin{array}{c} CH_3CHCOOCH_3 \\ | \\ \overset{+}{P}(C_6H_5)_3 \end{array}\right] I^- \quad (I)$$

$$RCH_2Br+2(C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCOOCH_3 \rightarrow (C_6H_5)_3\overset{+}{P}-\underset{\displaystyle RCH_2}{\overset{-}{C}}COOCH_3 + \underset{90\%}{[(C_6H_5)_3\overset{+}{P}-CH_2COOCH_3]Br^-};$$

for (II) R = $COOCH_3$ (75%); for (III) R = C_6H_5 (80%).

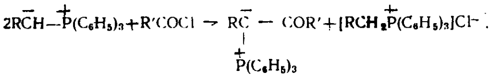
Upon alkaline hydrolysis (I) decomposes to acid, triphenylphosphine, and methanol:



$$[\underset{\displaystyle \overset{+}{P}(C_6H_5)_3}{CH_3CH}COOCH_3]I \rightarrow CH_3CH_2COOH+(C_6H_5)_3PO+CH_3OH.$$

II and III decompose under the same conditions forming succinic and hydrocinnamic acid respectively, in 90–100% yield. This is a new method for the synthesis of mono- and di-carboxylic acids.

Acid chlorides were found to be capable of analogous addition reactions[143].



$$2R\overset{-}{C}H-\overset{+}{P}(C_6H_5)_3+R'COCl \rightarrow R\underset{\displaystyle \overset{+}{P}(C_6H_5)_3}{\overset{-}{C}}-COR'+[RCH_2\overset{+}{P}(C_6H_5)_3]Cl^-.$$

The yield of acetylalkylidenetriphenylphosphorane is 60–80%. When R = C_6H_5, the resulting products were stable to hydrolysis, while the alkyl derivatives hydrolyse forming ketones. This is a new method for the preparation of ketones from acid chlorides and alkylidenetriphenylphosphoranes.

Auto-oxidation. Bestman[144] observed the formation of symmetrical olefines from alkylidenetriphenylphosphoranes as a result of auto-oxidation. Auto-oxidation of benzylidenetriphenylphosphorane yields 55% stilbene (35% *trans*- and 20% *cis*-form); similarly cinnamylidenetriphenylphosphorane yields 1,6-diphenylhexatriene. This reaction proceeds via the formation of an aldehyde which subsequently condenses with the excess of phosphorane:

$$C_6H_5\overset{-}{C}H-\overset{+}{P}(C_6H_5)_3 \xrightarrow{O_2} [(C_6H_5)PO+C_6H_5CHO] \xrightarrow{C_6H_5\overset{-}{C}H-\overset{+}{P}(C_6H_5)_3} C_6H_5CH=CHC_6H_5.$$

Reaction with $LiAlH_4$. In the reaction of lithium aluminium hydride with alkylidenetriphenylphosphoranes in tetrahydrofuran at -20°, hydrogen adds on to the carbon in the methylene group and a phenyl group is split off from the phosphorus atom[145]:

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}HR \xrightarrow{LiAlH_4} (C_6H_5)_2P(O)CH_2R,$$

$$\text{where } R=COCH_3,\quad COC_6H_5,\quad COC(CH_3)_2COCH(CH_3)_2.$$

Yields are not higher than 34–42%.

Reaction with metal salts. Seyferth[146,147] recently studied the reaction of methylenetriphenylphosphorane with the halides of the metals from groups II, IV, and V of the Periodic Table. This reaction results in the formation of phosphonium salts soluble in water. For instance, methylenetriphenylphosphorane and mercuric bromide gave a salt of the composition $[(C_6H_5)_3PCH_2HgCH_2P.(C_6H_5)_3][HgBr_3]_2$; under the same conditions trimethylbromosilane forms $[(C_6H_5)_3PCH_2Si(CH_3)_3]Br$, and dimethyldibromostannane forms $[(C_6H_5)_3PCH_2Sn(CH_3)_2CH_2P(C_6H_5)_3].[(CH_3)_2SnBr_4]$.

The above examples illustrate the trends in the further development of the Wittig reaction and its application in organic synthesis.

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VIBRATIONAL SPECTRA OF ORGANOPHOSPHORUS COMPOUNDS

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CONTENTS

I. INTRODUCTION

At the present time organophosphorus compounds are being intensively studied. This fact is related to their great theoretical importance and to their various applications in industry and agriculture. They have been used for some time as flotation agents, plasticisers, additives for lubricating oil, etc.. Since many organophosphorus compounds exhibit a specific physiological activity, their use as medical preparations is becoming more and more widespread. In recent years they have been widely used for chemical crop protection. Various phosphorothioates have proved particularly valuable, being considerably more effective than many previously known insecticides. The prospects in the development of the chemistry of organic phosphorus compounds, including polymers, are very good. The possibilities of practical utilisation of these compounds are far from exhausted and in some fields their application is only beginning.

In the synthesis of new organophosphorus compounds many problems arise in establishing their structure and studying their reactions. In particular, the study of tautomerism, isomerism, and molecular rearrangements in a series of organophosphorus compounds is of great theoretical and practical interest to organic chemistry. A wide range of physical and chemical methods is necessary to solve these and other problems. Among the physical methods, vibrational spectra are very important.

Many investigations have been reported of the vibrational spectra of organophosphorus compounds, mainly in recent years. In some of these, mostly qualitative in character, the spectra of compounds of known structure are analysed and the observed frequencies are assigned to the vibrations of individual bonds or groups of bonds. Many of these assignments have been made by comparison of the spectra of a large number of compounds and are well established; others are insufficiently well founded and cannot always be recommended for use in structure determination. In a number of publications on the vibrational spectra of organophosphorus compounds attempts are made to explain shifts in the so-called characteristic frequencies, when comparing the spectra of certain compounds with those of others. As a rule, the frequency shifts are ascribed to the influence of some particular factor, *e.g.* polarity of bonds, mass of atoms, etc.

Experimentally and theoretically it is well known that the characteristic vibration frequencies of bonds can change considerably when the intramolecular environment of the bonds to which these frequencies are assigned is changed. The reasons for changes in characteristic frequencies, even if one considers only isolated molecules, can be very varied.

If the frequency is not entirely characteristic of one co-ordinate, *i.e.* the vibration is not localised within a given bond or angle, it is highly probable that the frequency will be sensitive to changes in the force and kinematic parameters of all the co-ordinates of the vibration. The frequencies of such vibrations change markedly, for example, when the distribution of bonds in a group is altered. This property is of particular value in investigations of rotational isomerism of molecules based on vibrational spectra. When a vibration is localised preferentially within one bond (or angle), a considerable change of frequency with change in environment is brought about by a change in the force field of the bond itself. Changes in frequency, caused not by the direct participation of neighbouring bonds and groups in the vibration but by their influence on the electronic configuration of the bond, are of considerable interest in studies of the nature of bonds and the interaction of atoms.

It is very difficult to draw a definite conclusion, exclusively from experimental spectroscopic data, concerning the reasons for the shift of a frequency characteristic of some bond or group of bonds. In fact, even when only one atom in a molecule is exchanged for another, changes in many kinematic and force parameters occur (mass, interatomic distance, angles, force constants). One cannot therefore (with rare exceptions) compare the spectra of substances differing only in one parameter and thus trace its effect on frequency. To reach a firm conclusion, theoretical analysis of the molecular vibrations is essential as well as consideration of the experimental data.

This review discusses the interpretation of the vibrational spectra of organophosphorus compounds, the theoretical analysis of the vibrations of phosphorus-containing molecules, and the application of vibrational spectra to the solution of certain problems in the chemistry of organophosphorus compounds.

The Appendix lists the organophosphorus compounds whose vibrational spectra have been published.

II. ANALYSIS OF THE VIBRATIONAL SPECTRA OF ORGANOPHOSPHORUS COMPOUNDS. IDENTIFICATION OF VARIOUS GROUPS

1. The P=O Group

For structural and analytical studies of the chemistry of phosphorus compounds, the spectral characteristics of P=O and P=S groups are of great interest. For this reason most of the work on the vibrational spectra of organophosphorus compounds has been devoted to elucidation and analysis of the characteristic frequencies of these groups.

Arbuzov *et al.*[1], in a Raman spectral study of the structure of dialkyl phosphites, first suggested that the lines of medium intensity in the 1250–1260 cm^{-1} region for dialkyl phosphites and in the 1280–1300 cm^{-1} region for trialkyl phosphites were due to stretching vibrations of the P=O link. Later, this assignment was confirmed by the work of Meyrick and Thompson[2] on the infra-red and Raman spectra of dialkyl phosphites and esters of alkylphosphinic acids. The infra-red spectra of these compounds showed intense bands in the 1250–1260 cm^{-1} region which were absent in the spectra of trialkyl phosphites.

These investigations were continued by Gore[3] and by Daasch and Smith[4], who studied a large number of infra-red spectra of organophosphorus compounds of various types. Gore compared the spectra of trialkyl phosphates with those of trialkyl phosphorothioates. The chief difference between the spectra of these compounds was observed in the 1250–1300 cm^{-1} region, where the spectra of trialkyl phosphates contain intense absorption bands, ascribed to stretching vibrations of the P=O link.

Daasch and Smith[4] showed that the so-called P=O frequency can vary over a wide range according to the nature of the substituent on the phosphorus atom. Thus, in the spectrum of $(CH_3O)_3PO$ the P=O frequency is 1176 cm^{-1}; 1305 cm^{-1} in that of $(CH_3O)_2POF$; and, according to Gutowsky and Liehr[5], 1415 cm^{-1} in POF_3. Daasch and Smith concluded that the value of the P=O frequency is determined by the electronegativity of the substituent. Bell *et al.*[6] found a linear relation between the frequency of the stretching vibrations of P=O in infra-red and Raman spectra and the sum of the Pauling electronegativities of the halogens in the compounds POX_3. The authors ascribed this relation to the strong polarisation of the P=O bond due to its position between two atoms of such widely different electronegativities. As a result, the phosphorus atom acquires a positive charge and the oxygen atom a negative one. Therefore the P=O bond becomes very sensitive to the polar influences of substituents. This is reflected in the force constant of the bond and hence in the frequency of stretching vibration. To derive the relationship between the P=O frequency and the electronegativity sum, the authors used the infra-red spectra of three compounds: POF_3, $POCl_3$, and $POBr_3$. From the linear relationship obtained and the known frequencies of the stretching vibrations of the P=O bond in various organophosphorus compounds, the authors determined "shift constants" for various substituents. They identified these "shift constants" with the Pauling electronegativities of the substituents and, from their values for many radicals, far-reaching conclusions were drawn about the order of the P=O bond and its character in various phosphorus compounds.

It should be noted that there is no foundation for reducing the many factors responsible for the value of the frequencies of molecular vibrations to one, in this case to the polar factor. The change in frequency between one type of compound and another cannot be ascribed to a polar effect without first calculating the molecular vibrations and determining the amplitude of the vibrations and the sensitivity of the frequencies to a change in the force and kinematic parameters of the molecule. The change in the P=O frequency when substituents are replaced by others can be due not only to a change in the force constant of the bond, but to the fact that the vibration is not fully characteristic of this bond. It is extremely probable that this vibration is not characteristic of the isolated P=O bond but of a tetrahedron with a phosphorus atom at its centre and including this bond and other bonds and angles. Cotton *et al.*[7] consider that in such a case it would be more correct to use not the frequency of vibration but the force constants of the P=O bond in molecules with different substituents at the phosphorus atom. The many experimental data in the paper by Bell *et al.* confirm a more complex relationship between the P=O frequency and the nature of the substituents at the phosphorus atom. The spectra of compounds having identical "shift constants" should have had closely similar values of P = O stretching vibration frequencies. This however was not so. For example, compounds with a sum of electronegativities (ΣX) = 9 have P = O frequencies in the 1250 – 1315 cm^{-1} region, those with (ΣX) = 8 in the 1220 – 1260 cm^{-1} region, those with (ΣX) = = 9.3 in the 1270 – 1320 cm^{-1} region, and so on. Furthermore, the infra-red spectra of the overwhelming majority of organophosphorus compounds containing the P = O bond have an intense absorption band in the 1200 – 1320 cm^{-1} region. Therefore one cannot forecast P = O frequencies on the basis of "shift constants".

Objections can also be raised on other assumptions made by these authors. For calculating the so-called "shift constants" the infra-red spectra of substances in different states are used. In some cases P = O frequencies are taken from spectra of solid substances, in others from spectra of liquids and solutions. It is well known[8,9] that the state of a compound can have an appreciable influence on the position of the P = O band. Further, the absorption band assigned to the P = O stretching vibration is often a doublet. In order to obtain the best fit to a linear relationship, the authors arbitrarily use a single frequency. For the same reason they conveniently displace the straight line, initially drawn through three points, and change its slope. Finally, it should be noted that interpretation of the "shift constants" in terms of Pauling electronegativities of the substituents has no physical meaning.

As a result of this experimental work and that of Bellamy and Beecher[10-12], who studied the infra-red spectra of about 100 organic derivatives of phosphoric and phosphinic acids, the work of Holmstedt and Larsson[13], Bergmann *et al.*[14], Harvey and Mayhood[15], Baudler[16], and others[17-21], it is conclusively established that, when a molecule contains a P = O bond, the infra-red and Raman spectra contain a frequency in the 1180 – 1400 cm^{-1} region, while for the majority of compounds this interval is considerably narrower (1200 – 1320 cm^{-1}).

A theoretical analysis of the experimental data is essential as a basis for experimental assignments and for the correct interpretation of the changes in spectra when comparing one molecule with another. Mayants *et al.*[21-23] calculated the characteristic vibrations of a number of phosphorus-containing molecules and made a numerical analysis of the relation between these frequencies and the force and kinetic parameters of the molecule; these calculations were based on a theory of characteristic frequencies, developed by Mayants[24].

A calculation of the frequencies and modes of vibration of molecules of the type POX_3, namely $POCl_3$ and $POBr_3$, shows that the vibrations corresponding to the so-called P = O frequencies are not fully characteristic of the P = O bond. Other bonds and angles vary appreciably during this vibration. However, the observed dependence of the frequency of this vibration on various parameters shows that plausible changes in all the force constants (excluding the P = O bond force constant) cannot significantly change the P = O frequency. Numerical analysis of the dependence of the frequency on kinematic parameters[25] showed it to be extremely insensitive to changes in the mass of the atom X, the length of the P – X bond, and the bond angles.

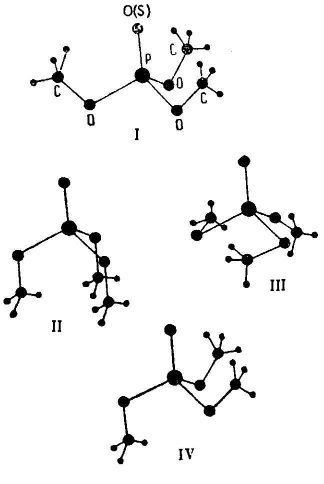
To clarify the part played in this vibration by more distant angles and bonds, the same authors calculated[23] the fully symmetrical vibrations of some of the possible conformations of the molecule $(CH_3O)_3PO$. The calculation showed that vibration involves primarily the P = O bond; some part in the vibration is played by P – O bonds nearest to the P = O bond and by the angles $\overset{P}{O{\diagup}\;\;{\diagdown\!\!\diagdown}O}$, $\overset{P}{O{\diagup}\;\;{\diagdown}O}$, and $\overset{O}{P{\diagup}\;\;{\diagdown}C}$; the remaining co-ordinates are hardly involved in this vibration and do not affect its frequency. Thus, taking into account the results of the calculations for $POCl_3$, $POBr_3$, and $(CH_3O)_3PO$, it can be stated that this vibration is highly characteristic of the P = O bond and the bonds and angles directly adjacent to it, *i.e.* it is localised within a tetrahedron. This is consistent with the experimental data on the vibration spectra of organophosphorus compounds. Table 1, taken from the paper cited above[23], lists the values of the P = O frequencies for certain types of phosphorus compound. The variation of the P = O frequencies in the spectra of compounds having phosphorus atoms with identical immediate environment, does not exceed 10 cm^{-1}. It must be remembered, however, that this conclusion is drawn from calculation of a mechanical model of an isolated molecule. It is not valid for compounds whose molecules are strongly associated or in which intramolecular hydrogen bonding exists. For example, the frequencies of the P = O stretching vibration in the spectra of dialkyl and trialkyl phosphates differ markedly, in spite of the identical immediate environment of the phosphoryl groups. A decrease of 40 – 50 cm^{-1} in the P = O frequency in dialkyl phosphates occurs as a result of an intermolecular hydrogen bond (see below).

TABLE 1. P = O frequencies in spectra of phosphorus compounds..

Compound	$\nu_{P=O}$, cm^{-1}	Lit. ref.	Compound	$\nu_{P=O}$, cm^{-1}	Lit. ref.
$POCl_3$	1290	3	CH_3POCl_2	1285	26
$(CH_3O)_2POCl$	1286	16	$C_2H_5POCl_2$	1285	26
$(C_2H_5O)_2POCl$	1289	16	$(C_2H_5O)C_2H_5P(O)SCH_3$	1215	20
$(C_3H_7O)_2POCl$	1291	16	$(C_2H_5O)C_2H_5P(O)SC_2H_5$	1215	20
$(CH_3O)_2PHO$	1258	16	$(C_4H_9O)C_2H_5P(O)SC_4H_9$	1215	20
$(C_2H_5O)_2PHO$	1257	16	$(C_2H_5O)_2P(O)SCH_3$	1258	19
$(C_3H_7O)_2PHO$	1254	16	$(C_2H_5O)_2P(O)SC_2H_5$	1257	18
$(C_4H_9O)_2PHO$	1258	16	$(C_2H_5O)_2P(O)SCH_2OCH_3$	1255	19
$(CH_3O)_2CH_3PO$	1243	2	$(C_2H_5O)_2P(O)SCH_2C_6H_5$	1254	19
$(C_2H_5O)_2CH_3PO$	1250	2	$(C_2H_5O)_2P(O)SCOOCH_3$	1263	19
(iso-$C_3H_7O)_2CH_3PO$	1249	2	$(C_2H_5O)_2P(O)SCH_2CH_2SC_2H_5$	1255	27
$(C_4H_9O)_2CH_3PO$	1250	18	$(CH_3O)_2POF$	1305	4
$(C_4H_9O)_2C_2H_5PO$	1250	18	$(C_2H_5O)_2POF$	1309	4
$(C_4H_9O)_2C_4H_9PO$	1250	4			
$(C_2H_5O)_2C_4H_9PO$	1243	10			

The fact that the spectra of many organophosphorus compounds show a doublet P = O band is of some interest. Gore[3] observed a doublet band in the spectra of phosphates containing the OC_2H_5 group and explained this by the proximity of the P = O and OC_2H_5 vibration frequencies. Later, Bellamy and Beecher[10] noted that doublets also occur in the spectra of certain triaryl phosphates, while Holmstedt and Larsson[13] observed them in organophosphorus compounds containing amino groups. This is evidence that both frequencies are connected with the P = O group. Mortimer[17] investigated the infra-red spectra of trimethyl, triethyl, and triphenyl phosphates in the crystalline and liquid states at various temperatures and in solution in iso-octane, carbon tetrachloride, carbon disulphide, acetone, and chloroform. The bands at 1290 cm^{-1} and 750 cm^{-1}, observed in the spectrum of crystalline trimethyl phosphate and assigned to P = O and P – O, split into the doublets 1290, 1275 cm^{-1}, and 755, 740 cm^{-1} respectively in the spectra of the liquid material and its solutions. The relative intensities at the maxima (J) of corresponding absorption bands vary appreciably with temperature and with the solvent. Thus J 1290/1275 and J 740/755 vary from 0.93 to 4.5 and from 0.26 to 0.67, respectively. When trimethyl phosphate is heated to 125° an increase in the intensities of the 1275 and 755 cm^{-1} bands is observed. Similar changes occur in the spectra of triethyl and triphenyl phosphate. The authors concluded that, in the liquid state and in solution, several rotational isomers of these phosphates existed, differing in the angle between the $O=P-O$ and $P-O-C$ planes. The frequencies 1290 and 740 cm^{-1} in the spectrum of trimethyl phosphate were ascribed to the conformation that is most stable at low temperatures and the frequencies 1275 and 755 cm^{-1} to a conformation whose concentration increases with rise in temperature.

The presence of two $P=O$ frequencies instead of one in the spectrum of liquid trimethyl phosphate could be explained both by a change in kinematics and by a change in the force field of the molecule on changing from one conformation to the other. A calculation[23] which assumes the equality of the force fields of four of the possible conformations (see diagram)† shows that $P=O$ practically coincides for them while the difference in frequency of the stretching vibrations of the single $P-O$ bonds in conformations I and III is close to the experimental value. Taking account of the possible errors in selecting values of the force constants and kinetic parameters cannot bring $\Delta\nu$ $P=O$ for the various conformations close to the experimental value. To explain the observed difference $\Delta\nu$ $P=O$, it was assumed that the force fields of different conformations are somewhat different, in particular because of differences in the force constants of the $P=O$ bond (~2%). This can arise from a very weak intramolecular interaction between the oxygen atom of the $P=O$ group and hydrogen of the methyl group in one isomer, which is absent in another isomer. The conditions for creating this interaction are most favourable in isomers I and IV and are absent in isomers II and III. Realisation of isomer II is improbable because of steric hindrance. The probable errors in selecting force constants likewise cannot appreciably affect the difference $\Delta\nu$ $P-O$ for the various conformations. Since the difference $\Delta\nu$ $P-O$ for conformations I and III is close to the observed value, it was suggested that the observed frequency 740 cm^{-1} relates to a conformation of type III. The frequency 755 cm^{-1} probably corresponds to a conformation of type I, so that the frequency 1290 cm^{-1} relates to conformation III and 1275 cm^{-1} to conformation I. This choice of a realisable type of conformation agrees with the assumption that their $P=O$ force constants differ; thus conformation I must correspond to a lower value of the constant and hence to a lower value of the $P=O$ frequency.



It might appear that the 1290, 1275 cm^{-1} doublet in the spectrum of trimethyl phosphate could arise from association of $(CH_3O)_3PO$ molecules and not because of the existence of different conformations, since the relative intensity of the bands at 1290 and 1275 cm^{-1} in the infra-red spectrum of a solution of trimethyl phosphate depends on its concentration. However, the hypothesis of $(CH_3O)_3PO$ association does not agree with a number of known facts.

1. The molecular weights of trialkyl phosphates, determined cryoscopically in benzene, are close to the theoretical values[30,31]: if there is an interaction between molecules of trimethyl phosphate, it must be a weak one.
2. If the doublet were caused by a weak intermolecular interaction, the doublet frequencies would not remain constant when passing from the pure liquid to solutions in different solvents and at different temperatures. The frequencies 1290 and 1275 cm^{-1} retain their value and do not depend greatly on the solvent and the temperature[17].
3. If there were association between trimethyl phosphate molecules the nature of the $P=O$ absorption band would differ from that observed. In the case of weak association between the oxygen atom of the $P=O$ group in one molecule and the hydrogen atoms of the methyl group in another, the $P=O$ band of lowest frequency should be more diffuse than the $P=O$ band in a non-associated molecule. This is not observed.
4. Finally, if one assumes a dipole–dipole interaction of the type $\begin{array}{c} O^{-}\cdots P^{+} \\ \| \qquad \| \\ P^{+}\cdots O^{-} \end{array}$ the spectrum should show, not two $P=O$ frequencies, but three, of which two should again be diffuse.

The concentration dependence of the relatively intense bands at 1290 and 1275 cm^{-1} does not contradict the hypothesis of the existence of different conformations of the trimethyl phosphate molecule. This dependence may be ascribed to the differing capacities of different rotational isomers for solvation by solvent molecules, as a result of which the equilibrium constant between different conformations, defined by the ratio of the activities, also depends on the concentration of the solution.

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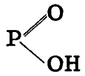
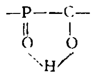
† Model I was first proposed by Gibling[28] for molecules of alkyl esters of phosphoric acid, on the basis of the good agreement between calculated and experimental values of the parachors, and was later supported by studies of the parachors by Arbuzov and Vinogradova[29].

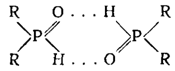
A further property of the P = O frequency is its sensitivity to any form of association of organophosphorus molecules either with themselves or with solvent molecules. Daasch and Smith[4] first noted that the maximum of the P = O band shifts by 50 – 80 cm^{-1} in the direction of lower frequencies compared with spectra of the corresponding esters of alkyl- and aryl-phosphonic acids, and the absorption band is more diffuse. This is accompanied by a large shift of the OH stretching vibrations band (see below). This was ascribed to the formation of an intermolecular hydrogen bond P = O ··· H – O. Bellamy and Beecher[11,12] confirmed the existence of association in a large number of spectra of compounds containing  $P(=O)OH$ groups and also concluded that P = O forms a hydrogen bond with the NH group. They observed that formation of a hydrogen bond was accompanied by an increase in intensity of the P = O band but no quantitative measurements were made. The infra-red spectra[25] of solutions of $(C_2H_5O)_2P(O)OH$, $(C_2H_5O)_3PO$, and $(C_2H_5O)_2C_2H_5PO$ show a noticeable solvent effect on the P = O frequency. Solvents containing hydroxyl and amino groups have a particularly marked effect. Thus in the spectra of substances in formamide solution the P = O frequencies are lower than those of the pure liquids and solutions in carbon tetrachloride, *e.g.* with $(C_2H_5O)_2P(O)OH$ the frequency drops from 1230 cm^{-1} to 1205 cm^{-1}, with $(C_2H_5O)_3PO$ from 1270 cm^{-1} to 1240 cm^{-1} and with $(C_2H_5O)_2.C_2H_5PO$ from 1265 cm^{-1} to 1220 cm^{-1}. Large shifts are also observed in the spectra of aqueous and alcoholic solutions. Bellamy *et al.*[9] studied the influence of many solvents, not containing hydroxyl or amino groups, on the P = O frequency in $POCl_3$ and $(CH_3O)_2PHO$. The greatest shift occurred with solutions in methylene iodide.

Cryoscopic determinations of the molecular weights of certain organophosphorus compounds in benzene and naphthalene[30,31] have shown that, in compounds of the type $(RO)_2PO(OH)$, the molecules are dimerised while, in compounds of the type $(RO)PO(OH)_2$, polymers of higher complexity are formed. In acetic acid the compounds are monomeric. With trialkyl phosphates, the molecules of which cannot form intermolecular hydrogen bonds, the experimental molecular weights agreed with the theoretical values. As was shown[25] with $(C_2H_5O)_2P(O)OH$, the degree of association of dialkyl phosphates depends very much on concentration. Increasing concentration increases association and the molecules are converted into di- and then poly-associated complexes.

Miller *et al.*[8] studied the infra-red spectra of dialkyl-α-hydroxyalkylphosphine oxides and dialkyl-α-hydroxyalkylphosphonates in the crystalline state and in CS_2 solution. The P = O and O – H frequencies in the spectra of the crystalline phosphine oxides occur in the regions 1100 – 1140 cm^{-1} and 3050 – 3100 cm^{-1} respectively; in the spectra of the alkyl phosphonates they occur in the regions 1230 – 1232 cm^{-1} and 3180 – 3250 cm^{-1}. The low values of these frequencies and their negligible enhancement in the spectra of the solutions were ascribed by the authors to intramolecular hydrogen bonding of the type:



The authors consider that the enhancement of the P = O frequency from 1150 to 1190 cm^{-1} in the spectra of the CS_2 solutions is caused by dipole – dipole association of the molecules, *e.g.* $P^+–O^-\cdots P^+–O^-$. Association of dialkylphosphinous acids by means of intermolecular hydrogen bonding of the type



they considered improbable, because an analogous change of P = O frequencies also occurs in the spectra of trialkylphosphine oxides. It was noted that the P – H frequency (see below) was lower in the spectra of solutions than in those of the crystalline compounds. With intermolecular hydrogen bonding the opposite should have been observed. The existence of association in compounds of this type is confirmed by the results of Kosolapoff and McCullough[32] on heats of mixing.

Vibrational spectra have been used to study the ability of phosphorus compounds to complex with metal cations[7,33–35]. Cotton *et al.*[7] examined the infra-red spectra of mixtures of trimethyl- and triphenyl-phosphine oxides with halides of Cd, Zn, Co, Cu, Mn, Ni, and Fe. Complex formation caused a diminution of the P = O stretching frequency by 40 – 70 cm^{-1}, and the absorption band broadened or split into two components. This is explained by the formation of a bond between the oxygen of the phosphoryl group and the metal ion and this, in turn, causes a reduction of the force constant of the P = O bond. Sheldon and Tyree[33] had earlier observed a similar phenomenon in the spectra of the crystalline addition products of $POCl_3$, $POBr_3$, and $(C_6H_5)_3PO$ with $TiCl_4$, $SnCl_4$, and $FeBr_2$.

Kinell *et al.*[35] investigated the Raman spectra of mixtures of $POCl_3$ and $PO(CH_3)_3$ with $SbCl_5$ in 1,2-dichloroethane solution. The spectra show that, in the ternary solution, all the $SbCl_5$ molecules react with $PO(CH_3)_3$, not with $POCl_3$, to form the complex $SbCl_5.PO(CH_3)_3$. This indicates that the donor properties of the phosphine oxide are greater than those of phosphorus oxychloride.

2. The P = S Group

The spectral characteristics of the P = S group are of considerable interest in the chemistry of organothiophosphorus compounds.

There are many studies of the vibrational spectra of compounds of this class. Thus, Gore[3] investigated more than thirty infra-red spectra of organothiophosphorus and organophosphorus compounds. The spectrum of $PSCl_3$ has an intense band at 748 cm^{-1} which is absent in the spectrum of $POCl_3$. The spectra of diethyl phosphorochloridothionate and diethyl phosphorochloridate differ markedly in the 660 and 1290 cm^{-1} regions. The presence, in the first compound, of a band at 660 cm^{-1} and, in the second, at 1290 cm^{-1} is explained by the presence of P = S and P = O bonds, respectively. In most cases, however, the absorption bands in the infra-red spectra could not be related to the thiono group in thiophosphorus compounds. Gore concluded that the P = S group did not have characteristic frequencies. The same conclusion was reached by Daasch and Smith[4], and Bellamy and Beecher[10]. In a number of other publications[19,27,36] the absorption due primarily to the P = S bond was not identified. Bellamy[37] concluded that the P = S absorption occurred in the 600 – 750 cm^{-1} region and varied considerably in intensity. The absence of a marked absorption in this region cannot therefore be taken as an indication of the absence of the P = S group in a molecule.

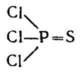
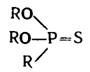
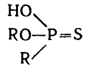
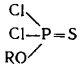
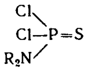
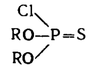
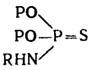
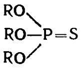
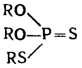
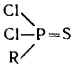
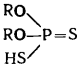
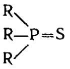
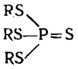
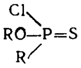
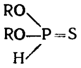
McIvor *et al.*[18] studied the infra-red spectra of 50 organothiophosphorus compounds: the thiono group was characterised by frequencies in the 740–830 cm^{-1} region. However, this conclusion is not supported by a comparison of the spectra of the thiono compounds with the spectra of the thiolo and oxygenated organophosphorus compounds quoted. For example, in the spectrum of CH_3PSCl_2 a band at 780 cm^{-1} was assigned by the authors to the P=S bond, but the spectrum of CH_3POCl_2 has a band at 770 cm^{-1}, of similar intensity. The spectra of diethyl phosphorochloridothionate and diethyl phosphorochloridate have absorption bands of comparable intensity in the 800 cm^{-1} region, but the band at 817 cm^{-1} in the spectrum of diethyl phosphorochloridothionate was assigned to the thiono group. The infra-red spectra of $(CH_3O)_2P(S)H$ and $(CH_3O)_2P(O)H$ contain bands of equal intensity at a frequency of 795 cm^{-1}, but the authors assigned this band in dimethyl phosphonothionate to the thiono group. Similarly, other assignments made by McIvor *et al.* are doubtful. Later[38], the authors themselves expressed doubts about their assignments; however, in a summarising table they still indicate the 740–830 cm^{-1} region as the region of P=S stretching vibrations.

Only a few studies of Raman spectra of thiophosphorus compounds have so far been made. From the work of Simon and Schulze[39], Delwaulle and François[40-42], and others[36,43], it is known that the P=S bond in phosphorochloridothioic acids produces intense lines in the Raman spectra, the frequencies of which coincide with those of the infra-red absorption bands. Simon and Schulze[39,44], and Michalski *et al.*[45] report the spectra of several trialkyl phosphorothionates but do not analyse them.

To determine the characteristic frequencies of the P=S group, Popov *et al.*[26] examined the infra-red and Raman spectra of a large number of organic phosphorothionates, together with the corresponding phosphorothiolates and phosphates. It was observed that, in the infra-red spectra of molecules of different types, the P=S absorption bands differ widely in intensity. In investigations of the structure of many organothiophosphorus compounds the use of infra-red spectra alone cannot therefore be recommended. In addition, one must take into account the possibility of P–S–R (R = alkyl) groups giving rise to intense bands in the P=S region. In the Raman spectra of all the organothiophosphorus compounds examined, the P=S bands are considerably more intense than the P=O bands. This is possibly due to the small polarity of this bond and its readier polarisability. The P=S bands in infra-red spectra of organothiophosphorus compounds often consist of two or three frequencies. By comparing the P=S and P=O absorption band, it was concluded that the complexity of the P=S bands was due, as in phosphoryl compounds, to rotational isomerism. In the spectra of analogous thiono and phosphoryl molecules, the P=O and P=S bands are identical in character. For example, in the spectra of $RPSCl_2$ and $RPOCl_2$ the P=S and P=O bands are single when R = CH_3 and complex when R = C_2H_5 and C_3H_7.

Analysis of the spectra of the compounds and published data show that the frequencies associated with the P=S group are in the 550–750 cm^{-1} region and only have a constant value when the environment of the phosphorus atom is identical. Table 2 gives the mean values of the characteristic P=S frequencies for different types of organothiophosphorus compounds.

TABLE 2.* P=S frequencies (cm^{-1}).

	750 cm^{-1}		580 cm^{-1}
			580 cm^{-1}
	700 cm^{-1}		670 cm^{-1}
	660 cm^{-1}		640 cm^{-1}
	610 cm^{-1}		655 cm^{-1}
	665 cm^{-1}		655 cm^{-1}
	550 cm^{-1}		685 cm^{-1}
	625 cm^{-1}		635 cm^{-1}

* R = alkyl radical.

Simultaneously with the work of Popov *et al.*[26], Hooge and Christen[46] determined the stretching vibration frequencies of the P=S group in the infra-red spectra of the compounds $X_3P=S$ (X = CH_3, C_2H_5, CH_3O, C_2H_5O, C_2H_5, C_2H_5S), and gave a theoretical analysis of this vibration. The assignment of frequencies in the spectra of compounds examined in both studies agree with each other. Hooge and Christen also assume that the doublet character of the P=S and P=O bands, observed in the spectra of many organophosphorus compounds, is due to rotational isomerism.

This work shows that the frequencies assigned to the P=S group remain constant only if the immediate environment of the phosphorus atom does not change. This conclusion was confirmed by Mayants *et al.*[22,23] by a calculation of the normal vibrations and a numerical analysis of the dependence of frequency on force and kinetic parameters of the molecules $PSCl_3$, $PSBr_3$, and four of the possible conformations of $(CH_3O)_3PS$.

Table 3 lists the P=S frequencies for different types of thiophosphorus compound. The P=S frequencies, like the P=O frequencies, remain constant within the limits of experimental error so long as the environment of the thiono group is unchanged. This rule has the same limitations as the analogous rule for the P=O frequencies (see p. 364).

The results of these calculations and experimental assignments of frequencies[22,23,26] contradict the conclusions of McIvor *et al.*[18,38], which were criticised above.

Hooge and Christen[46] calculated the P=S vibration frequencies for $(CH_3)_3P=S$, $Cl_3P=S$, $Br_3P=S$, $-O_3P=S$, and $S_3P=S$. Using the same P=S bond force constant for all the models, it was concluded that the P=S stretching vibration frequency for molecules of the type $X_3P=S$ depends only on the mass of the atoms X and the force constants of the P–X bonds. The conclusion concerning the

TABLE 3. P = S frequencies in spectra of thiophosphorus compounds.

Compound	$\nu_{P=S}$, cm^{-1}	Lit. ref.	Compound	$\nu_{P=S}$, cm^{-1}	Lit. ref.
$PSCl_3$	748	3	$(C_3H_7O)_2P(S)NHCH_3$	645	26
CH_3PSCl_2	664	26	$(C_4H_9O)_2P(S)NHCH_3$	645	26
$C_2H_5PSCl_2$	665	26	$(iso\text{-}C_3H_7O)_2P(S)NHCH_3$	637	26
$C_3H_7PSCl_2$	660	26	$(CH_3O)CH_3PSCl$	620	26
$(CH_3O)_3PS$	646	46	$(C_2H_5O)CH_3PSCl$	625	26
$(C_2H_5O)_3PS$	608	26	$(iso\text{-}C_3H_7O)CH_3PSCl$	629	18
$(C_2H_5O)_2P(S)OH$	618	46	$(CH_3O)P(S)SH$	654	18
$(C_2H_5O)_2P(S)OCH_2CH_2SC_2H_5$	607	27	$(C_2H_5O)_2P(S)SH$	654	26
$(C_2H_5O)_2P(S)OPO(OC_2H_5)_2$	609	26	$(CH_3O)_2P(S)SCH_3$	655	26
$(CH_3O)_2PHS$	636	4	$(C_2H_5O)_2P(S)SC_2H_5$	655	26
$(C_2H_5O)_2PHS$	633	26	$(C_2H_5O)_2P(S)SCH_2SC_3H_7$	655	26
$(CH_3O)_2PSCl$	660	26	$(C_2H_5O)_2P(S)SCH_2CH_2SC_3H_7$	656	26
$(C_2H_5O)_2PSCl$	660	26	$(CH_3S)_3PS$	685	46
$(C_3H_7O)_2PSCl$	665	26	$(CH_3S)_2(iso\text{-}C_3H_7S)PS$	685	46
$(C_4H_9O)_2PSCl$	667	26	$(C_2H_5S)_2CH_3SPS$	685	46
$(iso\text{-}C_3H_7O)_2PSCl$	656	26	$(C_2H_5S)_3PS$	685	46
$(CH_3O)_2P(S)NHCH_3$	635	26	$(C_3H_7S)_3PS$	685	46
$(C_2H_5O)_2P(S)NHCH_3$	638	26	$(C_4H_9S)_3PS$	685	46

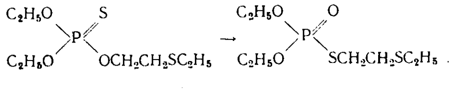
effect of the mass of the atoms X contradicts some of the data cited by the authors themselves; neither does it agree with the results of the calculation and analysis of the vibration frequencies of the molecules $PSCl_3$, $PSBr_3$, and $(CH_3O)_3PS$ made by Mayants *et al.*[22,23,25] Thus, according to the constant used by Hooge and Christen in their calculation, the force fields of $PSCl_3$ and $PSBr_3$ are effectively the same. The calculated P = S frequencies, in spite of the difference in mass of the chlorine and bromine atoms, are closely similar (750 and 736 cm^{-1} respectively) notwithstanding the conclusions of the authors. Where it has some effect, increase in mass must necessarily lower the frequency; however, the calculated P = S frequency in $(CH_3)_3P{=}S$ (555 cm^{-1}) is considerably lower than the frequency in $PSBr_3$ (736 cm^{-1}). The same is observed in the experimental vibrational spectra of these compounds (558 cm^{-1} and 718 cm^{-1} respectively).

The results of a more detailed and rigorous calculation[22,23,25] show that the so-called stretching vibration of the P = S bond is not confined only to this bond but is a more complex molecular vibration. In addition to P = S, the bonds and angles directly adjacent to the group play an appreciable part in this vibration. Therefore the force constants of PX, like other force constants of a tetrahedron with a phosphorus atom at the centre, have a definite influence on the P = S frequency. A quantitative estimate was also made[22,23,25] of the extent to which this vibration is characteristic, and the sensitivity of the frequency to variation of the force and kinematic parameters of the molecule was determined. According to these data, this frequency is most sensitive to variation of the force constant of the P = S bond. Likely changes in the values of other force constants cannot substantially affect the P = S frequency. Numerical analysis of the dependence of frequency on kinematic parameters proved that the effects of mass of the atoms X, of the length of the P – X bonds, and of the X – P – X and X – P = S angles, must be extremely small.

It can be seen from the above work on thiophosphorus compounds that vibrational spectra can, comparatively quickly and in most cases unambiguously, decide between a thiono or a thiolo structure in organothiophosphorus compounds. Vibrational spectra are therefore a useful means of investigation of thiono – thiolo isomerism, discovered by Pishchemuka[47] and Emmett and Jones[48] in trialkyl phosphorothioates.

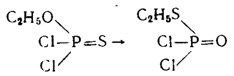
On heating, trialkyl phosphorothionates isomerise to trialkyl phosphorothiolates: $(RO)_3P{=}S \rightarrow (RO)_2(RS)P{=}O$. The difference in structure of the isomeric molecules has a substantial effect on their infra-red spectra. The marked difference in the spectra enables them to be used for qualitative and quantitative analysis both in the laboratory and in industry.

Henglein *et al.*[27] studied the isomerisation of the well-known insecticide *OO*-diethyl-*O*-ethylthioethyl phosphorothionate:



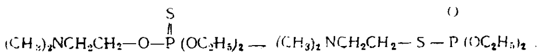
The quantity of thiolo isomer produced was determined chemically by oxidation with nitric acid and by means of infra-red spectroscopy; the results agreed well. The spectrum of *OO*-diethyl-*S*-ethylthioethyl phosphorothiolate, obtained by isomerisation, has an intense absorption band with a maximum at 1255 cm^{-1} associated with the P = O stretching vibration. The spectrum of the thiono isomer has no appreciable absorption in this region. The spectra of both compounds have a band at 1165 cm^{-1}, associated with vibrations of the $P{-}O{-}C_2H_5$ group. On isomerisation the position and intensity of this band remain unchanged. It can thus be used as an internal standard in quantitative analysis. The determination of isomer concentration by this method is very simple and exceptionally rapid.

Popov and Medenikova[49] used infra-red spectra to investigate the thermal isomerisation of ethyl phosphorodichloridothioate, an intermediate in the synthesis of a series of important organothiophosphorus insecticides.



In the spectra of ethyl phosphorodichloridothionate maintained at 120° for 1, 3, 4, 5, and 6 hours, it can be clearly seen that the bands characteristic of the groups $P{-}O{-}C_2H_5$ and P = S diminish in intensity with increase in the duration of heating, while the intensity of the P = O band of the thiolo isomer increases. After heating 6 h at 120° ethyl phosphorodichloridothionate has an infra-red spectrum similar to that of ethyl phosphorodichloridothiolate. For quantitative analysis the bands at 795 and 1270 cm^{-1} were chosen; these were convenient because they do not overlap any other bands and each is fairly intense only in the spectrum of one compound. The results of spectral analysis and refractometric measurements show that heating ethyl phosphorodichloridothionate for 6 h at 80° does not bring about any isomerisation; at 100° only a negligible amount of isomerisation occurs, while at 120° isomerisation is complete. The kinetics of the isomerisation are satisfactorily described by the equation for an autocatalytic reaction.

Tammelin[50] studied the isomerisation of *OO*-diethyl-*O*-ω-dimethylaminoethyl phosphorothionate by infra-red spectroscopy and paper chromatography. He showed that on heating for several hours at 100° the thiono isomer changes to *OO*-diethyl-*S*-ω-dimethylaminoethyl phosphorothiolate:



$$(CH_3)_2NCH_2CH_2{-}O{-}\overset{\overset{S}{\|}}{P}(OC_2H_5)_2 \rightarrow (CH_3)_2NCH_2CH_2{-}S{-}\overset{\overset{O}{\|}}{P}(OC_2H_5)_2.$$

3. The P = N Group

Of the compounds in which phosphorus forms multiple bonds, those containing a P = N group have been least studied.

Daasch[51] analysed the Raman and infra-red spectra of the trimer and tetramer of phosphonitrilic chloride. Intense bands at 1218 cm^{-1} for the trimer and 1315 cm^{-1} for the tetramer were assigned to vibrations of the respective rings. Analogous bands were observed in the same region in the spectra of other trimers: $P_3N_3Cl_5Br$ 1205 cm^{-1}, $P_3N_3Cl_4Br_2$ 1202 cm^{-1}, $P_3N_3Cl_2Br_4$ 1180 cm^{-1},[52] $P_3N_3(N_2H_3)_6$ and its benzaldehyde and salicylaldehyde derivatives 1218 cm^{-1}.[53] The spectra of aliphatic esters of trimeric nitrilophosphoric acid do not have intense bands in this region[4]. Shaw[54] investigated the spectra of a large number of trimeric and tetrameric phosphonitrilic derivatives: the frequencies assigned to vibrations of six-and eight-membered rings were in the 1180 – 1270 cm^{-1} region for the trimers and 1270 – 1330 cm^{-1} for the tetramers.

Kabachnik *et al.*[55] investigated the infra-red spectra of phosphorimidates $(RO)_3P = NC_6H_5$ and phosphonimidates $(RO)_2R'P = NC_6H_5$ (R and R′ = alkyl) containing a P = N group outside a ring. Intense bands in the 1350 – 1385 cm^{-1} region in the spectra of these compounds were assigned to P = N stretching vibrations. In the spectra of the isomeric anilidophosphates and anilidophosphonates there is no absorption in this region but an intense absorption occurs in the 1210 – 1270 cm^{-1} region, characteristic for compounds with a P = O group. To clarify the influence of substituents at the nitrogen atom on the absorption associated with the P = N vibration, the infra-red spectra of $(C_2H_5O)_3P = NC(O)CH_3$ and $(RO)_3P = NCH_3$ were obtained[55]. Absorption bands in the 1325 – 1385 cm^{-1} region were assigned to stretching vibrations of the P = N group. Horner and Oldiger[55a] studied the infra-red spectra of the compounds p-$R-C_6H_4-N=P(C_6H_5)_3$ (R = H, CH_3, CH_3O, Cl, $COOC_2H_5$, NO_2, and CN) and assigned to the P = N stretching vibration some absorption bands, very variable in intensity, in the 1160 – 1180 cm^{-1} region. The only basis for this was the assignment by Daasch[51] of a band at 1218 cm^{-1} to analogous vibrations of the molecule $(PNCl_2)_3$. It would possibly be correct to associate the P = N vibration in these compounds with the intense bands in the 1330 – 1370 cm^{-1} region, which is in good agreement with the data on phosphorimidates and phosphonimidates[55]. The correctness of the assignment by Horner and Oldiger of the bands in the 1330 – 1370 cm^{-1} region to N – C vibrations is doubtful.

Further accumulation of experimental data and theoretical consideration of the vibrations of phosphoronitrogen molecules is required before a final conclusion can be made concerning the characteristic nature of vibrations of the P = N group.

Associated with the question of identification of the P = N group is the question of structure and tautomerism of the N-substituted dialkyl phosphoramidates and phosphonamidates.

The tautomerism of the acid amides of pentavalent phosphorus are of some interest

This tautomerism is analogous to the lactam – lactim tautomerism.

The work of Bellamy and Beecher[11] and Holmstedt and Larsson[13] on the infra-red spectra of dialkyl N-alkylphosphoramidates shows that the tautomeric equilibrium in these substances is displaced towards the amide form (I).

In order to confirm the possibility of a tautomerism of this type (I ⇌ II) in a series of phosphoronitrogen compounds, Kabachnik *et al.*[56] displaced the equilibrium by introducing substituents of different electrophilic character at the nitrogen atom. The following N-substituted phosphoramidates and phosphonamidates were investigated and their infra-red spectra studied:

$$(C_2H_5O)_2P(O)NHCOCH_3,$$
$$(C_2H_5O)CH_3P(O)NHCOCH_3,$$
$$(C_2H_5O)C_2H_5P(O)NHCOCH_3,$$
$$(C_2H_5O)_2P(O)NHP(O)(OC_2H_5)_2,$$
$$(C_2H_5O)_2P(O)NHSO_2CH_3.$$

The spectroscopic data show that the amide form (I) predominates in the N-acetyl-substituted phosphoramidate and phosphonamidates. Thus intense absorption bands are observed in the 1200 – 1250 cm^{-1} and 3100 cm^{-1} regions, which are assigned to P = O and N – H vibrations, respectively.

The spectra of diethyl-N-diethylphosphoryl-phosphoramidate and diethyl-N-methanesulphonyl-phosphoramidate are different in appearance. In the spectrum of the first, absorption bands at ~ 1250 cm^{-1} and ~ 1390 cm^{-1} are assigned to stretching vibrations of P = O and P = N respectively. In that of the second, the band at 1390 cm^{-1}, characteristic of P = N, remains. Bands at 1235 cm^{-1} and 1315 cm^{-1} are ascribed to symmetric and asymmetric vibrations of the sulphonyl group. In addition, the spectra of both compounds have very diffuse bands in the 3000 cm^{-1} region, which are assigned to vibrations of hydrogen-bonded hydroxyl groups. When these compounds are deuterated their spectra change only in the hydroxyl group region: the intensity of the bands at 2700 cm^{-1} and 3000 cm^{-1} diminishes and new bands appear in the 2170 – 2320 cm^{-1} region. The presence of OH and P = N bands and the absence of clearly defined NH and P = O bands shows that the tautomeric equilibrium in these two compounds is displaced towards the imidol form (II).

Thus the introduction of the more electrophilic substituents, the phosphoryl and methanesulphonyl radicals, at the nitrogen atom in phosphoramidates displaces the tautomeric equilibrium towards the imidol form and proves the tautomerism of this type of compound.

4. The P – O – R Group

The experimental study of the vibrational spectra of organophosphorus compounds enabled a number of other assignments of bands to individual bonds and groups of bonds to be made.

In an investigation of the infra-red spectra of aliphatic esters of phosphoric and alkylphosphonic acids, Daasch and Smith[4] established the connection between the P – O – C group and a strong absorption band in the 1030 – 1050 cm^{-1} region. The extensive studies of Bellamy and Beecher[10-12] confirmed this assignment. At present, the spectra of a large number of alkyl phosphates and other compounds containing the P – O – C group are known (see Appendix); in all cases there is a very intense absorption band in the 995 – 1050 cm^{-1} region, the overwhelming majority of compounds absorbing at 1030 cm^{-1}.

In the same way that frequencies ascribed to C–O–C (alkyl) and C–O–C (aryl) bonds in ethers differ appreciably from each other, there is a marked difference between the frequencies for analogous P–O–C bonds. This difference was demonstrated by Bellamy and Beecher[10] with the spectra of triphenyl, diphenylethyl, phenyldiethyl, and triethyl phosphate. At the same concentration and in the same cell, a progressive weakening and then the complete disappearance of the 1200 cm^{-1} band was observed; at the same time the 1030 cm^{-1} band, absent in triphenyl phosphate, increased in intensity. Later it was established[11,12] that frequencies assigned to the P–O–C (aryl) group occurred in the range 1190–1240 cm^{-1} in the spectra of aromatic phosphates, phosphines, and phosphites.

Up to the present time, the spectra of only a few compounds containing the P–O–C (acyl) group have been studied[19,20]. It is very probable that the intense absorption band in the 1180–1200 cm^{-1} region in the spectra of these compounds is associated with this group. Thus, the experimental data show that the P–O–C frequencies are extremely sensitive to the type of substituent at the carbon atom. However, they remain practically unchanged in the spectra of organic phosphates, phosphorothionates, and phosphorimidates, and compounds of trivalent phosphorus.

Several publications discuss the more detailed assignment of frequencies in the 1000–1050 cm^{-1} region in spectra of alkyl phosphates. Thus Bergmann *et al.*[14] suggested that the absorption in this region was due to asymmetric vibration of the three P–O–C groups. The band at 980 cm^{-1} is assigned to the symmetrical vibrations of these groups. However, if this were the case, one would have expected a shift of the absorption band in spectra of compounds with two or one P–O–C groups: this is not observed.

Bellamy and Beecher[10-12] assigned the band in the 1000–1050 cm^{-1} region to the (P)O–C vibration and that at 980 cm^{-1} to the P–O(C) vibration. Baudler[16], Meyrick and Thompson[2], and others[17] assign a band in the 730–800 cm^{-1} region to the P–O(C) vibration.

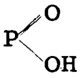
Ketelaar and Gersmann[57] considered the vibration of a P–O–C group isolated from the rest of the molecule and concluded that, in molecules of phosphoric acid esters, the vibrations corresponding to P–O and C–O bonds in the P–O–C group are to a considerable extent isolated, the greater frequency being associated with the C–O vibration. Considering the unjustified assumptions made in the calculation, the authors' conclusions cannot be regarded as substantiated. A full calculation and analysis[23] of the vibration frequencies of the molecules $(CH_3O)_3PO$ and $(CH_3O)_3PS$ show that in these molecules local (P)O–C, P–O(C), and even P–O–C vibrations are absent. Frequencies in the 1000–1050 cm^{-1} and 730–800 cm^{-1} regions can only very provisionally be identified with O–C and P–O vibrations because, although the C–O bond (1000–1050 cm^{-1}) and the P–O bond (730–800 cm^{-1}) play the major part in these vibrations, the bonds and angles of the organic part of the molecule also vary appreciably. At the same time, the phosphoryl group in $(CH_3O)_3PO$ and the thiono group in $(CH_3O)_3PS$ take practically no part in these vibrations.

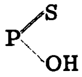
Analysis of the frequencies shows, on the one hand, their great sensitivity to changes in the force constants of the organic part of the molecule and, on the other hand, their small sensitivity to changes in the phosphorus part. This is in agreement with experiment. The so-called (P)O–C frequencies differ substantially in spectra of compounds containing alkyl, aryl, and acyl substituents at the phosphorus atom but coincide in spectra of compounds with P=O, P=S, or P=N groups and also in spectra of compounds of 5- or 3-valent phosphorus. The P–O(C) frequencies in spectra of trialkyl phosphates and trialkyl phosphorothionates change when one alkyl radical is exchanged for another. Calculation and experiment[17,23] show that the P–O frequencies differ by 15 cm^{-1} in rotational isomers of the molecule $(CH_3O)_3PO$, indicating that the vibration is sensitive to change in the angle of rotation of the methoxyl groups about the P–O bond.

The data of Daasch and Smith[4] show that in the spectra of compounds containing $(P)O-C_2H_5$ groups there is, in addition to the intense band at 1030 cm^{-1}, another sharp band of medium intensity at 1160 cm^{-1}. Bellamy and Beecher[10-12] confirmed this and noted that a similar band, but of greater intensity, appears in spectra of compounds containing the (P)O–C(aryl) group. In 70 compounds studied by them, containing a group of this kind, the band appears in the 1156–1163 cm^{-1} region. The presence in a spectrum of a band in this region and an intense band in the 1200 cm^{-1} or 1030 cm^{-1} region identifies one of these groups. For the $(P)O-CH_3$ group, there is also a characteristic band at 1190 cm^{-1} which, according to much of the data[4], is very constant and can be used as confirmation of the presence of methoxyl groups in phosphorus compounds.

Baudler[16] studied the Raman spectra of 22 compounds of the following types: $(RO_3)P$, $(RO)_2PX$, $ROPX_2$, $(RO)_3PO$, $(RO)_2POX$, and $(RO)_2POH$, where R = alkyl, X = Cl or Br. Lines of low intensity in the 950–1070 cm^{-1} region were assigned to the (P)O–C(alkyl) group; lines of frequency 1190 and 1160 cm^{-1} in cases where R = CH_3 and C_2H_5, were not observed in the Raman spectra.

5. The O–H and S–H Groups

It was noted above that the stretching vibration frequency of OH is shifted considerably to lower values as a result of intermolecular hydrogen bonding in compounds containing  $P{\overset{O}{\underset{OH}{<}}}$ groups. The corresponding absorption band in the infra-red spectra of dialkyl phosphates is very diffuse and occurs[4,10,12] in the 2560–2700 cm^{-1} region. This band persists in solutions in non-polar solvents. In the Raman spectrum of Cl_2POOH a diffuse band at 2819 cm^{-1} is assigned[58] to OH stretching vibrations. The spectrum of Cl_2POOD does not have a band at 2819 cm^{-1} but has a low-intensity OD stretching vibration band at 2093 cm^{-1}.

In spectra of compounds containing the  $P{\overset{S}{\underset{OH}{<}}}$ group[18,19] the absorption band that can be assigned to the OH stretching vibration is found in the 3100–3150 cm^{-1} region. There is no doubt that such low values for the OH frequencies are connected with association, while the diffuse nature of the absorption bands is evidence of intermolecular interaction between molecules of the organophosphorus acids. The association of alkyl alkylphosphonothioic acids is confirmed by cryoscopic data[20,25]. The molecular weight of acids of the (RO)P(S)OH type in benzene considerably exceeds the theoretical value, while corresponding exactly to it in phenol. The infra-red spectrum of alkyl alkylphosphonothioic acids heated to 90° show a shift of the absorption maximum by 60 cm^{-1} to higher frequency. Molecules of dialkyl phosphoric and phosphorothioic acids are also associated[25,30,31]. A study of the concentration dependence of the association of these compounds[25] shows that the degree of association of dialkyl phosphates greatly exceeds that of dialkyl phosphorothioates. The more stable intermolecular hydrogen bond in diethyl phosphate also brings about a greater shift of the absorption maximum of the OH stretching vibration (2640 cm^{-1}) compared with diethyl phosphorothioate (3120 cm^{-1}).

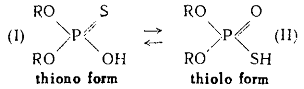
Molecules of dialkyl phosphorothioates, like molecules of the half esters of alkylphosphonothioic acid, can form a hydrogen bond by interaction between a proton and either the thiono group (O−H····S = P) or the oxygen atoms of the ester groups ($\text{O-H}\cdots\text{O}\langle^{\text{P}}_{\text{R}}$). To clarify this question, a study of the spectra of alkyl alkylphosphonothioic acids and cryoscopic measurements would be useful. The absence of ester groups in these acids would enable conclusions to be made concerning the interaction of a proton with the thiono group. Existing data allows one only to state that association of the type OH····S = P is either absent or very weak and that the intermolecular hydrogen bonding is mainly with oxygen atoms. This proposition is based on the position of the P = S frequencies in the spectra of phosphorus thio-acids. In the case of association with the thiono group, the P = S frequency should be markedly lower than in the corresponding ester; this occurs with dialkyl or trialkyl phosphates, for example, or with the esters and half esters of alkylphosphonic acids. In fact, the observed P = S frequencies[46] for diethyl phosphorothioate (618 cm^{-1}) and the ethyl ester of ethylphosphonothioic acid (586 cm^{-1}) practically coincide with the P = S frequencies for, respectively, trialkylphosphorothionates and dialkyl esters of alkylphosphonothioic acids; this is expected for molecules with identical immediate environments of the phosphorus atom and in the absence of strong intermolecular hydrogen bonding with the thiono group.

A few spectra of compounds containing the P−S−H group are known. Thus the infra-red spectra of phenyl phenylphosphonodithioic and ethyl ethylphosphonodithioic acids have been studied[59]. The spectra of the solid and fused compounds and also of their concentrated solutions have bands at 2420 and 2560 cm^{-1} which, by analogy with the spectra of mercaptans, were assigned to stretching vibrations of the thiol group. On dilution of the solutions and raising the temperature, the intensity of the diffuse 2420 cm^{-1} band diminishes appreciably. The authors explain the existence of two bands and the diffuse nature of the 2420 cm^{-1} band by the formation of polymeric complexes $(R_2PSSH)_n$ associated by SH····S hydrogen bonds. The doublet character of the 2420 cm^{-1} band in the spectra of ethereal solutions of phenyl phenylphosphonodithioic acid is related to the existence of two forms of association, SH····S and SH····O(ether). The infra-red spectra of pure dialkyl phosphorotetrathioic acids[60] have a diffuse SH stretching band at 2435 cm^{-1}. The 2435 cm^{-1} band disappears in spectra of solutions of the acids in carbon tetrachloride and a sharp band is found at 2545 cm^{-1}. This is considered to be caused by intermolecular hydrogen bonding SH····S = P which breaks down on dilution[60].

According to cryoscopic data[25], the molecular weight of diethyl phosphorodithioate in benzene, in the range permitted by the method, does not depend on concentration and agrees with the theoretical value. This shows that even if the molecules of acid are associated at higher concentrations, this is due only to a weak interaction, which is easily destroyed by the molecules of inert solvent. The infra-red spectrum of diethyl phosphorodithioate[18,25] and also the spectra of other dialkyl phosphorodithioates[18] has a diffuse doublet with maxima at 2540 and 2475 cm^{-1}. The spectrum of the acid in acetone has bands with maxima at 2500 and 2425 cm^{-1}. The spectrum of diethyl phosphorodithioate in carbon tetrachloride under the same conditions has sharp bands at 2590 and 2565 cm^{-1}. The doublet character of the bands cannot be due to intermolecular association in this case, since the acid is monomeric[25]. It is possible that the appearance of two S−H frequencies is due to the formation of two rotational isomers, in one of which hydrogen bonding occurs with an oxygen atom of the ester groups. This is confirmed by the fact that the spectra of thiophosphorus compounds whose molecules have no oxygen atoms show only one S−H frequency in inert solvents.

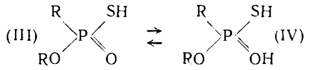
The question of structure and tautomerism of dialkyl phosphorothioates and half esters of alkyl phosphonothioic acids is closely related to the identification of P = O, P = S, O−H, and S−H groups.

The dialkyl phosphorothioates can be represented by two tautomeric forms, differing in the position of a hydrogen atom



Because of the rapid interconversion in this thiono−thiolo tautomeric system, the equilibrium cannot be studied by purely chemical means.

The tautomerism of the half esters of alkyl phosphonothioic acids is of the same type:



Kabachnik *et al.* studied the infra-red spectra of diethyl phosphorothioate[25] and a series of half esters of alkyl phosphonothioic acids[61]. In the spectra of these compounds there are no P = O and S−H bands of the thiolo isomer; instead there are intense diffuse bands with maxima in the 3100−3140 cm^{-1} region which can certainly be assigned to associated hydroxyl groups. The spectrum of diethyl phosphorothioate[46] also has a band at 618 cm^{-1} and that of ethyl hydrogen ethylphosphonothioic acid has a band at 586 cm^{-1} assigned to P = S stretching vibrations. Thus the spectra show that the favoured tautomeric forms are thiono forms (I) and (III). This aspect of thiono−thiolo tautomerism has been studied in greater detail by other methods[62−64].

Owing to the dual reactivity of salts of dialkyl hydrogen phosphorothioic and alkyl alkylphosphonothioic acids, it is not possible to draw any conclusions about the structure of the salts from the structure of the reaction products. Gore[3] studied the infra-red spectrum of crystalline potassium diethyl phosphorothioate and, on the grounds that there was no absorption in the 1200−1320 cm^{-1} region, concluded that it had a thiono structure. Kabachnik *et al.*[19,26] studied the infra-red spectra of crystalline sodium diethyl phosphorothioate and its solutions in absolute alcohol and chloroform. The spectra were similar to those of the potassium salt.

The spectra of the salts have a band in the 600−610 cm^{-1} region which is connected with the presence of a P = S group. Thus the alkali metal salts of dialkyl phosphorothioates have a similar, evidently thiono, structure.

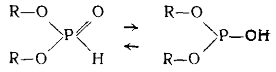
The infra-red spectra of the solid sodium salts of half esters of alkylphosphonothioic acids[21] and their solutions in absolute alcohol also show appreciable absorption in the 1200–1300 cm^{-1} region, which may be taken as evidence of the absence of the P=O bond. Further, a band at 580 cm^{-1} confirms their thiono structure. The structure of the salts of monothio acids of phosphorus has not yet been adequately studied.

Kabachnik and Mastryukova[65] showed that alkylation of the sodium and potassium salts of dialkyl phosphorothionic acids with ethyl bromide yielded thiolo derivatives. Hoegberg and Cassaday[66] came to the same conclusion from a study of the infra-red spectra of alkylation products. The alkylation products of the sodium salts of the half esters of alkylphosphonothioic acids also have a thiolo structure[20,21]. The spectra of these compounds have intense absorption bands in the 1215–1225 cm^{-1} region which are undoubtedly associated with P=O stretching vibrations. The products of acylation of sodium diethyl phosphate with acetyl chloride and propionyl chloride[19] do not absorb in the 1200–1300 cm^{-1} region. This establishes that they are thiono derivatives, *i.e.* acylation, in contrast to alkylation, proceeds without transfer of the reaction centre.

6. The P–H Group

The frequency of the P–H stretching vibration in liquid phosphine is[67] 2306 cm^{-1}. The Raman spectra of six dialkyl hydrogen phosphites, studied by Arbuzov *et al.*[1] have, in this region, an extremely intense broad band, the centre of which is at practically the same frequency near 2435 cm^{-1}. The authors assigned this band at 2435 cm^{-1} to the P–H stretching vibration and ascribed its somewhat diffuse nature to strong intermolecular interaction of the type P–H····O. Meyrick and Thompson[2] showed that the P–H stretching vibration in infra-red spectra is associated with a band of medium intensity at 2435 cm^{-1}. Daasch and Smith[4] studied the infra-red spectra of $C_6H_5(OH)P(O)H$, $CH_3C_6H_4(OH)P(O)H$, $C_2H_5C_6H_4(OH)P(O)H$, $C_{10}H_7(OH)P(O)H$, $C_6H_5(C_2H_5O)P(O)H$, $(C_2H_5O)_2P(O)H$, $(C_4H_9O)_2P(O)H$, and found the P–H frequencies to be in the 2350–2440 cm^{-1} region. This assignment is confirmed by the fact that when hydrogen in the P–H group is replaced by deuterium, the band at 2381 cm^{-1} in the spectrum of phenylphosphonous‡ acid disappears and a new one appears at 1750 cm^{-1}, which can without doubt be assigned to P–D stretching vibrations. According to Simon and Feher[68] the Raman spectra of the alkali salts of phosphorous acid have the P–H stretching vibration at 2396 cm^{-1}. In a study of isotopic substitution in phosphorous acid in acid solution, Simon and Schulze[69] observed in the Raman spectra a diminution of intensity of the P–H band at 2485 cm^{-1} and an increase in intensity of the P–D band at 1744 cm^{-1}. In two months the intensity of both bands became equal. In the Raman spectrum[26] of $(C_2H_5O)_2P(S)H$ the P–H stretching vibration frequency is 2407 cm^{-1}; in the infra-red spectrum[70] of $(C_6H_5O)_2P(O)H$ it is 2420 cm^{-1}. Miller *et al.*[8], in an analysis of the infra-red spectra of a number of dialkylphosphinic acids, noted that the P–H stretching vibration frequency was sensitive to the nature of the substituent at the phosphorus atom and to the electronic state of the phosphoryl group. The authors made an unsuccessful attempt to relate P–H frequencies to the so-called "shift constants" obtained by Bell *et al.*[6] Houalla and Wolf[71] quote data on the integral intensities of the P–H stretching absorption bands for a number of dialkyl hydrogen phosphites. Because the intensities were close in value, in the range 0.6–0.7 × 10^4 mole^{-1} cm^{-2}, they concluded that the P–H bonds in the compounds studied were identical in nature. On considerable dilution, the P–H frequencies are enhanced by only 10–15 cm^{-1} compared to the pure liquids. This indicates the low capacity of the hydrogen atom in a P–H bond for hydrogen bonding.

The question of structure and tautomerism of organic derivatives of phosphorous acid is closely linked to the identification of the P–H group. Dialkyl hydrogen phosphites may be depicted in two tautomeric forms, in one of which phosphorus is pentavalent (I) and in the other, trivalent (II)


(I) (II)

In the work of Arbuzov *et al.*[1], mentioned earlier, Raman spectra were used to establish the structures of dialkyl hydrogen phosphites. The P–H and P=O stretching vibration frequencies found by the authors in spectra of the liquid compounds confirmed that these compounds had a structure based on pentavalent phosphorus. In addition, narrow weak bands at 3150 cm^{-1} were found in the spectra of dipropyl and dibutyl hydrogen phosphites, which were assigned to stretching vibrations of associated OH groups in molecules containing a trivalent phosphorus atom. The authors thus concluded that dialkyl hydrogen phosphites existed in two tautomeric forms, the equilibrium being displaced towards form I.

Later Meyrick and Thompson[2] studied the Raman and infra-red spectra of dimethyl, diethyl, and di-isopropyl hydrogen phosphites. The spectra contained only bands specific for form I and the compounds studied were assigned structures based on pentavalent phosphorus.

Daasch[72] studied the infra-red spectra of liquid and crystalline dialkyl hydrogen phosphites and their solutions in dioxan and triethylamine. When the temperature, state of aggregation, and medium were changed, no absorption bands were observed in the spectra of diethyl, dibutyl, and di-iso-octyl hydrogen phosphites that could be associated with the formation of OH groups, which would have indicated the marked displacement of the tautomeric equilibrium towards form II. Baudler[73] came to the same conclusion in a study of the Raman spectra of dialkyl hydrogen phosphites (R = CH_3, C_2H_5, C_3H_7, and C_4H_9).

Thus, from the results of spectroscopic studies it may be considered as established that the position of tautomeric equilibrium of dialkyl hydrogen phosphites is strongly displaced towards the form containing a pentavalent phosphorus atom. Only in the work of Arbuzov *et al.*[1] were bands found in the spectra of dialkyl hydrogen phosphites that could be ascribed to vibrations of molecules of form II. However, these results have not been confirmed by later investigations.

Some interesting results, confirming the presence of a tautomeric equilibrium of the type I ⇌ II in phosphonites, have recently been published by Griffiths and Burg[74]. The infra-red spectrum of ditrifluoromethylphosphonous acid

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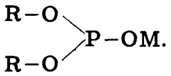
‡ The term alkyl phosphonous acid has been used in the translation since it is closest to the original Russian nomenclature, although these compounds are probably better described as alkyl phosphinic acids (Ed. of Translation).

had no P=O and P−H absorption band corresponding to a molecule based on pentavalent phosphorus, but did have an intense band at 3620 cm^{-1}, assigned to the free stretching vibrations of the hydroxyl groups of the form $(CF_3)_2P-OH$. This shows that, when a strong electron-acceptor substituent is introduced into the molecule, the tautomeric equilibrium shifts towards the form containing trivalent phosphorus (II).

Numerous chemical investigations show that dialkyl hydrogen phosphites do not, in most cases, display properties characteristic of trivalent phosphorus compounds. The chemical properties of diphenyl hydrogen phosphite, studied by Kabachnik and Polikarpov[70], on the other hand, definitely testify to the presence of an appreciable quantity of form II in equilibrium with form I. However, the infra-red spectra of diphenyl hydrogen phosphite, studied by the same authors, favour the structure with the pentavalent phosphorus atom. It should be borne in mind that the absence of a band characteristic of molecules of the other form does not mean the complete absence of a tautomeric equilibrium but only that the concentration of that form is less than a few parts per cent.

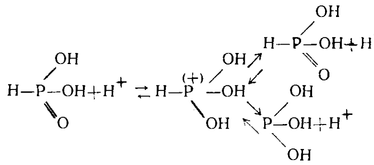
The structure of salts of dialkyl hydrogen phosphites is of some interest. Daasch[72] studied the infra-red spectra of the following dialkyl phosphite salts: $(C_2H_5O)_2PONa$, $(C_2H_5O)_2POAg$, $(C_4H_9O)_2PONa$, $(C_4H_9O)_2POAg$, and $(C_4H_9O)_2POK$ in the crystalline state and in cyclohexane solution. The spectra of the salts of different metals are very similar and differ considerably from the spectra of the corresponding dialkyl hydrogen phosphites. They have no P=O stretching vibration bands. This establishes that they are derivatives of trivalent phosphorus:



$$\begin{matrix}R-O\\R-O\end{matrix}\!\!>\!P-OM.$$

The covalent structure of the salts studied by Daasch is supported by their solubility in non-polar solvents (limited, it is true, but quite sufficient for obtaining infra-red spectra). Daasch's conclusion concerning the structure of dialkyl phosphite salts cannot, however, be extended to salts of other acids derived from tervalent phosphorus. Thus, the infra-red spectrum of the sodium salt of trifluoromethylphosphonous acid, obtained by Bennett, Emeléus, and Haszeldine[75] corresponds completely to the formula $CF_3P(O)H(ONa)$ [*i.e.* sodium trifluoromethylphosphinate (Ed. of Translation)] and is inconsistent with $CF_3P(OH)(ONa)$. The spectrum contains bands at 2381 cm^{-1} and 1242 cm^{-1}, associated with P−H and P=O stretching vibrations. Salts of phosphorous acid itself apparently also have a structure based on pentavalent phosphorus. Simon and Schulze[69] made a detailed study of the structure of the barium salt of phosphorous acid. After prolonged exposure, the Raman spectrum of solid $BaHPO_3$ contained a P−H stretching vibration band. Earlier, Simon and Feher[68] obtained Raman spectra of the alkali salts of phosphorous acid. They also found P−H frequencies in the spectra of KH_2PO_3 (2396 cm^{-1}) and K_2HPO_3 (2314 cm^{-1}). From a study of the spectra of the alkali salts of phosphorous acid in crystalline form and in aqueous solutions, Tsuboi[76] also concluded that P−H bonds were present in the salt molecules. The author assigned frequencies to vibrations of PO_3 groups and the P−H anion, having C_{3v} symmetry.

Simon and Schulze[69] studied the tautomerism of phosphorous acid. Raman spectra of H_3PO_3 in alkaline and in acid solutions were identical. The spectrum of an alkaline solution of H_3PO_3 in heavy water, recorded two months after the solution was prepared, had no P−D stretching vibration bands. In acid solution, the P−D band appears within 24 h from the preparation of the solution, and after two months the P−D and P−H bands are of equal intensity. The isotopic exchange takes place only in an acid medium; it is catalysed by H$^+$ and apparently proceeds according to the following scheme:



The authors suggest that both tautomeric forms of H_3PO_3 exist but that the concentration of the form $P(OH)_3$ is negligible.

7. The P−O−P, P−X and Other Groups

In the literature on the vibrational spectra of phosphorus compounds many other experimental assignments are discussed and attempts are often made to find a characteristic frequency for each bond in the molecule. Since this is not possible in principle, the assignments by many authors are extremely nominal and have a limited applicability.

Bergmann *et al.*[14] studied the infra-red spectra of tetramethyl, tetraethyl, and tetraisopropyl pyrophosphate and compared them with the spectra of the appropriate phosphates. Merely on the grounds that the spectra of the pyrophosphates contained bands at 970, 939, and 950 cm^{-1} respectively, which were not found in the spectra of the phosphates, the authors assigned these bands to asymmetric vibrations of the P−O−P group, in spite of the fact that phosphates also have intense absorption bands in this region. For example, the spectrum of tri-isopropyl phosphate has bands at 995 and 931 cm^{-1} and that of triethyl phosphate has one at 974 cm^{-1}. Holmstedt and Larsson[13], having evidently found no substantial difference in the infra-red spectra of phosphates and pyrophosphates in the 930−970 cm^{-1} region, proposed that the vibration of the pyrophosphate P−O group appears in the 700 cm^{-1} region. Their assignments too are insufficiently well founded, since they were obtained from the spectra of only two compounds. Other conclusions[10,15,18] concerning the characteristic nature of vibrations of the pyrophosphate group are also open to doubt.

Authentic characteristic frequencies of the P−C bond in the spectra of aliphatic compounds have not been established. Daasch and Smith[4] associate the vibration of the group with absorption in the 650−760 cm^{-1} region. However, many organophosphorus compounds that have no P−C group absorb in this region. Daasch and Smith[4] also obtained the spectra of a large number of phosphorus-containing aromatic compounds with the P−C (aryl) group. In all cases sharp bands of medium intensity were found in the 1435−1450 and 995−1005 cm^{-1} regions. These bands were assigned to vibrations of the $P-C_6H_5$ bond, but the authors point out that they could with equal justification be ascribed to vibrations of the benzene ring.

Phosphorus trichloride[77] has two absorption bands, 488 and 511 cm^{-1}, which correspond to P−Cl stretching vibrations. The spectrum of $POCl_3$ [3,4,37] similarly has two bands at 486 and 582 cm^{-1}; that of $PSCl_3$ [3,26,87] has two at 430 and 540 cm^{-1}, corresponding to the symmetrical and doubly degenerate P−Cl vibrations. Daasch and Smith[4] studied the infra-red spectra of seven other organophosphorus compounds containing the P–Cl group. The spectra of molecules containing two atoms of chlorine had bands in the 433–500 and 500–572 cm^{-1} regions. The spectrum of diphenylchlorophosphine oxide, as would be expected, has only one band in this region at 521 cm^{-1}. Bands corresponding to P–Cl stretching vibrations are usually very intense in both infra-red and Raman spectra. Daasch and Smith also studied the infra-red spectra of six fluorine-containing phosphorus compounds and made a tentative assignment of the P–F stretching vibrations in pentavalent phosphorus compounds to the 850–900 cm^{-1} region and in tervalent phosphorus compounds to the 750–900 cm^{-1} region. Other authors[5,79] give an analysis of the infra-red spectra of PF_3 (bands at 892 cm^{-1} and 860 cm^{-1} are assigned to symmetrical and asymmetrical P–F vibrations), PF_5, and POF_3.

The spectra of compounds with P–Br and P–I bonds have not received much study. The P–Br stretching vibration frequencies[77] in PBr_3 are 380 and 400 cm^{-1}, in $POBr_3$ 340 and 488 cm^{-1}, and in $PSBr_3$ [40,24] 299 and 438 cm^{-1}. Baudler[16] obtained the Raman spectra of $(C_6H_5O)PBr_2$ and $(C_6H_5O)_2PBr$. Very intense bands in the 370 and 410 cm^{-1} region were assigned to the P–Br stretching vibration.

Calculation of the normal vibrations of the molecules $POCl_3$, $POBr_3$, $PSCl_3$, and $PSBr_3$ [22,24] confirms the experimental assignments of frequencies to P–X (X = = halogen) bonds. The values of these frequencies are determined mainly by the P–X force constants. Determination of the sensitivity of frequency to isotopic variations in the mass of the chlorine atoms[24] shows that, in the molecules $POCl_3$ and $PSCl_3$, the frequencies of symmetrical vibration with ^{37}Cl atoms should be ~10 cm^{-1} less and those of asymmetric vibration ~5 cm^{-1} greater than with ^{35}Cl atoms.

The assignment of frequencies to other bonds and groups is also discussed in the literature. Thus, attempts have been made to find characteristic frequencies for the stretching vibrations of P–S,[18] P–S–P,[18] P–N,[11,13] the deformation vibrations of H–P=O, O–P–O, etc.[16,73] The data concerning these groups are not very reliable and cannot as yet be applied.

Thus, a large quantity of experimental data has been accumulated on the vibrational spectra of organophosphorus compounds, and has formed the basis of many assignments of frequencies to various groups. In some cases, the experimental data have been examined theoretically; this has made possible the interpretation of the changes occurring in the spectra between one molecule and another.

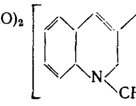
APPENDIX

In this section of the review are listed the phosphorus compounds whose vibrational spectra has been published up to the middle of 1960.

The substances are divided into four groups, *viz.* organic phosphates, compounds containing a carbon-phosphorus bond, phosphites, and certain inorganic phosphorus compounds whose spectra could be of some interest in a study of organic phosphorus compounds. After the formula of the compound the literature reference is given and an indication of the type of spectrum studied (infra-red spectrum IR, Raman spectrum R). [*i*- stands for iso-, as in the original Russian text (Ed. of Translation)].

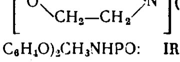
Phosphates

$(CH_3O)_3PO$: IR^{4,14,17}, R^{1,16}; $(C_2H_5O)_3PO$: IR^{3,10,14,17}, R$^{1,16,26\ 45}$; $(C_3H_7O)_3PO$: IR^{14}, R^{1}; $(i\text{-}C_3H_7O)_3PO$: IR^{14}, R^{80}; $(C_4H_9O)_3PO$: IR^{10,14,81,82}, R^{1,16}; $i\text{-}C_4H_9O)_3PO$: R^{1}; $(C_4H_9CH(C_2H_5)CH_2O)_3PO$: IR^{11,12}; $(cyclo\text{-}C_6H_{11}O)_3PO$, $(p\text{-}NO_2C_6H_4CH_2O)_3PO$, $(C_4H_9CH(C_2H_5)CH_2O)(C_2H_5O)_2PO$, $(C_4H_9CH(C_2H_5)CH_2O)_2(C_2H_5O)PO$: IR^{11}; $(C_{18}H_{37}O)_3PO$: IR^{12}; $(CH_3O)_2P(O)OCH{=}CCl_2$: IR^{83}, $(CH_2Cl{-}CH_2O)_3PO$: IR^{10}; $(C_2H_5O)_2P(O)OCH{=}CCl_2$: IR^{84}; $(C_2H_5O)_2P(O)OCCl{=}CCl_2$: IR^{85}; $(C_6H_5O)(C_2H_5O)_2PO$: IR^{3,10}; $(p\text{-}CH_3C_6H_4O)(C_2H_5O)_2PO$: IR^{3}; $(p\text{-}NO_2C_6H_4O)_2(C_2H_5O)PO$: IR^{3,10,86}, R^{86}; $[(p\text{-}COONa)C_6H_4O](C_6H_5O)_2PO$, $[(m\text{-}COONa)C_6H_4O](C_2H_5O)_2PO$, $(CH_3O)_2$ $m\text{-}[N(CH_3)_3{}^+]C_6H_4OPO$, $(C_2H_5O)_2[m\text{-}C(O)OC_6H_4CH_2]C_6H_4OPO$: IR^{57}; $(C_2H_5O)_2p\text{-}$ $\text{-}(C_2H_5C_6H_{12}C_6H_4OPO$: IR^{11}; $(C_2H_5O)_2(o\text{-}NO_2C_6H_4O)PO$, IR^{3}; $(C_2H_5O)_2(p\text{-}ClC_6H_4O)PO$,

$(C_2H_5O)_2$  PO: IR^{57};

$(i\text{-}C_4H_9O)_2(p\text{-}C_4H_9CH(C_2H_5)CH_2{-}C_6H_4O)PO$: IR^{11}; $(CH_3O)(p\text{-}NO_2C_6H_4O)_2PO$, IR^{57}; $(C_2H_5O)(C_6H_5O)_2PO$: IR^{10}; $(C_2H_5O)(p\text{-}NO_2C_6H_4O)_2PO$: IR^{57}; $(C_6H_5O)_3PO$: IR^{4,10,17,82,87} $(p\text{-}CH_3C_6H_4O)_3PO$, $(m\text{-}CH_3C_6H_4O)_3PO$: IR^{10,87}; $(o\text{-}CH_3C_6H_4O)_3PO$: IR^{10}; $(p\text{-}NO_2C_6H_4O)_3PO$: IR^{57}; $(CH_3O)(C_2H_5O)POOH$: IR^{4}; $(C_2H_5O)_2POOH$: IR^{9,26,57} $(i\text{-}C_3H_7O)_2POOH$: IR^{80}, R^{80}: $(C_4H_9O)_2POOH$, $(i\text{-}C_4H_9O)_2POOH$, $(C_5H_{11}O)_2POOH$, $(i\text{-}C_5H_{11}O)_2POOH$, $(C_6H_5CH_2)_2POOH$, $(C_4H_9CH(C_2H_5)CH_2O)_2POOH$: IR^{12}; $[(CH_3)_3CCH(CH_3)C_2H_4O]_2POOH$: IR^{11}; $(C_6H_5O)_2POOH$, $[p\text{-}CH_3C(CH_3)_2CH_2C(CH_3)_2{-}C_6H_4O]_2POOH$: IR^{30,31}; $(p\text{-}C_8H_{17}{-}$ ${-}C_6H_4O)_2POOH$: IR^{12}; $(NO_2C_4H_8O)_2POOH$: IR^{30,31}, $(CH_3O)_2PO_2Na$, $(CH_3O)_2PO_2K$, $(CH_3O)_2PO_2Ag$, $[(CH_3O)PO_2]_2Ba$, $(CH_3O)_2PO_2\overset{+}{N}H_3C_6H_{11}$, $(C_2H_5O)_2PO_2Na$, $(C_2H_5O)_2PO_2K$, $(C_2H_5O)_2PO_2Ag$, $[(C_2H_5O)_2PO_2]_2Ba$, $(C_2H_5O)_2PO_2\overset{+}{N}H_3C_6H_{11}$: IR^{88}; $(i\text{-}C_3H_7O)_2PO_2Na$: IR^{35,68}; $(i\text{-}C_3H_7O)PO_2K$, $(i\text{-}C_3H_7O)_2PO_2Ag$, $[(i\text{-}C_3H_7O)_2PO_2]Ba$, $(i\text{-}C_3H_7O)_2PO_2\overset{+}{N}H_3C_6H_{11}$: IR^{88}; $(C_4H_9O)_2PO_2Li$, $(C_4H_9O)_2PO_2Na$: IR^{89}; $(C_4H_9O)_2PO_2Ag$: IR^{12,89}; $[(C_4H_9O)_2PO_2]_2Ba$, $[(C_4H_9O)_2PO_2]_2Mn$, $[(C_4H_9O)_2PO_2]_2Cu$, $(C_4H_9O)_2PO_2Ni$, $[(C_4H_9O)_2PO_2]_2Pb$, $[(C_4H_9O)_2PO_2]_2Hg$, $(C_4H_9O)_2PO_2Hg$, $[(C_4H_9O)_2PO_2]_3La$, $[(C_4H_9O)_2PO_2]_3Y$, $[(C_4H_9O)_2]PO_2]_3Ce$, $[(C_4H_9O)_2PO_2]_4Ce$, $[(C_4H_9O)_2PO_2]_3Fe$, $[(C_4H_9O)_2PO_2]_3Bi$, $[(C_4H_9O)_2PO_2]_4Zr$, $[(C_4H_9O)_2PO_2]_6U$: IR^{89}; $[(i\text{-}(C_4H_9O)_2PO_2]Pb$, $[(i\text{-}C_5H_{11}O)_2PO_2]_2Pb$; $[C_4H_9CH(C_2H_5)CH_2O]_2PO_2Ag$: IR^{11}; $(C_6H_5CH_2O)PO_2Ag$: IR^{11,12}; $[(C_6H_5CH_2O)_2PO_2]_2Pb$: IR^{12}; $(C_6H_5O)_2PO_2Ag$, $(C_6H_5O)PO_3Ag_2$: IR^{11}; $[(p\text{-}NO_2C_6H_4O)_2PO_2]_2Pb$, $(C_6H_5O)PO_3Pb$, $[(p\text{-}C_8H_{17}\cdot C_6H_4O)_2PO_2]_2Pb$: IR^{12}; $(2,4,6\text{-}Cl_3C_6H_2O)_2PO_2Ag$: IR^{12}; $CH_3C(O)OPO_3Li_2$: IR^{57}; $(CH_3O)_2P(O)OP(O)(OCH_3)_2$: IR^{4,14}, R^{90}: $(C_2H_5O)_2P(O)OP(O)(OC_2H_5)_2$: IR^{4,13,14,18}, R^{90}; $(C_3H_7O)_2P(O)OP(O)(OC_2H_5)_2$ IR^{14,18}; $(i\text{-}C_3H_7O)_2P(O)OP(O)(Oi\text{-}C_3H_7)_2$: IR^{14}; $(C_4H_9O)_2P(O)OP(O)(OC_4H_9)_2$, IR^{4,14}: $(C_6H_5CH_2O)_2P(O)OP(O)(OCH_2C_6H_5)_2$: IR^{11}; $(CH_3O)_2POF$: IR^{4}; $(CH_3O)_2POCl$: IR^{18}; R^{16}; $(C_2H_5O)_2POCl$: IR^{3,4,10,13,18}, R^{16}; $(C_2H_5O)_2POCN$: IR^{18}; $(C_3H_7O)_2POCl$: IR^{18}, R^{16}; $(i\text{-}C_3H_7O)_2PO$: IR^{38,80}, R^{38,80}; $(i\text{-}C_3H_7O)_2POCl$: IR^{18,80}, R^{80}; $(CH_3O)_2P(O)P(O)(CH_3O)_3$: R^{91}; $(C_6H_5O)_2P(O)P(O)(OC_6H_5)_2$: IR^{92}, R^{92}; $(C_2H_5O)_2P(O)SCH_3$: IR^{19}; $(C_2H_5O)_2P(O)SC_2H_5$: IR^{3,18,57}, R^{26,45}; $(C_2H_5O)_2P(O)SC_5H_{11}$: IR^{3}; $(C_2H_5O)_2P(O)SCH_2CH_2SC_2H_5$: IR^{27}, R^{26}; $(C_2H_5O)_2P(O)SCH_2C_6H_5$: IR^{19}; $(C_2H_5O)_2P(O)SC_6H_5$, IR^{3}; $(C_2H_5O)_2P(O)SC(O)OCH_3$: IR^{19}; $(C_4H_9O)_2P(O)Si(CH_3)_3$: IR^{93}; $(C_6H_5O)_2POCl$: IR^{10}, R^{16}; $(C_6H_5O)POCl_2$; IR^{10}. R^{58}; $(C_2H_5S)POCl_2$: IR^{26}; $(C_3H_7S)POCl_2$, $(C_4H_9S)POCl_2$: IR^{38}; $(C_2H_5S)_2(O)OC_2H_5$: IR^{3}; $(C_2H_5S)_2POCl$: R^{26}; $(C_2H_5S)_3PO$: IR^{18,87}; $(CH_3O)_3PS$: IR^{4}; $(C_2H_5O)_2P(S)OCH_3$: IR^{19} $(C_2H_5O)_3PS$: IR^{3,18}, R^{26,45}; $(C_2H_5O)_2P(S)OC_6H_{13}$: IR^{3}; $(C_2H_5O)_2P(S)OCH_2CH_2SC_2H_5$: IR^{27}, R^{26}; $(C_2H_5O)_2P(S)OCH_2C_6H_5$: IR^{19}: $(C_2H_5O)_2P(S)OC_6H_5(C_2H_5O)_2P(S)OC_6H_4{-}p\text{-}CH_3$: IR^{3}; $(C_2H_5O)_2P(S)OC_6H_4{-}p\text{-}NO_2$: IR^{3,10,86}, R^{86}; $(C_2H_5O)_2P(S)OC_6H_4{-}o\text{-}NO_2$: IR^{3}; $(C_2H_5O)_2P(S)OC(O)CH_3$, $(C_2H_5O)_2P(S)OC(O)C_2H_5$: IR^{19}; $(CH_3O)_2PSOH$: IR^{39}; $(C_2H_5O)_2PSOH$: IR^{18,57}; $(C_2H_5O)_2PSOK$: IR^{8}; $(C_2H_5O)_2PSONa$: IR^{19,26}; $(C_2H_5O)_2PSO\overset{+}{N}H(C_2H_5)_3$: IR^{18,38}; $(C_3H_7O)_2PSO^-\overset{+}{N}H(C_2H_5)_3$, $(C_4H_9O)_2PSO^-\overset{+}{N}H(C_2H_5)_3$: IR^{38}; $(p\text{-}NO_2C_6H_4O)_2P(S)OC_2H_5$: IR^{10,57}; $(p\text{-}NO_2C_6H_4O)_3PS$: IR^{57}; $(CH_3O)_2P(S)OP(O)(OCH_3)_2$, $(C_2H_5O)_2P(S)OP(O)(OCH_3)_2$, $(CH_3O)_2P(S)OP(O)(OCH_3)_2$: IR^{18}; $(C_2H_5O)_2P(S)OP(O)(OC_2H_5)_2$: IR^{18,26}, R^{45,90}; $(C_3H_7O)_2P(S)OP(O)(OC_3H_7)_2$: IR^{18,38}; $(C_4H_9O)_2P(S)OP(O)(OC_4H_9)_2$, $(i\text{-}C_3H_7O)_2P(S)OP(O)(Oi\text{-}C_3H_7)_2$: IR^{18}; $(C_2H_5O)_2P(S)OP(S)(OC_2H_5)_2$: IR^{18,57}; $(CH_3O)_2P(S)NHCH_3$, $(C_2H_5O)_2P(S)NHCH_3$, $(C_3H_7O)_2P(S)NHCH_3$, $(i\text{-}C_3H_7O)_2P(S)NHCH_3$, $(C_4H_9O)_2P(S)NHCH_3$; IR^{28}; $(C_2H_5O)_2P(S)N(CH_3)_2$: IR^{38,94}; $(C_2H_5O)_3P(S)N(C_2H_5)_2$, $(C_2H_5O)_2P(S)N(C_3H_7)_2$, $(C_3H_7O)_2P(S)N(C_2H_5)_2$, $(C_3H_7O)_2P(S)N(C_3H_7)_2$, $(i\text{-}C_3H_7O)_2P(S)N(C_2H_5)_2$, $(i\text{-}C_3H_7O)_2P(S)N(C_3H_7)_2$, $(i\text{-}C_3H_7O)_2P(S)N(i\text{-}O_3H_7)_2$, $(C_4H_9O)_2P(S)N(C_2H_5)_2$, $(C_4H_9O)_2P(S)N(C_3H_7)_2$, $[(C_2H_5)_2NCH_2CH_2O](C_2H_5O)P(S)N(CH_3)_2$, $[(C_2H_5)_2NCH_2CH_2O]\text{-}$ $\text{-}(C_3H_7O)P(S)N(CH_3)_2$: IR^{38}; $(CH_3O)_2PSCl$: IR^{18,26}; $(C_2H_5O)_2PSCl$: IR^{3,18,26}, R^{26}; $(C_3H_7O)_2PSCl$: IR^{18,26}; $(i\text{-}C_3H_7O)_2PSCl$: IR^{18,26,37}; $(C_4H_9C)_2PSCl$: IR^{18,26}; $CH_3O)PSCl_2$: IR^{18}; $(C_2H_5O)PSCl$; IR^{18,26,39}, R^{26}; $(C_2H_5O)(CH_3)_2NPSCl$, $(C_4H_9O)(CH_3)_2NPSCl$: IR^{33}; $(CH_3)_2NPSCl_2$: IR^{26,38}, R^{26}; $(C_2H_5)_2NPSCl_2$: IR^{38}; $(CH_3O)_2P(S)SCH_3$: IR^{18}; $(C_2H_5O)_2P(S)SC_2H_5$: IR^{18,26}, R^{26}; $(C_2H_5O)_2P(S)SC_5H_{11}$; IR^{3}; $(C_2H_5O)_2P(S)SCH_2SC_3H_7$; IR^{26}; $(C_2H_5O)_2P(S)SCH_2CH_2SC_2H_5$: IR^{26}, R^{26}; $(C_2H_5O)_2P(S)SCH_2CH_2SC_3H_7$: IR^{26}; $(C_2H_5O)_2P(S)SC_6H_5$, $(C_2H_5O)_2P(S)SC_6H_4{-}p\text{-}CH_3$: IR^{3}; $(C_2H_5O)_2P(S)SC(O)OC_5H_{11}$: IR^{9}; $(CH_3O)P(S)SH$: IR^{18,33,95}; $(C_2H_5O)_2P(S)SH$: IR^{3,18,26,38,98}, R^{26}; $(C_3H_7O)_2P(S)SH$, $(i\text{-}C_3H_7O)_2P(S)SH$, $(C_4H_9O)_2P(S)SH$: $(C_2H_5O)_2P(S)SNa$: IR^{38}; $(C_2H_5O)_2P(S)SK$; $(C_2H_5O)_2P(S)SP(S)(OC_2H_5)_2$, $(i\text{-}C_3H_7O)_2P(S)SP(S)(Oi\text{-}C_3H_7)_2$, $[(C_2H_5)_2NCH_2CH_2S]C_2H_5OP(S)N(CH_3)_2$, $[(C_2H_5)_2NCH_2CH_2S]\text{-}$ $\text{-}C_3H_7OP(S)N(CH_3)_2$, $(i\text{-}C_3H_7S)PSCl_2$; IR^{38}: $(CH_3S)_3PS$, $(C_2H_5S)_2(CH_3S)PS$: IR^{96};

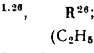
$(C_2H_5S)_3PS$: IR^{8,96}; $(C_3H_7S)_3PS$, $(i\text{-}C_3H_7S)(C_2H_5S)(CH_3S)PS$, $(i\text{-}C_3H_7S)_2(CH_3S)PS$, $(i\text{-}C_3H_7S)_3PS$, $(C_4H_9S)_3PS$: IR^{96}; $(CH_3S)_3P(S)SH$; $(CH_3S)(C_2H_5S)P(S)SH$, $(CH_3S)(C_3H_7S)P(S)SH$, $(CH_3S)(i\text{-}C_3H_7S)P(S)SH$: IR^{60}; $(CH_3O)P(O)NH_2$, $(C_2H_5O)P(O)NH_2$: IR^{13,38}; $(C_2H_5O)_2P(O)N(CH_2)_2$: IR^{94}; $(C_2H_5O)_2P(O)N(CH_3)_2$: IR^{15}; $(C_2H_5O)_2P(O)NHC(O)CH_3$: IR^{97}; $(C_2H_5O)_2P(O)NH(C_6H_5)$: IR^{10}; $(C_2H_5O)_2P(O)NCH_3(C_6H_5)$; $(C_2H_5O)_2P(O)NC_2H_5(C_6H_5)$: IR^{55}; $(C_2H_5O)_2P(O)OP(O)[N(CH_3)_2]_2$: IR^{15}; $(C_2H_5O)_2P(O)N(C_2H_5)P(O)[N(CH_3)_2]_2$, $(C_2H_5O)_2P(O)N(C_2H_5)P(O)(OC_2H_5)_2$, $(C_3H_7O)_2P(O)N(CH_2)_2$: IR^{94}; $(i\text{-}C_3H_7O)_2P(O)NH_2$, $(i\text{-}C_3H_7O)_2P(O)NHCH_3$, $(i\text{-}C_3H_7O)_2P(O)N(CH_3)_2$: IR^{80}, R^{80}; $(i\text{-}C_3H_7O)_2P(O)N(CH_2)_2$, $(i\text{-}C_3H_7O)_2P(O)N(C_2H_5)P(O)(O\,i\text{-}C_3H_7)_2$, $(i\text{-}C_3H_7O)_2P(O)N(C_2H_5)P(O)(OC_3H_7)_2$: IR^{94}; $(C_6H_5CH_2O)_2NH_2PO$, $(C_6H_5CH_2O)_2C_6H_5NHPO$, $(C_6H_5CH_2O)_2C_6H_5NCH_3PO$, $(o\text{-}C_2H_5NHC_6H_4O)(C_6H_5CH_2O)_2PO$,



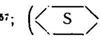
$(C_3H_5CH_2O)PO$, $(C_6H_5O)_2NH_2PO$, $(C_6H_5O)_2C_6H_5NHPO$: IR^{11}; $(p\text{-}Cl\cdot C_6H_4O)_2CH_3NHPO$: IR^{57}; $(C_6H_5CH_2O)_2C_6H_5CH_2NHPO$: IR^{11}; $(C_2H_5O)(CH_3)_2NP(O)OP(O)N(CH_3)_2(OC_2H_5)$: IR^{18}; $(C_2H_5O)(CH_3)_2NPOOH$: IR^{38}; $(CH_3)_2N]_2P(O)OP(O)[N(CH_3)_2](OC_2H_5)$: IR^{15}; $(C_2H_5O)(CH_3)_2NPOCl$: IR^{13,38}; $(C_2H_5O)(CH_3)_2NP(O)CN$: IR^{13}; $[(CH_3)_2N]_2P(O)(OC_2H_5)$: IR^{15}; $[(CH_2)_2N]_2P(O)(OC_4H_9)$: IR^{94}; $(C_6H_5O)(NH_2)_2PO$: IR^{11}; $(p\text{-}ClC_6H_4NH)NH_2P(O)OH$: IR^{98}; $(C_6H_5O)(C_6H_5NH)_2PO$: IR^{11}; $(p\text{-}ClC_6H_4O)(C_6H_5NH)_2PO$: IR^{57}; $[(CH_3)_2N]_2P(O)OP(O)[N(CH_3)_2]_2$, $(C_6H_5NH)_2POOH$, $(C_6H_5NH)_2PO_2Ag$: IR^{10}; $(CH_3)_2NPOCl_2$, $[(CH_3)_2N]_2POF$: IR^{10}; $[(CH_3)_2N]_2POCl$: IR^{15}; $[(CH_3)_2N]_3PO$, $[(C_2H_5)_2N]_3PO$: IR^{87}; $(C_2H_5O)_3PNC_6H_5$, $(C_2H_5O)_3PNC(O)CH_3$: IR^{56}; $(C_2H_5O)_2O(OH)NP(O)(OC_2H_5)_2$, $(C_2H_5O)_2P(OD)NP(O)(OC_2H_5)_2$, $(C_2H_5O)_2P(OH)NSO_2CH_3$, $(C_2H_5O)_2P(OD)NSO_2CH_3$: IR^{97}; $(C_3H_7O_3)PNC_6H_5$, $(i\text{-}C_3H_7O)_3PNC_6H_5$, $(C_4H_9O)_3PNC_6H_5$, $(C_2H_5O)_2C_6H_5NHPNC_6H_5$, $(C_3H_7O)_2C_6H_5NHPNC_6H_5$: IR^{55}; $P_3N_3Cl_6$: IR^{4,51,54}, R^{51}; $P_3N_3Cl_4[N(CH_3)_2]_2$, $P_3N_3Cl_4[N(C_2H_5)_2]_2$, $P_3N_3Cl_4[NHCH_3)_2$, $P_3N_3Cl_4(C_6H_5)_2$, $P_3H_3Cl_3[N(C_2H_5)_2]_3$, $P_3N_3Cl_2[N(CH_3)_2]_4$, $P_3N_3[N(CH_3)_2]_6$, $P_3N_3(N_2H_3)_6$, $P_3N_3Br_6$: IR^{54}; $P_3N_3(OCH_3)_6$: IR^{4,54}; $P_3N_3(OC_2H_5)_6$, $P_3N_3(OC_3H_7)_6$, $P_3N_3(O\,i\text{-}C_3H_7)_6$, $P_3N_3(OC_8H_{17})_6$: IR^{4}; $P_3N_3(CH_3)_6$: IR^{90}; $P_4N_4Cl_8$: IR^{4,51,54}, R^{51}; $P_4N_4Br_8$, $P_4N_4Cl_4(C_6H_5)_4$, $P_4N_4(OCH_3)_9$, $P_4H_4[N(CH_3)_2]_8$: IR^{54}; $P_4N_4(CH_3)_8$: IR^{99}; $(PNCl_2)_x$, $[PN(OC_2H_5)_2]_x$: IR^{4}; $[(CH_3)_3SiO]_3PO$: R^{100} $[(CH_3)_2NCH_2CH_2O](C_2H_5O)_2PO$, $[(CH_3)_2NCH_2CH_2S](C_2H_5O)_2PO$, $[(CH_3)_2NCH_2CH_2S](i\text{-}C_3H_7O)PO$, $[(CH_3)_2NCH_2CH_2O](C_2H_5O)_2PS$: IR^{50}; $[HSi(C_2H_5)_2O]P(O)(OC_2H_5)_2$, $[HSi(C_2H_5)O_2]_2(C_2H_5O)PO$, $(C_2H_5)_3SiOSi(C_2H_5)_2O](C_2H_5O)_2PO$, $[(C_2H_5)_3SiOSi(C_2H_5)_2O]_2(C_2H_5O)PO$ $[(C_2H_5)_3SiO]C_2H_5SiO.P(O)(OC_2H_5)_2$, $[(C_2H_5)_3SiO]_3SiOP(O)(OC_2H_5)_2$, $(C_2H_5O)_2P(O)OSi[OSi(C_2H_5)_3]_2$; IR^{101}.

Compounds Containing a Carbon – Phosphorus Bond

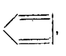
$(CH_3O)_2P(O)CH_3$: IR^{2}; $(CH_3O)_2P(O)C(O)CCl_3$: IR^{85}; $(CH_3O)_2P(O)C(OH)HCCl_3$: IR^{83}; $(CH_3O)_2P(O)CHCCl_2OP(O)(OCH_3)_2$: IR^{85}; $(C_2H_5O)_2P(O)CH_3$: IR^{2}; $(C_2H_5O)_2P(O)C_2H_5$: IR^{2,10}, R^{26}; $(C_2H_5O)_2P(O)C_4H_9$: IR^{10}; $[(C_2H_5O)_2P(O)CF_3$: IR^{38}; $(C_2H_5O)_2P(O)CCl_3$, $(C_2H_5O)_2P(O)C_6H_5$; $(C_2H_5O)_2P(O)C_6H_4\text{—}p\text{-}Cl$: IR^{4}; $(C_2H_5O)_2P(O)C(O)CH_3$: IR^{57}, R^{16}; $(C_2H_5O)_2P(O)CH_2C(O)CH_3$: IR^{102}; $(C_2H_5O)P(O)(CH)(CCH_3)_2$: IR^{57}; $(C_2H_5O)_2P(O)C(O)(CH_2)_{12}CH_3$: IR^{103}; $(C_2H_5O)_2P(O)C(O)C_6H_5$: IR^{57}; $(C_2H_5O)_2P(O)CH_2C(O)C_2H_5$, $(C_2H_5O)_2P(O)CH(CH_3)C(O)CH_3$: IR^{102}; $(C_2H_5O)_2P(O)C(OH)(CH_3)_2$, $(C_2H_5O)_2P(O)C(OH)(CH_2)_4CH_2$, $(C_2H_5O)_2P(O)CH(OH)C_6H_5$, $(C_2H_5O)_2P(O)CH(OH)C_6H_4\text{—}p\text{-}NO_2$, $(C_2H_5O)_2P(O)CH(OH)C_6H_4\text{—}3\text{-}NO_2$, $(C_2H_5O)_2P(O)CH(OH)C_6H_4\text{—}4\text{-}NO_2$, $(C_2H_5O)_2P(O)CH(OH)C_6H_4\text{—}2\text{-}Cl$: IR^{8}; $(C_3H_7O)_2P(O)CH_3$: IR^{2}; $(i\text{-}C_3H_7O)_2P(O)CH_3$: IR^{80}, R^{80}; $(i\text{-}C_3H_7O)_2P(O)C_2H_5$: IR^{2}; $(C_4H_9O)_2P(O)CH_3$, $(C_4H_9O)_2P(O)C_2H_5$: IR^{18}; $(C_4H_9O)_2P(O)C_4H_9$: IR^{4}; $(p\text{-}NO_2C_6H_4O)_2P(O)C_2H_5$: IR^{57}; $(C_2H_5O)CH_3OP(O)P(O)CH_3(OC_2H_5)$, $(C_2H_5O)C_2H_5P(O)OP(O)C_2H_5(OC_2H_5)$, $(i\text{-}C_3H_7O)CH_3P(O)OP(O)CH_3(O\,i\text{-}C_3H_7)$, $(i\text{-}C_3H_7O)C_2H_5P(O)OP(O)C_2H_5(O\,i\text{-}C_3H_7)$, $(s\text{-}C_4H_9O)CH_3P(O)OP(O)CH_3(O\,s\text{-}C_4H_9)$, $(s\text{-}C_4H_9O)C_2H_5P(O)OP(O)C_2H_5(O\,s\text{-}C_4H_9)$: IR^{15}; $CH_3OCH{=}C(POCl_2)CCl{=}CH_2$, $C_2H_5OCH{=}C(POCl_2)CCl{=}CH_2$, $C_3H_7CCH{=}C(POCl_2)CCl{=}CH_2$, $C_4H_9OCH{=}C(POCl_2).CCl{=}CH_2$: IR^{104}; $(CH_3O)_2P(O)C{\equiv}CH$, $(C_2H_5O)_2P(O)C{\equiv}CH$, $(i\text{-}C_3H_7O)_2P(O)C{\equiv}CH$: IR^{132}; $(C_2H_5O)_2P(O)CCH_3(OC_2O_5)C(O)CH_3$, $(C_2H_5O)_2P(O)CC_2H_5(OC_2H_5)C(O)C_2H_5$, $(C_2H_5O)_2P(O)CC_3H_7(OC_2H_5)C(O)C_3H_7$, $(C_2H_5O)_2P(O)CC_4H_9(OC_2H_5)C(O)C_4H_9$: R^{105}; $(C_2H_5O)C_2H_5P(O)SCH_3$: IR^{20}; $(C_2H_5O)CH_3P(O)SC_2H_5$: IR^{20,21,26}; $(C_2H_5O)C_2H_5P(O)SC_2H_5$: IR^{20,21,26}, R^{26}; $(C_2H_5O)C_3H_7P(O)SC_2H_5$, $(C_2H_5O)C_4H_9P(O)SC_2H_5$, $(C_2H_5O)CH_3P(O)SCH_2OCH_3$: IR^{21}; $(C_4H_9O)C_2H_5P(O)SC_4H_9$: IR^{20}; $[(CH_3)_3SiO]_2P(O)C_4H_9$: IR^{93}; CH_3POCl_2: IR^{18,38}; $C_2H_5POCl_2$: IR^{11,18,26}, R^{26}; **cyclo-**$C_6H_{11}POCl_2$: IR^{10}; $(C_4H_9O)C_4H_9P(O)NHC_6H_5$: IR^{55}; $(C_2H_5O)PO(CH_3)_2$: IR^{57};



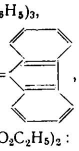
CH_3POCl: IR^{18}; $C_6H_5POCl_2$: IR^{4}; $CH_3PO(OH)_2$: R^{106}; $C_4H_9PO(OH)_2$: IR^{4}; $C_6H_5PO(OH)_2$: IR^{4,11}; $C_6H_5PO(OD)_2$, $p\text{-}ClC_6H_4PO(OH)_2$: IR^{4}; $(C_6H_5CH_2)NH_2PO(OH)$: IR^{11}; $CH_3PO_3Na_2$: R^{106}; $(C_6H_5O)NH_2C_6H_4PO_2Ag$: IR^{11};



CH_3PO_2Na: IR^{18}; $CF_3PO(OH)(ONa)$, $CF_3PO_3Na_2$: IR^{75}; $CH_3PO_3Na_2\cdot 6H_2O$: IR^{107}; $CH_3PO_3K_2$: IR^{106}; CH_3PO_3Ag, CH_3PO_3Mg, CH_3PO_3Ba, $CH_3PO_3Ca\cdot 2H_2O$, $CH_3PO_3Sr.2H_2O$, CH_3PO_3Pb: IR^{107}; $C_4H_9PO_2(OH)^{+}NH_3C_6H_5$: IR^{93}; $(CH_3)_2PO(OH)$: IR^{57,106}; $(C_6H_5)_2PO(OH)$, $(C_6H_5CH_2)_2PO(OH)$, $(2,4,6\text{-}Cl_3C_6H_2)_2PO(OH)$, $(p\text{-}CH_3C_6H_4)C_2H_5PO(OH)$, $(p\text{-}NO_2\text{—}C_6H_4)_2PO(OH)$, $(o\text{-}CH_3O\text{—}C_6H_4)_2PO(OH)$: IR^{10}; $(CH_3)_2PO_2Li$: IR^{107}; $(CH_3)_2PO_2Na$: IR^{106,107}; $(CH_3)_2PO_2K$: IR^{106}; $(CH_3)_2PO_2K.xH_2O$, $[(CH_3)_2PO_2]Ca.xH_2O$, $[(CH_3)_2PO_2]Sr.xH_2O$; $[(CH_3)_2PO_2]Ba.xH_2O$: IR^{107}; $(C_6H_5)_2POCl$: IR^{4}; $(CH_3)_3PO$: IR^{4,7,108}, R^{35}; $(CH_3)_3PO(+SbCl_5)$, $(CH_3)_3PO(+POCl_3+SbCl_5)$: R^{35}; $(C_2H_5)_3PO$: IR^{46}; $(m\text{-}CH_3\text{—}C_6H_4CH_2)_3PO$: IR^{3}; $(o\text{-}CH_3\text{—}C_6H_4)_3PO$: IR^{87}; $(C_6H_5CH_2)_2P(O)CH(OH)C_6H_4\text{—}2\text{-}Cl$, $(C_6H_5CH_2)_2P(O)C(OH)(CH_3)_2$, $(C_6H_5CH_2)_2P(O)CH(OH)CH(CH_3)_2$, $(C_6H_5CH_2)_2P(O)C(OH)(CH_3)C_2H_5$, $(C_6H_5CH_2)_2P(O)CH(OH)C_3H_7$, $(C_8H_{17})_2P(O)CH(OH).C_6H_4\text{—}2Cl$, $(C_8H_{17})_2P(O)CH(OH)C_6H_4\text{—}2\text{-}NO_2$, $(C_8H_{17})_2P(O)CH(OH)C_6H_5$, $(C_8H_{17})_2P(O)C(OH)(CH_2)_4CH_2$, $(C_8H_{17})_2P(O)C(OH)(CH_3)_2$: IR^{8}; $(C_6H_5)_3PO$: IR^{4,7,23,33,82,109}; $(C_6H_5)_3PO^{18}$: IR^{34}; $(C_6H_5)_3PO$ (+ **chloronil**): IR^{110}; $[(C_6H_5)_3PO]_2SnCl_4$, $[(C_6H_5)_3PO]_2SnBr_4$, $[(C_6H_5)_3PO]_2TiCl_4$, $[(C_6H_5)_3PO]_2.FeBr_2$: IR^{38}; $(p\text{-}CH_3\text{—}C_6H_5)_3PO$: IR^{3}; $(o\text{-}NO_2\text{—}C_6H_4)_3PO$: IR^{57}; $C_6H_5P(O)(NHNHC_6H_5)_2$: IR^{4}; $(CH_3O)(C_2H_5O)P(S)C_2H_5$: IR^{20}; $(C_2H_5O)_2P(S)CH_3$: IR^{20,21,38}; $(C_2H_5O)_2P(S)C_2H_5$: IR^{20,26,38}, R^{26}; $(i\text{-}C_3H_7O)_2P(S)CH_3$: IR^{18,38}; $(C_4H_9O)_2P(S)C_2H_5$: IR^{20}; $(C_2H_5O)[CH_3C(O)O]P(S)C_2H_5$: IR^{21}; $(C_2H_5O)CH_3PS(OH)$, $(C_2H_5O)C_2H_5PS(OH)$, $(C_2H_5O)C_3H_7PS(OH)$, $(C_2H_5O)C_4H_9PS(CH)$: IR^{20}; $(C_2H_5O)CH_3PS(ONa)$, $(C_2H_5O)C_2H_5PS(ONa)$: IR^{21,28}; $(C_2H_5O)C_3H_7PS(ONa)$, $(C_2H_5O)C_4H_9PS(ONa)$: IR^{21}; $(C_2H_5O)CH_3PSO^{+}NH(C_2H_5)_3$, $(C_2H_5O)CF_3PS(ONa)$: IR^{38}; $(i\text{-}C_3H_7O)CH_3P(S)OP(O)CH_3(O\,i\text{-}C_3H_7)$: IR^{19}; $(CH_3O)CH_3PSCl$, $(C_2H_5O)CH_3PSCl$: IR^{26}; $(i\text{-}C_3H_7O)CH_3PSCl$: IR^{18,38}; CH_3PSCl_2: IR^{18,26,38}, R^{28}; $C_2H_5PSCl_2$: IR^{38,46,26}; $C_3H_7PSCl_2$: IR^{26,38}; $i\text{-}C_3H_7PSCl_2$, $C_4H_9PSCl_2$: IR^{38}; $C_6H_5PSCl_2$: IR^{3,4}; $C_6H_5PS[N(CH_3)_2]_2$, $C_6H_5PS[N(C_2H_5)_2]_2$, $C_6H_5PS[N(i\text{-}C_3H_7)_2]_2$, $C_6H_5PS[N(C_4H_9)_2]_2$, $C_6H_5PS[N(C_{10}H_{21})_2]_2$: IR^{4}; $(C_2H_5)CH_3PS(OH)$, $(C_2H_5)CF_3PS(OH)$, $(CH_3CHFCH_2)CH_3PS(OH)$, $(FH_2C\text{—}C_2H_4)CH_3PS(OH)$, $(C_2H_5)CH_3PSCl$, (**cyclo-**$C_6H_{11})CH_3PSCl$, $(FH_2CCH_2)CH_3PSCl$, $(FH_2CC_2H_4)CH_3PSCl$: IR^{38}; $(i\text{-}C_3H_7O)CH_3P(S)OCH_3P(S)OCH_3P(S)(O\,i\text{-}C_3H_7)$: IR^{18}; $(C_3H_7O)CH_3P(S)OCH_3P(S)OCH_3P(O)(OC_3H_7)$: IR^{33}; $[(CH_3)_2NCH_2CH_2O](C_2H_5O)CH_3PO$, $(CH_3)_2NCH_2CH_2S](C_2H_5O)CH_3PO$: IR^{50}; $(C_2H_5)_2PS(SH)$, $(C_6H_5)_2PS(SH)$: IR^{59}; $(CH_3)_4P_2S_2$: IR^{57,111}; $(C_2H_5)_4P_2S_2$, $(C_3H_7)_4P_2S_2$, $(C_4H_9)_4P_2S_2$, $(i\text{-}C_4H_9)_4P_2S_2$: IR^{111}; $(CH_3)_3PS$, $(C_2H_5)_3PS$: IR^{46}; $(C_2H_5O)CH_3P(O)N(CH_3)_2$, $(C_2H_5O)CH_3P(O)N(C_2H_5)_2$: IR^{15}; $(C_2H_5O)CH_3P(O)NHC(O)CH_3$, $(C_2H_5O)C_2H_5P(O)NHC(O)CH_3$: IR^{97}; $(C_3H_7O)CH_3P(O)N(CH_3)_2$, $(i\text{-}C_3H_7O)CH_3P(O)N(CH_3)_2$, $(C_4H_9O)CH_3P(O)N(CH_3)_2$, $[(CH_3)_2N]_2CH_3PO$, $[(C_2H_5)_2N]_2CH_3PO$: IR^{15}; $(C_6H_5NH)_2C_6H_5PO$: IR^{4}; $(C_3H_7O)_2C_2H_5PNC_6H_5$, $(i\text{-}C_3H_7O)_2CH_3PNC_3H_5$, $(C_4H_9O)_2CH_3PNC_6H_5$, $(C_4H_9O)_2C_2H_5PNC_6H_5$, $(C_4H_9O)_2C_3H_7PNC_6H_5$, $(C_4H_9O)_2C_4H_9PNC_6H_5$, $(C_2H_5O)_2C_6H_5PNC_6H_5$, $(C_3H_7O)_2C_6H_5PNC_6H_5$: IR^{55}; $p\text{-}CH_3OC_6H_4NP(C_6H_5)_3$, $p\text{-}Cl\text{—}C_6H_4NP(C_6H_5)_3$, $C_6H_5NP(C_6H_5)_3$, $p\text{-}CH_3C_6H_4NP(C_6H_5)_3$, $p\text{-}CO_2C_2H_5\text{—}C_6H_4NP(C_6H_5)_3$, $p\text{-}NO_2C_6H_4NP(C_6H_5)_3$, $p\text{-}CN\text{—}C_6H_4NP(C_6H_5)_3$, $(C_6H_5)_3P=$



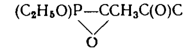
, $(C_6H_5)_3P=$



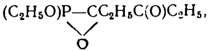
, $(C_6H_5)_3PC(SO_2C_6H_5)_2$, $(C_6H_5)_3PC(CN)_2$, $(C_6H_5)_3PC(CN)CO_2CH_3$, $(C_6H_5)_3PC(CO_2C_2H_5)_2$: IR^{55a}.

Phosphites

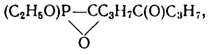
$(CH_3O)_3P$: IR^{2}, R^{16}; $(C_2H_5O)_3P$: IR^{2,3,4,10}, R^{16}; $(i\text{-}C_3H_7C)_3P$: IR^{2,112}; $(C_4H_9O)_3P$: IR^{4}; $(C_2H_5O)_2[C_4H_9\text{—}CH(C_2H_5)CH_2O]P$, $(C_2H_5O)[C_4H_9CH(C_2H_5)CH_2O]_2P$, $[C_4H_9CH(C_2H_5)CH_2O]_3P$, $[(CH_3)_3CCH_2CH(CH_3)CH_2O]_3P$: IR^{10}; $(C_6H_5O)_3P$: IR^{4,10,82}; $(C_2H_5O)_2C_2H_5P$: IR^{4};



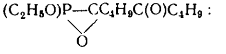
$(C_2H_5O)P\text{—}CCH_3C(O)CH_3$ (with $\overset{}{O}$ bridging P and C),



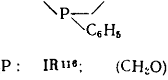
$(C_2H_5O)P\text{—}CC_2H_5C(O)C_2H_5$,



$(C_2H_5O)P\text{—}CC_3H_7C(O)C_3H_7$,



$(C_2H_5O)P\text{—}CC_4H_9C(O)C_4H_9$: R^{105}; $(CH_3O)_2PCl$, $(C_2H_5O)_2PCl$, $(C_3H_5O)_2PCl$, $(C_6H_5O)_2PBr$, CH_3OPCl_2: R^{16}; $C_2H_5OPCl_2$: IR^{10}, R^{16}; $C_6H_5OPCl_2$, $C_6H_5OPBr_2$: R^{16}; $(CH_3S)_3P$: IR^{96}; $C_2H_5PCl_2$: IR^{4}; CH_3PH_2, SiH_3PH_2: IR^{113}; $(CH_3)_2PH$: IR^{114}, R^{114}; $(C_2H_5)_2PH$: R^{115}; $(CF_3S)_2PH$: IR^{116}; $(CH_3)_3P$: IR^{117,119}, R^{118,119}; $(C_2H_5)_3P$: IR^{46,120,121}, R^{115}; $(CH_2{=}CH)_3P$: IR^{120,121}; $(C_2H_5)_2C_6H_5P$: IR^{4}; $(C_6H_5)_3P$: IR^{4,82,109,122}



, IR^{122}; $P(CN)_3$: IR^{123,124}; $(CF_3)_2POP(CF_3)_2$: IR^{74}; $(CF_3S)_3P$: IR^{116}; $(CH_3O)_2PHO$: IR^{2,9,18}, R^{1,2,16}; $(C_2H_5O)_2PHO$: IR^{2,3,4,8,18,72}, R^{1,2,16}; $(C_3H_7O)_2PHO$; IR^{18}, R^{1,16}; $(i\text{-}C_3H_7O)_2PHO$: IR^{18,80}, R^{1,80}; $(C_4H_9O)PHO$: IR^{4,18,72}, R^{1,16}; $(i\text{-}C_4H_9O)_2PHO$: R^{1}; $(C_6H_5CH_2)_2PHO$: IR^{10,11}; $[(CH_3)_3CCH(CH_3)O]_2PHO$: IR^{11}; $[(CH_3)_3CCH_2CH(CH_3)O]_2PHO$: IR^{10}; $(C_8H_{17})_2PHO$: IR^{8}; $(CH_3O)C_4H_9PHO$: IR^{93}; $(C_{10}H_7)(HO)PHO$: IR^{4}; $(C_{18}H_{37})(HO)PHO$: IR^{8}; $(C_6H_5)(DO)PDO$, $(C_6H_5)(HO)PHO$, $(C_2H_5O)C_6H_5PHO$, $(p\text{-}CH_3C_6H_4)(HO)PHO$, $(p\text{-}C_2H_5\text{—}C_6H_4)(HO)PHO$: IR^{4}; $(CF_3)_2POH$: IR^{74}; $(C_2H_5O)_2PONa$, $(C_4H_9O)_2PONa$, $(C_4H_9O)_2POK$, $(C_2H_5O)_2POAg$, $(C_4H_9O)_2POAg$: IR^{72}; $(CF_3)HP(O)ONa$: IR^{75}; $(C_6H_5)_3PHFeCl_4$, $[(C_6H_5)_3P]_2HgCl_3$: IR^{109}; $(CH_3O)_2PHS$: IR^{18}; $(C_2H_5O)_2PHS$: IR^{18}, R^{26}; $(C_2H_5)_2NPF_2$: IR^{4}; $(CH_3)_2NPCl_2$: IR^{15}; $(C_2H_5O)_2PN(CH_3)_2$: IR^{84}, $[(CH_3)_3SiO]_2P(O)H$, $[(C_2H_5)_3SiO]_2P(O)H$, $[CH_3(C_3H_7)_2SiO]_2P(O)H$; R^{100}.

Inorganic Phosphorus Compounds

PH_3: IR^{125}; PF_3: IR^{5,79}; PF_5: IR^{5}; PCl_5: IR^{126}, R^{126}; POF_3: IR^{5}; $POCl_3$: IR^{3,4,9,33,92}, R^{35,92}; $POCl_3(+SbCl_5)$: R^{58}; $(POCl_3)_2TiCl_4$, $POCl_3.TiCl_4$, $(POCl_3)_2SnCl_4$: IR^{33}; Cl_2FPO, Cl_2PCOH, Cl_2PCOD: R^{58}; $POBr_3$: IR^{4,33}, R$^{40-42}$; $PSCl_3$: IR^{3,78}, R^{26}; FCl_2PS: IR^{4}; $(POBr_3)_2TiBr_4$, $(POBr_3)FeBr_2$: IR^{33}; $(NH_2)_3PO$, $(NH_2)_3PS$; $(NH_2)_2ClPO$: IR^{11}; $(NH_4)_2HPO_4$: R^{127}; $(NH_4)PO_2F_2$, $(NH_4)_2PO_3F.H_2O$, $Li_2PO_3F.3H_2O$, Na_2PO_3F, K_2PO_3F, $CaPO_3F.xH_2O$, $SrPO_3F.xH_2O$, $BaPO_3F$, $PbPO_3F$: IR^{107}; $H_4P_2O_7$, $Na_4P_2O_7.10H_2O$, $Na_3HP_2O_7.H_2O$, $Na_2H_2P_2O_7$, $Na_4P_2O_7.10H_2O$, $Na_3HP_2O_7.9H_2O$, $Na_3HP_2O_7$, $Na_2H_2P_2O_7$, $NaH_3P_2O_7$: IR^{128}; P_2H_4: R^{129}; $P_2O_3Cl_4$: R^{130}; $P_4O_4Cl_{10}$: IR^{92}, R^{92}; H_3PO_3, KH_2PO_3, K_2HPO_3: R^{106}; P_2O_5, (P_2O_{25}), P_2S_5: IR^{3}; K_2HPO_4 $Zn_3(PO_4)_2$, Ag_3PO_4, Tl_3PO_4, Na_2PO_3F, K_2PO_3F, Ag_2PO_3F, $Na_2H_2P_2O_7$, $K_2H_2P_2O_7$, $K_2D_2P_2O_7$, $K_4P_2O_7.xH_2O$, $Ag_4P_2O_7$, $Tl_4P_2O_7$, $Zn_2NaP_3O_{10}$, $Ag_5P_3O_{10}$, $Ag_3P_3O_9$,

$Tl_3P_3O_9$, $Ag_4P_4O_{12}$, $Na_2PO_3NH_2$, $ZnPO_3NH_2$, $Ag_2PO_3NH_2$, $Tl_2PO_3NH_2$, $Zn[PO_2(NH_2)_2]_2$, $Na_4P_2O_6NH$, $K_2H_2P_2O_6NH$, $K_2D_2P_2O_6ND$, $K_4P_2O_6NH$, $Zn_2P_2O_6NH$, $Ag_4P_2O_6NH$, $Ag_4P_2O_6NAg$, $Tl_4P_2O_6NH$, $Na_5P_3O_8(NH)_2$, $Zn_2NaP_3O_8(NH)_2$, $Tl_5P_3O_8(NH)_2$, $K_3P_3O_7(NH)_2$, $Ag_3P_3O_7(NH)_2$, $Tl_3P_3O_7(NH)_2$, $Tl_3P_3O_7(NH)_2TlOH$, $H_3(PO_3NH)_3$, $NaH_2(PO_3NH)_3 . 2H_2O$, $Na_3(PO_2NH)_3 . 4H_2O$, $K_3(PO_2(NH)_3$, $K_3(PO_2ND)_3$, $A_3(PO_2NH)_3$, $Tl_3(PO_2NH)_3$, $Tl_3(PO_2NH)_3TlOH$, $(NH_4)_2H_2(PO_2NH)_4$, $(NH_4)(PO_2NH)_4 \cdot 4H_2O$, $Na_2H_2(PO_2NH)_4$, $Na_4(PO_2NH)_4 . 3H_2O$, $K_4(PO_2NH)_4$, $Ag(PO_2NH)_4$, $Tl_4(PO_2NH)_4$, $P(O)(NH_2)_3$, $P(S)(NH_2)_3$: IR[131].

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EFFICIENCY CRITERIA IN GAS CHROMATOGRAPHY

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PART I

The study of the operating characteristics of chromatographic apparatus and of the efficiency of the resulting separations is of great relevance to the development of this important technique for physicochemical analysis. Contemporary gas chromatography includes a variety of different methods, each of which involves numerous parameters. Industrial concerns in many countries are marketing very diverse chromatographic assemblies, the types of which already exceed several dozen.

One is often faced with the problem of comparing different methods and their analytical results and thus defining the optimum experimental parameters. Unfortunately, the literature is strangely silent on the selection of the correct procedures for evaluating the effectiveness of the operation of chromatographic equipment, in spite of the large number of *ad hoc* criteria suggested by different authors. The necessary distinction between apparatus parameters and characteristics of the separation process is not always made. Many important questions (for instance, the effect of the ratio of the concentration of components) are not analysed in sufficient detail.

The present article attempts a critical survey of the efficiency characteristics for the chromatographic process which have been proposed, and suggests ways of improving on them. The reader is assumed to be familiar with the basic concepts of the theory of chromatography, given in Keulemans' monograph[1] and in an article by one of the present authors, previously published in this journal[2].

Before the criteria given in the literature can be correctly classified, it is necessary to specify them. Considerable divergence of opinion is evident from the many papers on this subject. The number of necessary criteria must be determined by the number of essential characteristics of the apparatus and of the process. One should first of all evaluate the extent of separation from the final chromatogram. However, as will be shown below, one cannot rely on a single criterion for characterising the degree of separation. According to the nature of the chromatographic curve, three criteria may present themselves: these make up one group, since they all characterise the degree of separation. However, the overall separation effect does not provide a sufficiently detailed description of the various aspects of the operation of a particular apparatus.

The selectivity of the adsorbent (or solvent) is an essential characteristic and the main design parameter of the apparatus. Selectivity considerations make up the second group of chromatographic criteria. For a given selectivity, the separation is limited by the spreading of the bands. Experimental parameters (gas flow rate, particle size, pressure, column geometry, etc.) as well as characteristics of the sample injector and of the detector have a considerable effect on the spreading of the bands.

The third group of criteria describes those properties of the column which are largely independent of the sorbent, being determined by the kinetics and the dynamics of the process and by the properties of the detector and the injector. These criteria describe the extent to which band spreading can be suppressed in a given apparatus.

All these groups of criteria are needed to characterise the degree of separation. Some characteristics of the apparatus, however, do not affect the degree of separation. The most important of these are the resistance to gas flow and the time required for the analysis. Automation, and industrial process control, require short analysis times. The fourth group of criteria will characterise all the properties of the chromatographic equipment, including the degree of separation, the resistance to gas flow, and the analysis time.

We shall discuss these four groups of criteria in the order given above.

PART II

The degree of separation is a measure of the purity of a fraction, expressed by the dimensionless quantity θ which gives the proportion of the main component in a particular fraction. This quantity is derived from the most characteristic features of the chromatogram.

The chromatogram for a component with a linear adsorption isotherm is defined by three quantities: the position of the maximum (*e.g.* the retention volume, v_g, per unit column area), the concentration at the maximum, c_m, and the parameter β, which describes the shape of the chromatogram by means of the equation

$$c = c_m e^{-\beta x^2} \tag{1}$$

where x is measured from the ordinate of the maximum.

The so-called band width μ (distance between points at which $c = c_m/e$) is related to the quantity β:

$$\mu = 2\sqrt{\frac{1}{\beta}}. \tag{2}$$

For a chromatogram characterised by a single parameter all the other characteristics are expressed in terms of these three (v_g, c_m, and β).

θ must obviously depend on differences in v_g, not on the absolute values of v_g, since the degree of separation is not affected by displacing the chromatogram along the volume axis.

The values of β for neighbouring components may be assumed identical, since β is generally independent of the nature of the component in turbulent diffusion, and all other processes which can lead to band spreading have very similar β values for components in close proximity.

The degree of separation may depend on the ratio between c_{m_1} and c_{m_2} ($\Phi = c_{m_1}/c_{m_2}$) but not on the absolute values of c_m, since θ does not vary with concentration in the case of a linear isotherm. Being a dimensionless quantity, θ may depend on dimensionless expressions.

From the three chromatogram parameters discussed above we can construct two dimensionless expressions: Φ and $K = \Delta v_g\sqrt{\beta}$.

Thus,

$$\theta = f(\Phi, K). \tag{3}$$

It must be stressed that Φ and c_m refer to the peaks of pure components. Φ therefore gives the ratio of the starting materials in the original mixture.

Methods for evaluating K and Φ from the chromatogram and for deducing the degree of separation will now be discussed.

The procedure used for analysing the chromatogram will depend on the completeness of the separation achieved. If the separation is good, Δv_g and μ may be determined directly from the chromatogram. In this case it is advantageous to replace K by a new criterion[3,4] differing from K by some factor:

$$K_1 = \frac{\Delta v_g}{\mu_1 + \mu_2} = \frac{\Delta v_g}{2\mu}. \tag{4}$$

When separation is incomplete neither Δv_g nor μ can be measured, since the appearance of the maxima is altered when two peaks are in close proximity. If the chromatogram has a minimum we can choose the quantities $c_{\min}$ (concentration at the minimum) and c_m as the basic parameters.

Two criteria based on this approach[5,9] are discussed in the literature:

$$K_2 = \frac{c_{m_1} + c_{m_2}}{c_{\min}}, \tag{5}$$

$$K_B = \frac{c_B - c_{\min}}{c_B}, \tag{6}$$

where c_B is the concentration corresponding to the intersection of the straight line joining the two maxima with the ordinate passing through the minimum (see Fig. 1).

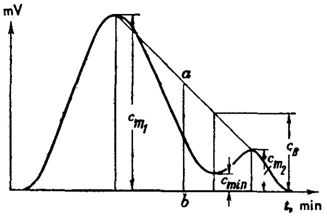

Fig. 1. Definition of the criteria K_2 and K_B.

It can readily be shown that if $\Phi \simeq 1$

$$K_B = \frac{K_2 - 2}{K_2}.$$

Finally, if the separation is very poor, and no minimum appears on the chromatogram, the values of Δv_g and μ may be calculated from the shape of the chromatogram.

For small values of Δv_g the expression

$$c = c_{m_2}[\Phi e^{-\beta x^2} + e^{-\beta (x - \Delta v_g)^2}]$$

is reduced to the form

$$\ln \frac{c_{m_2}}{c} = \beta x^2 - \ln \Phi - \ln\left(1 + \frac{1}{\Phi}\right) - \frac{2x\beta\Delta v_g}{1 + 1/\Phi}. \tag{7}$$

If Φ is known, or if $\Phi \simeq 1$, β and Δv_g may be determined and the criterion K_1 calculated by fitting Eqn. (7) to the experimental chromatogram. All the criteria discussed here may be expressed in terms of any one of them. Thus, it can be shown that for $\Phi \simeq 1$, $K_2 = 2e^{4K_1^2}$ and therefore $K_B = 1 - e^{-4K_1^2}$.

Thus, if Φ is known, the criterion K_1 is in principle calculable for any chromatogram. Since $\theta = f(K, \Phi)$, Φ must be kept constant when comparing different methods or discussing the effect of various parameters. All the expressions are considerably simplified if $\Phi = 1$. In particular, if Δv_g is large, a quantitative relationship between θ and K_1 can easily be derived:

$$\theta = \frac{1}{4\sqrt{\pi}K_1} e^{-4K_1^2}.$$

If Φ varies between experiments, comparison of the criteria will lead to an incorrect evaluation of the difference in the degree of separation. The criterion which is least sensitive to the value of Φ will therefore be the most satisfactory from this point of view. K_B has this property. The criterion K_B has a twofold advantage over K_2: not only does K_B vary between more physically meaningful limits than K_2 (K_2 varies between +1 and ∞, K_B between 0 and 1), but K_B also varies little with Φ. The use of K_2 can therefore only be recommended in cases when $\Phi \simeq 1$. The difference between K_2 and K_B can be appreciated from Fig. 1. In place of $c_B - c_{min}$, K_2 contains double the value of the ordinate ab, which equals the arithmetic mean of the maxima. Obviously, if $\Phi \neq 1$, c_m should be compared with c_B or $c_B - c_{min}$ rather than with ab. On these grounds we can think of the criterion K_B as a modified form of K_2 which is less sensitive to Φ.

The criterion K_1 may also be modified so as to decrease its sensitivity to Φ. Let $c_{m_1} > c_{m_2}$. In this case we measure μ not between the points at which the concentration is c_{m_1}/e, as is done when calculating K_1, but between points on the first peak of concentration c_{m_2}/e. The resulting criterion $\left(K_1 = \frac{\Delta x}{\mu_1 + \mu_2}\right)$ is considerably less sensitive to Φ.

If we wish the criteria to have certain specified values (for example, we may wish to control K_1, the purity of the fraction), the values of the parameters of the chromatographic experiment must be under our control.

We shall derive the relationship between K_1 and these values for the simplest case ($\Phi = 1$). It is known that

$$\Delta x = \Gamma_2 L (m - 1), \tag{8}$$

where $m = \Gamma_1/\Gamma_2$ and Γ is Henry's constant used in the calculation of the amount of adsorption per unit volume of the tube:

$$\mu_1 = 4\Gamma_1 \sqrt{\frac{DL}{\alpha}}, \qquad \mu_2 = 4\Gamma_2 \sqrt{\frac{DL}{\alpha}}. \tag{9}$$

Here α is the linear velocity of the carrier gas, D is the effective coefficient of longitudinal diffusion, which we assume to be the same for both components, and L is the length of the column.

It follows that

$$K_1 = \frac{1}{4}\frac{m - 1}{m + 1}\sqrt{\frac{L\alpha}{D}}.$$

If the values of A in the equation $\Gamma = Ae^{Q/RT}$ are the same for both components, $\Delta Q \ll RT$, and $\Gamma_1 = \Gamma_2$, we have[7]

$$K_1 = \frac{\Delta Q}{8RT}\sqrt{\frac{L\alpha}{D}},$$

where D/α characterises the spreading of the bands in the particular apparatus. Applying the well-known formula $2D/\alpha = H$, where H is the height of a theoretical plate, we have

$$K_1 = \frac{1}{4}\frac{m - 1}{m + 1}\sqrt{\frac{2L}{H}}. \tag{10}$$

Therefore, in order to achieve a given value of K_1 (or a given fraction purity) we require a certain minimum length L:

$$L = 8K_1^2\left(\frac{m + 1}{m - 1}\right)^2 H, \tag{11}$$

$$N = 8K_1^2\left(\frac{m + 1}{m - 1}\right)^2, \tag{12}$$

where $N = L/H$ is the number of plates.

Röck[8] derived a similar formula for the criterion K_B:

$$N = \left(\ln \frac{4}{1 - K_B}\right)\left(\frac{m + 1}{m - 1}\right)^2. \tag{13}$$

It can be seen that if the values of K_B (or K_1) and H are given, the required length is described by a factor which we shall call, after Purnell[9], the selectivity coefficient K_c:

$$K_c = \frac{m - 1}{m + 1}.$$

K_c refers to a single separation. This coefficient vanishes when there is no separation of the components, and tends to one if separation is complete.

It must be remembered, when comparing the efficiency of different methods, that the Henry coefficients (Γ) refer to sorption by unit volume of the tube. A decrease in the absolute value of the coefficient Γ (*e.g.* by decreasing the amount of stationary phase) will therefore lead to a decrease in K_c.

If κ_1 is the fraction of the cross-sectional area occupied by the stationary phase and κ is the fraction of free space we have, as will be shown in Part III,

$$\Gamma = \kappa + \Gamma_i \kappa_1,$$

where Γ_i describes the sorption by unit volume of the stationary phase. Hence

$$m = \frac{\kappa + \Gamma_{i_1}\kappa_1}{\kappa + \Gamma_{i_2}\kappa_1}. \tag{14}$$

We can see that if the Henry coefficient is small a decrease in κ_1 for a given stationary phase will sharply lower the value of m and therefore also of K_c, and consequently increase the length required. For large values of Γ_i we can neglect κ and write

$$m = \frac{\Gamma_{i_1}}{\Gamma_{i_2}}.$$

Consequently, the separation coefficient K_c is independent of the amount of stationary phase. However, if κ and Γ_i are both small, a decrease in κ_1 will considerably impair the separation, since if $\kappa_1 = 0$, $m = 1$, and $K_c = 0$, and the required length $L \to \infty$. This conclusion, first put forward by Purnell, stresses the inadequacies of capillary chromatography in comparison with the conventional gas–liquid variant.

We shall illustrate this point by considering two typical examples taken from gas–liquid and capillary chromatography respectively.

If the stationary phase is the same in the two cases and the true Henry coefficients are 30 and 20 respectively, we shall have $\kappa = 0.5$ and $\kappa_1 = 0.1$ for the gas–liquid chromatography. Then

$$m = \frac{30 \times 0.1 + 0.5}{20 \times 0.1 + 0.5} = 1.4.$$

For the capillary chromatography $\kappa = 1$, $\kappa_1 = 10^{-2}$, whence

$$m = \frac{30 \times 10^{-2} + 1}{20 \times 10^{-2} + 1} = 1{,}1,$$

and the K_c values will be 0.17 and 0.045 respectively. A greater column length is needed in the second case in spite of the fact that the H values are the same.

Formulae (11) and (12) express the length, or the plateage L/H, required if the criterion K_1 is to have the stated value. At $\Phi = 1$, K_1 uniquely determines the degree of separation, θ.

In general, as has already been pointed out, $\theta = f(\Phi, K)$. The most obvious choice of a separation condition in this case is:

$$\Delta x > \frac{\mu_1 + \mu_2}{2}. \tag{15}$$

However, when $\Phi \neq 1$, the width of the band corresponding to the first component, which is also the major component, must be measured at the concentration c_{m_2}/e:

$$\mu_2 = 4\Gamma_2 \sqrt{\frac{DL}{\alpha}}$$

and

$$\mu_1 = 4\Gamma_1 \sqrt{\frac{DL}{\alpha} \ln \frac{c_{m_1} e}{c_{m_2}}} = 4\Gamma_1 \sqrt{\frac{DL}{\alpha}(1 + \ln \Phi)}.$$

Making use of (15):

$$\Gamma_2 L \left(\frac{\Gamma_1}{\Gamma_2} - 1 \right) > 2\Gamma_2 \sqrt{\frac{DL}{\alpha}} + 2\Gamma_1 \sqrt{\frac{DL}{\alpha}(1 + \ln \Phi)}.$$

After some manipulation, and substituting H for $2D/L$, we obtain:

$$L > H \frac{2[1 + m\sqrt{1 + \ln \Phi}]^2}{(m-1)^2}. \tag{16}$$

Condition (15) corresponds to the requirement that $K > 1/2$. For $\Phi = 1$ Eqn. (16) corresponds to Eqn. (11).

Formula (16) differs from that derived by van Deemter[10] in that the value of Φ is considered.

The variation of N_Φ/N_1 with Φ is shown in Fig. 2 for m close to 1. N_Φ/N_1 is the increase in plateage required if the ratio between the two components is changed from 1 to Φ. The variation of N_1 with Φ may be determined by comparing (15) and (11) for a given value of θ, whence:

$$\frac{N_\Phi}{N_1} = \frac{[1 + m\sqrt{1 + \ln \Phi}]^2}{(1 + m)^2}. \tag{17}$$

N_Φ/N_1 gives the increase in N_1 needed to change from $\Phi = 1$ to $\Phi = \Phi$, keeping the degree of separation constant. The formula is only true when the separation is good. It shows that an increase in Φ makes the requirements in N much more stringent. Thus, if $m = 0.5$ and $\Phi = 100$, $N_\Phi/N_1 = 2.2$.

Formula (17) predicts that the increase in N with Φ depends on the value of m, and decreases when the difference in adsorbability increases.

Lu P'ei-chang[11] adopted $\sqrt{\ln (c_{m_1}/c_{\min})}$, *i.e.* $\ln\sqrt{N_2/2}$, as the separation criterion for the case $\Phi = 1$ and $c_{m_1} = c_{m_2}$. He showed that his criterion was the product of two factors, S and F:

$$\sqrt{\ln \frac{c_{m_1}}{c_{\min}}} = SF. \tag{18}$$

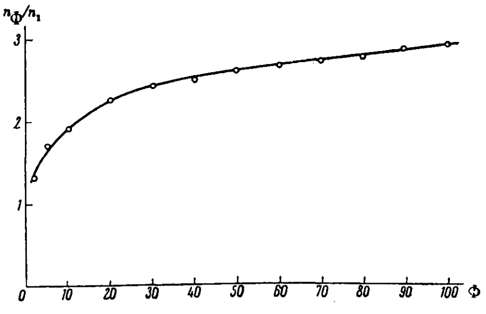

Fig. 2. Variation of n_Φ/n_1 with Φ.

TABLE 1.

Type of chromatography	S	F
Adsorption development	$\frac{V_{g_2}-V_{g_1}}{V_{g_2}+V_{g_1}}$	$\sim D^{0.5}\alpha^{0.5}L^{0.5}$
Gas-liquid	$\frac{V_{g_2}-V_{g_1}}{V_{q_1}^{0.5}+V_{g_2}^{0.5}}$	$2.75_g^{0.5}\alpha^{0.42}$
Chromathermography	$\frac{Q_2-Q_1}{\sqrt{Q_1}+\sqrt{Q_2}}$	$\frac{1}{\sqrt{2R}}\sqrt{\frac{\alpha}{D_{\mathrm{eff}}\gamma}}$

S is determined by the statistical characteristics of the column, F by the spreading of the bands, *i.e.* by the kinetics and the dynamics of the process.

Lu P'ei-chang's values for S and F are set out in Table 1 for different types of chromatography: R is the gas constant, γ is the temperature gradient, and q is the amount of stationary phase.

Lu P'ei-chang's factorisation has the desirable effect of distinguishing the influence of experimental parameters (F) from the properties of the adsorbent (S).

PART III

The second group of criteria characterises the column selectivity.

It was shown in the above discussion that the criteria K are expressed as the products of factors which are separately determined by statistical and by kinetic characteristics. Formulae (10), (13), and (18) show these properties. The selectivity of the column is given in every case by the criterion:

$$K_c = \frac{m-1}{m+1}. \tag{19}$$

K_c is obviously a characteristic of the column rather than of the adsorbent, since both m and K_c decrease, as was shown above, if the amount of adsorbent is decreased.

The value of m can be determined directly from the retention volumes by means of the formula:

$$m = \frac{v_{g_1}}{v_{g_2}}.$$

In addition to (19), a number of other selectivity criteria are to be found in the literature. Thus, Janak[12] suggests making use of the difference in retention volumes, $\Delta v_g = v_{g_1} - v_{g_2}$. This is of doubtful value, since it is the relative difference in retention volume which is important, not its absolute value. The requirement in Δv_g depends on v_g itself, since H is proportional to Γ and therefore also to v_g, and a small value of Δv_g is sufficient if the v_g values are small. Consequently, the requirements in Δv_g are less stringent if the materials are not readily adsorbed.

It may not be out of place to stress that in the case of non-linear isotherms not all the criteria discussed, such as v_g, are applicable.

In a number of publications[1,13] m is used directly as a selectivity criterion. K_c is to be preferred, however, not only because it varies over more physically meaningful limits (from 0 to 1 instead of from 0 to ∞), but also because the separation criteria follow directly from it through formulae (10), (11), and (12).

Selectivity criteria have on occasions been defined on the basis of the distribution coefficients Γ_i rather than in terms of the ratio of the coefficients Γ. This procedure is less attractive, since it is the selectivity of the column as a whole which is important, not that of the sorbent. In practice, this concerns the method used for determining the Henry coefficient from the chromatogram, and, in particular, the need for introducing the dead space correction into the calculation of the retention volume. The literature has little to offer on these questions. We shall therefore confine our attention to the Henry coefficients, which may be derived directly from chromatographic experiments. Considering only the v_g measurement, we can only derive the Henry coefficient which appears in the formulae presented above, *i.e.*

$$\Gamma = \frac{v_g}{w},$$

where w is the volume of the column or, if v_g is expressed per unit cross-sectional area, the column length. Γ defines the capacity of unit volume of the column: it is related to Γ_i, which expresses the capacity of unit volume of the stationary phase.

Let, as before, κ be the fraction of free volume, κ_1 the fraction of the volume occupied by the solvent. In the case of adsorption chromatography we have

$$\kappa_1 = 1 - \kappa.$$

The capacity of unit volume is then given by

$$\kappa \times c + \kappa_1 \times \Gamma_i \times c, \tag{20}$$

and therefore $\Gamma = \kappa + \kappa_1\Gamma_i$. The smallest value of Γ is obviously given by κ. If κ_1 tends to zero, Γ assumes the universal value κ for all substances.

The values of κ and Γ_i cannot be determined from measurements of v_g alone. A knowledge of v_{g_0}, the retention volume of a virtually non-adsorbed component, such as hydrogen or helium, is also required. In this case

$$\kappa = \frac{v_{g_0}}{w}.$$

From Eqn. (20),

$$\Gamma_i = \frac{\Gamma - \kappa}{\kappa_1} = \frac{v_{g_i}/w - v_{g_0}/w}{\frac{v_{\mathrm{liq}}}{w}}$$

where v_{liq} is the volume of the stationary phase.

Thus

$$\Gamma_i = \frac{v_g - v_{g_0}}{v_{\mathrm{liq}}}. \tag{21}$$

The Henry coefficient calculated per unit volume of adsorbent, Γ_a, is occasionally of interest:

$$\Gamma_a = \frac{v_g - v_{g_0}}{v_a} \tag{22}$$

where v_a is the volume of the adsorbent.

Finally the capacity of the support is sometimes referred to unit free volume:

$$\Gamma' = \frac{v_g - v_{g_0}}{w\kappa} = \Gamma_i \frac{\kappa_1}{\kappa}. \tag{23}$$

The most direct and useful characteristic is undoubtedly Γ. This quantity can be calculated without measuring v_{g_0} and subtracting it from v_g. The use of Γ in calculations is to be recommended.

When the properties of the solvent or the adsorbent are being studied, the need sometimes arises to use formulae (21)–(23). Thus, low values are obtained if the heat of adsorption is derived from the temperature variation of Γ.

PART IV

Two criteria have so far been suggested for describing band spreading in a column. The criterion most commonly used in the literature is H, the height of a theoretical plate, or N, the number of theoretical plates[14]. The other criterion is the effective longitudinal diffusion coefficient, D. The two criteria are related by the following well-known expression

$$H = \frac{2D}{\alpha},$$

and are therefore equivalent.

The values of H and D are calculated from measurements of v_g and μ. Replacing Γ by v_g/L we obtain the familiar relation

$$\frac{D}{\alpha} = \frac{1}{16} L \left(\frac{\mu}{v_g}\right)^2,$$

whence

$$H = \frac{1}{8} L \left(\frac{\mu}{v_g}\right)^2,$$

or the number of theoretical plates

$$N = \frac{L}{H} = 8 \left(\frac{v_g}{\mu}\right)^2.$$

Many other similar methods of calculating H and N are available. They have been reviewed by Glueckauf[3] and by Struppe[15].

In the calculation of v_g, and even of μ, an unnecessary correction is often made for the retention volume of the dead space. This correction is justified only if the dead volume is located outside the packing.

Conceptually, the theoretical plate approach has the advantage of generality, as it is unrelated to any specific mechanism of band spreading. However, this formal generality can lead to an erroneous interpretation. Since the selectivity coefficient does not appear in the expression for the plate height, it is not possible to characterise the separation efficiency of the apparatus by means of the latter quantity. In this respect the quantity D has certain advantages over H, since its physical significance is clear, and it is not likely to be incorrectly interpreted.

It is not always true to say that decreasing H (or increasing N) must necessarily improve the separation. For instance, H always decreases when the quantity of solvent is decreased in cases where inner diffusion is the controlling process. The selectivity criterion is also decreased and the number of plates required for the separation will now increase, as indicated by Eqn. (10).

We shall now consider how the separation criterion K_1 (and therefore also the purity of the fraction, θ) varies when the amount of solvent is decreased in gas–liquid and in capillary chromatography. This requires an analysis of the dependence of the selectivity criterion K_c and the plate height H on the amount of solvent. We shall discuss the case, typical in gas–liquid chromatography, of combined turbulent and inner diffusion[2].

In this case

$$H = A + C\alpha,$$

where A represents the turbulent diffusion, and is independent of the amount of material, and

$$C = \frac{8}{\pi^2} \frac{\Gamma'\delta^2}{(1+\Gamma')^2 D_{\text{liq}}}.$$

In this formula δ is the thickness of the film, D_{liq} is the inner diffusion coefficient, and Γ' is given by Eqn. (23) in terms of κ and κ'.

To calculate the variation of κ with δ we require the volume of solvent per unit volume of the packing, given by

$$\frac{1-\kappa}{{}^4/_3\pi r^3} \times 4\pi r^2\delta.$$

The first factor defines the number of spherical particles per unit volume, the second factor gives the volume of the layer of solvent on each particle.

The quantity $\frac{3(1-\kappa)\delta}{r}$ gives the required value of κ_1, since it is calculated per unit area and per unit volume of packing.

Thus

$$C\alpha = \frac{Z\delta^3}{(1+M\delta)^2}$$

and

$$H = A + \frac{Z\delta^3}{(1+M\delta)^2}, \tag{24}$$

where Z and M are constants.

To calculate K_1 we require to know the function $m = f(\delta)$. It follows from what has been said above that

$$m = \frac{\kappa + 3\left(\frac{1-\kappa}{r}\right)\delta\Gamma_1}{\kappa + 3\left(\frac{1-\kappa}{r}\right)\delta\Gamma_2}.$$

If $\Gamma_1 = \Gamma_2 + \Delta\Gamma$ and $\Delta\Gamma$ is small, we have

$$m = 1 + \frac{3(1-\kappa)\delta}{r}\Delta\Gamma \text{ and } K_c = \frac{3(1-\kappa)\delta}{r}\frac{\Delta\Gamma}{\Gamma}.$$

Therefore

$$K_1 = \frac{\delta(1+M\delta)}{\sqrt{A(1+M\delta)^2 + Z\delta^3}}.$$

It can be seen that K_1 goes through a maximum. This is particularly evident when Γ is small and $\mu \to 0$. In this case

$$K_1 = \frac{\delta}{\sqrt{A + Z\delta^3}}.$$

Thus, an increase in the amount of material is beneficial at low values of δ, in spite of the fact that it invariably decreases the number of plates, because the resulting gain in selectivity will offset the loss introduced by the increased spreading.

PART V

It is arguable whether an overall criterion of the performance of a chromatographic apparatus, which included the efficiency of separation, the resistance to flow, and the analysis time, would be desirable.

Some attempts have been made in the past to derive general criteria for complicated assemblies. On the whole, they have not been very successful. It is better to find separate answers to the various questions (for example, to that of speed) than to search for a general criterion. This does not mean that one should consider only the separation efficiency when comparing different chromatographic procedures.

Golay[16] introduced the so-called performance index of the column (*PI*) to describe the advantages of capillary chromatography over the gas–liquid variant. His approach can be summarised as follows. One must obviously express the optimum conditions (minimum plate height $H_{\min}$) in a form which involves the basic experimental parameters, such as the pressure drop Δp, the width of the band, etc., since Golay's index must necessarily involve the pressure drop. We know that the pressure drop can be expressed as

$$p_1^2 = p_0^2 + \frac{16\eta}{r^2} p_0 L \alpha$$

where p_0 and p_1 are the outlet and the inlet pressures, η is the viscosity, r is the radius of the capillary column, v_0 is the outlet velocity, and L is the length of the column.

In addition, we shall consider the half-width of the band (Δt^x, expressed in seconds) under conditions of carrier gas velocity corresponding to minimum plate height.

Golay, taking only longitudinal and radial diffusion into consideration, expresses the plate height by the formula:

$$H = 2\frac{D}{\alpha} + \frac{1 + 6\Gamma' + 11\Gamma'^2}{24(1+\Gamma')^2} \times \frac{\alpha r^2}{D} \cdot$$

From the condition $\partial H/\partial\alpha = 0$ we have:

$$H_{\min} = \left(\frac{1 + 6\Gamma' + 11\Gamma'^2}{3(1+\Gamma')^2}\right)^{1/2} r \,. \tag{25}$$

It should be noted that the minimum plate height in capillary chromatography is a function of the radius of the capillary. From Eqn. (25) Golay obtains an expression for Δt_x:

$$\frac{\Delta t_x^2}{t_x^2} = \frac{144 \ln 2\, (p_1^2 - p_0^2)(p_1^2 + p_0^2)\, \eta\alpha p_0 h}{(p_1^3 - p_0^3)\, r^2} \cdot$$

Introducing the retention time for the non-adsorbed component:

$$t_a = \frac{(p_1{}^3 - p_0^3)\, r^2}{24\eta\alpha^2 p_0^2},$$

Golay obtains an expression for the viscosity in terms of the quantities under discussion:

$$\eta = \frac{1}{64(\ln 2)^2}\left(\frac{\Delta t_x}{t_x}\right)^4 \frac{t_a}{C_\kappa}\, \frac{16}{27}\, \frac{(p_1^3 - p_0^3)^3}{(p_1^4 - p_0^4)^2},$$

where

$$C_\kappa = \frac{8}{3}\, \frac{1 + 6\Gamma' + 11\Gamma'^2}{(1+\Gamma')^2},$$

or, approximately,

$$C_\kappa = \frac{4}{3}\left(1 + 15\frac{\Gamma}{1+\Gamma}\right) \cdot$$

We make the further approximation

$$\frac{(p_1^3 - p_0^3)^3}{(p_1^4 - p_0^4)^2} = \Delta p = p_1 - p_0 \,.$$

The maximum error in this treatment arises when Δp is large, and amounts to 40%:

$$\eta \times {}^1/_3 \times 2^{10} (\ln 2)^2 \simeq \frac{\Delta t_x^4 \times t_a \Delta p}{t_x^3\left(t_x - \frac{15 t_a}{16}\right)} \cdot$$

Golay calls this quantity, which is proportional to the viscosity, the performance index of the column:

$$PI = \frac{\Delta t_x^4 \times t_a \times \Delta p}{t_x^3\, (t_x - t_a{}^{15}/_{16})} \cdot \tag{26}$$

Since *PI* increases with the width of the band, it must increase when the optimum velocity is replaced by realisable velocities and when subsidiary factors conducive to spreading, which had not been considered, become appreciable (*e.g.* inner diffusion).

The expression for *PI* may be re-written as follows:

$$PI = \left(\frac{\Delta t_x}{t_x - t_a}\right)^4 \frac{(t_x - t_a)^4\, t_a}{t_x^4 \left(t_x - \frac{15 t_a}{16}\right)} t_x \Delta p \,.$$

The first term describes the spreading in the column and therefore varies inversely as the column efficiency; the third term expresses the price which has to be paid for this efficiency, since it involves the work expended and the time required for the analysis.

PI is dimensionally a viscosity, and its numerical value equals the viscosity under optimum conditions (for helium, *PI* = 0.08 poise). The larger the performance index, the worse the performance of the column [$\Delta t_x/(t_x - t_a)$, or the analysis time, will be large, or much work will be expended]. *PI* is not a function of the dimensions of the column: it depends only on the nature of the solvent. Representative *PI* values for gas–liquid chromatography are 4 orders of magnitude higher than the minimum calculated value, whereas in capillary chromatography the discrepancy is only 2 powers of ten.

Golay's method of comparing different techniques is not particularly successful. One should certainly not compare different methods under conditions of minimum plate height: conditions of optimum separation should be chosen instead (optimum K_1, for instance).

The choice of conditions corresponding to a minimum H implies a constant length of packed column. However, it follows directly from Eqn. (10) that if L is constant K_1 is a maximum when H is a minimum. It should be noted that constant length is frequently assumed in publications dealing with the choice of parameters[17,18].

If the work expended is chosen as the main characteristic an expression is obtained in which the other parameters (analysis time, resistance to flow) play a more or less fortuitous part.

The inadequacy of Golay's criterion is best illustrated by pointing to an example in which the separation is impaired by decreasing *PI*. It is well known, for instance, that the separation is worse at higher temperatures in spite of the fact that *PI* decreases.

Different methods are best compared under their respective most favourable conditions, keeping constant whatever parameter is dictated by practical considerations.

The main practical requirement is undoubtedly a reasonably short analysis time (t); the second involves the resistance to flow (Δp).

Among the most characteristic requirements is the ability, essential in industrial chromatographic practice, to carry out the analysis in a stated time.

From Eqn. (10), introducing the relationship between the analysis time and the length of the column $t = L\Gamma/\alpha$, we obtain

$$K_1 = \frac{\sqrt{2}}{4} K_c \sqrt{\frac{t\alpha}{\Gamma H}}\,.$$

Expressing H in terms of α,

$$K_1 = \frac{\sqrt{2}}{4} K_c \sqrt{\frac{t}{\Gamma\left(\frac{A}{\alpha} + \frac{B}{\alpha^2} + C\right)}}\,.$$

We see from this equation that for a given analysis time K_1 increases with flow rate and therefore with length of the column, but that it cannot go on increasing indefinitely. There is a maximum limiting value of K_1 ($K_{\max}$) which may be realised in the given time.

If $\alpha \to \infty$

$$K_{\max} = \frac{\sqrt{2}}{4} K_c \sqrt{\frac{t}{\Gamma C}}\,. \tag{27}$$

Different methods are best compared in terms of the value of $K_{\max}$. The choice of a method is then dictated by the quantity

$$\nu_{\text{I-II}} = K^{\text{I}}_{\max}/K^{\text{II}}_{\max}$$

$$\nu_{\text{I-II}} = \frac{K_c^{\text{I}}}{K_c^{\text{II}}} \sqrt{\frac{\Gamma^{\text{II}}}{\Gamma^{\text{I}}}} \sqrt{\frac{C^{\text{II}}}{C^{\text{I}}}}\,. \tag{28}$$

In the case of readily adsorbed materials, for which K_c decreases little if at all on going over to the capillary chromatographic technique, the last term in Eqn. (28) settles the verdict in favour of capillary chromatography as compared with the gas–liquid method.

The shortest time in which a given value of K_1 may be achieved can be derived from Eqn. (27):

$$t_{\min} = \frac{8K_1^2\Gamma C}{K_c^2}\,. \tag{29}$$

Equations similar to (28) have been derived by Purnell[9] and by Loyd, Ayers, and Karasek[19].

If the resistance is given, the product $L\alpha = M_1$ must be treated as constant. In this case, it follows from (10) that

$$K_1 = \frac{\sqrt{2}}{4} K_c \sqrt{\frac{M_1}{\alpha H}}\,,$$

or

$$K_1 = \frac{\sqrt{2}}{4} K_c \sqrt{\frac{M}{A\alpha + B + C\alpha^2}}\,.$$

Thus, K_1 will decrease as α increases:

$$K_{\max} = \frac{\sqrt{2}}{4} K_c \sqrt{\frac{M_1}{B}}\,.$$

To compare different methods one determines the quantity

$$\nu_{\text{I-II}} = \frac{K_c^{\text{I}}}{K_c^{\text{II}}} \sqrt{\frac{B_{\text{II}}}{B_{\text{I}}}}\,.$$

In general, we shall need to fix the time (primarily) but also the resistance. In every concrete case we can define the product

$$t^n \Delta p^m = M_2,$$

which must be kept constant at a specified value, with the condition that $m + n = 1$. As before, using Eqn. (10), we obtain

$$K_1 = \frac{\sqrt{2}}{4} K_c \sqrt{\frac{M_2}{\Gamma^{\frac{n}{n+m}}} \times \frac{1}{A\alpha^{\frac{m-n}{m+n}} + B\alpha^{\frac{-2n}{m+n}} C\alpha^{\frac{2m}{m+n}}}}$$

In this case the optimum rate does not equal 0 or ∞ as in the earlier examples. A finite optimum value may be assigned to the rate (and therefore to the column length), so as to maximise K_1.

It should be stressed that the whole of this discussion of the relative advantages of different methods involves the assumption that the ratio of the concentrations of the components is close to unity ($\Phi = 1$). In the more general case the expressions should contain Φ.

A few practical cases will now be considered in order to illustrate the conclusions reached above on the usefulness of various criteria of the performance of chromatographic apparatus.

As we have pointed out, the very large plateage of capillary columns does not necessarily lead to improved separations, since the smaller volume of stationary phase in these columns entails a decrease in the selectivity coefficient. Tables 2 and 3 illustrate this state of affairs. The significance of the quoted values is defined in the tables.

In spite of the fact that the number of plates considered normal in capillary chromatography is higher than in the gas–liquid technique by about an order of magnitude, we see that the criterion K_1 is smaller. For example, in the system propane–butane on diatomite coated with liquid paraffin the number of theoretical plates for propane is 680. The same solvent, used in capillary chromatography, gives 50 times as many plates (33 600) but a smaller separation criterion: $K_1 = 6.1$ in gas–liquid chromatography, 2.0 in capillary chromatography. This is a consequence of the smaller selectivity coefficient K_c of the capillary technique.

Since the selectivity coefficient in capillary chromatography increases with thickness of the stationary phase, the value of K_1 will increase with amount of solvent. Thus, the separation criterion K_1 can be varied from 1.5 to 3.4 by changing the concentration of the solution of dibutyl phthalate in petroleum ether, used for coating the capillary, from 10% to 30%.

The selectivity coefficient can be increased by increasing the distribution coefficient whilst keeping constant the amount of solvent: replacing the dibutyl phthalate by petroleum jelly in gas–liquid chromatography results in an increase in K_1 too large to be accounted for by the increased plateage alone.

The relative effects of selectivity coefficient and of plate height depend on the nature of the mixture considered. Fig. 3 shows the variation of K_1^2 with N for the separation of a mixture of heptane and hexane by silicone oil supported on celite. The number of plates was calculated for heptane. The percentage of solvent is shown for each experimental point.

TABLE 2.

Substonce	Gas-liquid chromatography																	
	diatomite + 20% dibutyl phthalate						diatomite + 25% dibutyl phthalate						diatomite + 25% paraffin oil					
	L, cm	v, cm^{3}min^{-1}	v_g, cm^3	μ, cm^3	N	K_1	L, cm	v, cm^{3}min^{-1}	v_g, cm^3	μ, cm^3	N	K_1	L, cm	v, cm^{3}min^{-1}	v_g, cm^3	μ, cm^3	N	K_1
Propane	200	17.5	61.5	3.7	1500	3.4	1000	25	156	12.5	860	5.0	1000	25	166	15.0	680	6.1
Butane			97.7	6.9	1070				330	22.8	1200				412.5	25	1500	

TABLE 3.

Substance	Capillary chromatography																													
	in petroleum ether																													
	10% dibutyl phthalate						30% dibutyl phthalate						5% paraffin oil						8% paraffin oil						15% paraffin oil					
	L, cm	v, cm^3 × ×min^{-1}	v_g, cm^3	μ, cm^3	N	K_1	L, cm	v, cm^3 × ×min^{-1}	v_g, cm^3	μ, cm^3	N	K_1	L, cm	v, cm^3 × × min^{-1}	v_g, cm^3	μ, cm^3	N	K_1	L, cm	v, cm^3 × ×min^{-1}	v_g, cm^3	μ, cm^3	N	K_1	L, cm	v, cm^3 × ×min^{-1}	v_g, cm^3	μ, cm^3	N	K_1
Propane	3200	0.8	6.0	0.2	5200	1.5	4500	0.5	8.7	0.3	4650	3.4	4700	0.1	5.3	0.1	15700	1.5	4700	0.1	7.8	0.1	33600	2.0	4700	0.6	9.0	0.1	11300	2.0
Butane			6.7	0.2	4600				11.2	0.4	4300				5.6	0.1	17400				8.2	0.1	37000				10.0	0.3	6200	

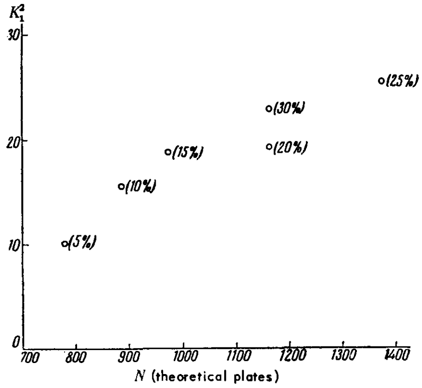

Fig. 3. Variation of K_1^2 with N for hexane–heptane mixtures.

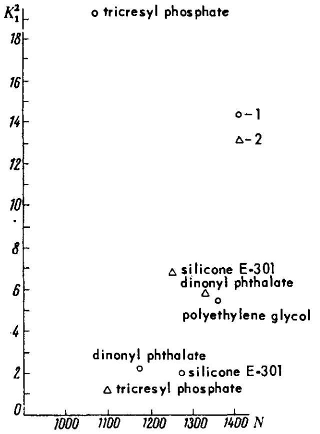

Fig. 4 Variation of K_1^2 with N for the following mixtures:
1) toluene–octane; 2) methylcyclohexane–octane.

From Eqn. (12), K_1^2 should be proportional to N if the selectivity coefficient is constant. For this particular mixture the relationship is more or less obeyed, but it fails completely with toluene–octane and methylcyclohexane–toluene mixtures, whose separation needs a higher selectivity (Fig. 4).

In these experiments the plateage was controlled by varying the solvent (as specified with each experimental point). A small change in the number of plates causes a sharp drop in K, since the separation in this case is largely determined by the selectivity rather than by the plateage.

The small thickness of the film in capillary chromatography introduces some substantial advantages in spite of the decreased selectivity. For readily adsorbed substances, the process of outer mass transfer is dominant in capillary chromatography. It follows that H and N are independent of the value of Γ_1 if the material is readily adsorbed. In the opposite case (sparingly adsorbed material) inner diffusion is the controlling process, and H increases with

Γ_i whilst N decreases. A decrease in N with Γ_i once again leads to a decrease in K_1, but with readily adsorbed substances the separation is improved more substantially than with weakly adsorbed materials if Γ_i is increased, *e.g.* the temperature is decreased, or the film thickness is increased.

The analysis and the results which have been presented demonstrate that a correct choice of method and of experimental parameters must involve both the static and the kinetic aspects of the separation criteria, which often present conflicting requirements.

To maximise the separation criterion certain conditions have to be fixed. A fixed analysis time is perhaps the commonest practical requirement, but we have considered the more general case in which limitations are imposed on the resistance to flow as well as on the time of the analysis.

For a fixed analysis time the separation criterion increases to a limiting value with flow rate. If the resistance to flow is fixed, the criterion decreases with flow rate to some other optimum value. High flow rates are desirable in the former case, low rates in the latter. The kinetic characteristics of the column are determined, in the two cases, by inner diffusion and by longitudinal diffusion, respectively.

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THE DIELECTRIC INVESTIGATION OF MOLECULAR RELAXATION IN POLYMERS

G.P.Mikhailov and T.I.Borisova

CONTENTS

I. INTRODUCTION

Owing to the structural peculiarities of polymers, molecular relaxation, a process representing the establishment of a statistical equilibrium, is one of the main factors determining their mechanical, electrical, and other properties[1].

The literature now contains a great deal of experimental data on the investigation of relaxation processes in polymers by both dielectric and mechanical methods, on the basis of which several conclusions can be reached about the nature and the mechanism of relaxation. This is done by comparing the structure of macromolecules with the temperature and the frequency dependence of the dielectric and the mechanical losses, characterised by the tangent of the loss angle, tan δ, and by the dielectric permittivity ϵ' (or by the elastic modulus in the case of the mechanical properties).

High polymers are characterised by the occurrence of several processes of molecular relaxation, which are due to the thermal motion of different types of kinetic units, which may be portions of the main chain of the polymer (segments), side-radicals, or simply certain groups of atoms, that behave as independent units in the thermal motion. All such kinetic units can be described by their most probable relaxation time τ; units of a single type, which have complicated molecular interactions with their environment, can yield a spectrum of relaxation times. At the present time, however, no rigorous theory of molecular relaxation in polymers yet exists. Therefore the only method for arriving at general conclusions is to compare the structure of the polymer with the above properties.

A peculiarity of relaxation observed by the dielectric method is that the energy of the electric field applied to a polymer specimen is dissipated mainly in relaxation regions containing polar groups. Dipoles taking part in thermal motion acquire a preferential orientation in the direction of the electric field. As a result, two maxima usually appear in the frequency (or temperature) variation of tan δ for polymers. The dielectric permittivity also undergoes marked changes, increasing with rise in temperature and falling with increase in frequency.

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A peculiarity of relaxation observed by the dielectric method is that the energy of the electric field applied to a polymer specimen is dissipated mainly in relaxation regions containing polar groups. Dipoles taking part in thermal motion acquire a preferential orientation in the direction of the electric field. As a result, two maxima usually appear in the frequency (or temperature) variation of tan δ for polymers. The dielectric permittivity also undergoes marked changes, increasing with rise in temperature and falling with increase in frequency.

Molecular relaxation, observed by the method of dielectric losses and polarisation, may be divided into two main types – the relaxation of polar radicals or of a polar monomer unit of the macromolecule, and relaxation of these same polar radicals together with portions of the main chain, *i.e.* the relaxation of segments[1]. This has been established for polymers of very different structures, linear and branched, containing rings in the chain, partly crystalline or completely amorphous (for example, polymers of vinyl chloride, methyl methacrylate, and its homologues, methyl acrylate and its homologues, cellulose esters, carbonates, amides, etc.).

In most papers on dipole dielectric losses the view is developed that one type of relaxation, due to the mobility of polar side-radicals or, in conformity with the terminology which we have adopted, to dipole–radical losses, can occur only within a definite temperature range corresponding to the vitreous state of the polymer, whereas a second type, so-called dipole–elastic losses, occurs only in polymers above the embrittlement point T_c. This is probably because the frequencies commonly used to measure tan δ and ϵ' correspond to relaxation times τ of dipole–radical losses at temperatures below T_c and to those of dipole–elastic losses above T_c. In the case of poly(methyl methacrylate), however, we have been able to observe dipole–radical losses at a frequency of 5 Mc/s at 190°, *i.e.* 85° above T_c.[2,3]

It can thus be accepted that dipole–radical losses are not peculiar to relaxation in the vitreous state of polymers, but, as was to be expected, can be observed in the rubber-like state if the period of the applied field is comparable with the relaxation time of these types of losses at the given temperature.

Nevertheless, with several polymers (the halogenated styrenes) it has not yet been possible to detect any appreciable dipole–radical losses at frequencies between 10 and 10^{10} c/s.[4] The molecular forces due to interaction between the benzene rings are apparently so strong that there is hardly any orientation of the CCl dipole in an electric field within this temperature and frequency range.

This hypothesis is supported by relaxation data obtained by the dielectric loss method by Müller and Huff with stretched polystyrene films, for which dielectric losses having maxima were observed below T_c.[5] The stretching of polystyrene opens up the structure of the polymer, thereby increasing the mobility of the phenyl groups.

Thus the dipole–radical losses observed in high polymers represent that type of molecular relaxation which is due to movement of polar side-groups while the main chain remains fixed during the time of observation (*i.e.* during a time comparable with the period of oscillation of the applied field). This determines the characteristic laws of dipole–radical losses. For example, the position of tan δ_{max} (or ϵ''_{max}) for different temperatures and frequencies for losses of this type is independent of the presence of impurities of low molecular weight (external plasticisers)[6], and also of the stretching of the specimen[7]. Internal plasticisation (copolymerisation) may, as will be shown below, give different effects depending on how the mobility of the polar side-group is changed.

If the period of the applied field is sufficiently long, dipole–elastic losses due to movement of portions of the main chain together with the polar attachments, *i.e.* to segmental thermal motion in the polymer, can be observed at certain temperatures. The laws characteristic of this type of loss will, of course, be determined by the relaxation behaviour of a corresponding set of kinetic units (segments), which cannot be very long. Willbourn has shown that, in the case of linear polymers, a segment can consist of 3 or 4 methylene groups[8]. No essential differences arose in the study of relaxation processes in branched and in unbranched polymers[9]. This also suggests that the kinetic units are considerably shorter than the distances between the points at which branching occurs, so that the latter have no effect on the mobility of the segments.

The position of tan δ_{max} for dipole–elastic losses as a function of frequency and temperature is greatly affected by the introduction of substances of low molecular weight, the relaxation time of the process being reduced. Cross-linking of the macromolecules has the opposite effect, impeding their movement and increasing the relaxation time of the dipole–elastic losses[10,11].

According to the few published data, the stretching of polymer specimens, which leads to orientation of the main chains, increases the relaxation time for the dipole–elastic losses[7], but this is probably not a general rule. The work of Kargin and Slonimskii[12] shows that under certain conditions stretching loosens the polymer structure, increases intermolecular distances, and weakens the interactions[12]. In such cases the relaxation times of the processes should fall.

Change in the chemical structure of the monomeric unit in the polymer chain has a still greater effect on the dipole–elastic than on the dipole–radical losses. Introduction both of polar and of non-polar groups, which may be added either directly to the main chain or to the side-group, is of importance here.

Hoff *et al.*[13] have made this type of observation on a series of polymethacrylates. Deutsch *et al.*[14] have shown that replacement of an α-methyl group is poly(methyl methacrylate) by a polar group such as Cl, which occupies about the same volume, retards the segmental motion of the macromolecules to a still greater extent. Polar effects are intensified when CH_3 is replaced by CN. Increase in the length of the side-group, also contributes to an increase in mobility of the chain segments by diminishing the molecular interaction. For successive members of a homologous series, the region in which tan δ for dipole–elastic losses passes through a maximum is systematically shifted to lower temperatures.

Recently great attention has been paid to the examination of the spectrum of relaxation times in the mechanical and dielectric study of relaxation processes. Here must be mentioned in the first instance the work of Ferry and his collaborators[15,16]. The method of reduced variables, suggested by Ferry, Williams, and Landel, enables the distribution of τ to be calculated.

Unfortunately, the range of application of this method is limited to cases in which the form of the distribution function for τ does not change with temperature – this is its chief premise. Our work has shown that, at a given temperature, at least two relaxation processes may occur in a polymer, which are caused by the presence of two independent sets of units with their own relaxation times[2,3].

The temperature coefficient of relaxation, or, as it is usually called, the apparent activation energy, can differ almost tenfold for the two processes. As a result, the distribution spectra of relaxation times for the two processes may approach one another and overlap in a certain temperature–frequency range. In this region, of course, the relation $\epsilon'' = \varphi(t^\circ)$ will continuously change its form with variation of temperature, thus making it impossible to apply Ferry's method. Such a situation is observed with polymers of homologous series of alkyl methacrylates and chlorinated alkyl acrylates, poly(methyl acrylate), poly(vinyl acetate), [17] etc.

In this case the formal theory of Cole and Davidson[18] can be used to resolve the partly superposed processes and to examine them separately.

II. EFFECT OF STRUCTURE OF POLYMER CHAINS ON MOLECULAR RELAXATION

1. Copolymers of Methyl Methacrylate and Methyl Acrylate with Styrene

The influence of chain structure on molecular relaxation is clearly shown in the dielectric properties of copolymers. By varying the percentage of one of the components in the copolymer, it is possible to change both the flexibility of the chain and the nature of the molecular interaction.

We shall describe results obtained in an investigation of dielectric losses and polarisation in copolymers of methyl methacrylate (MMA) with styrene (ST)[19] and of methyl acrylate (MA) with styrene[20].

Figs. 1 and 2 illustrate respectively the relationships $\tan\delta = \varphi(t^\circ)$ at a frequency of 20 c/s for MMA–ST copolymers of four concentrations by weight, and the functions $\tan\delta = \varphi(f)$ for a few copolymers of MMA with different styrene contents. In this temperature and frequency range, all specimens exhibit two regions of molecular relaxation where $\tan\delta$ passes through a maximum.

In conformity with the accepted terminology, dielectric losses at temperatures below T_c (= 110° for PMMA) must be regarded as dipole–radical losses, while those observed above the temperature of vitrification and caused by relaxation of the polymer chain are termed dipole–elastic losses.

Fig. 2 shows that the plots of $\tan\delta = \varphi(f)$ also exhibit two regions in which $\tan\delta$ passes through a maximum, the high-frequency part of the curves being associated with dipole–radical losses, and the low-frequency portion with dipole–elastic losses. These results, like those of several other investigations, show that dipole–radical processes are by no means peculiar to the vitreous state of polymers, but under suitable experimental conditions can be observed also in polymers which are in the rubberlike state.

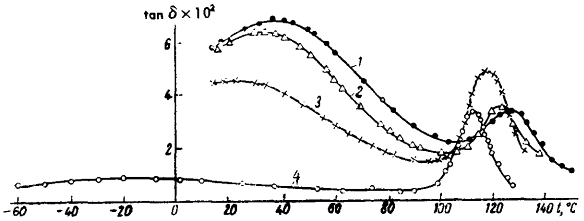


Fig. 1. Plots of $\tan\delta = \varphi(t^\circ)$ at a frequency of 20 c/s for MMA–ST copolymers containing different proportions of MMA: 1) 100%; 2) 93.3%; 3) 80.5%; 4) 24.4%.

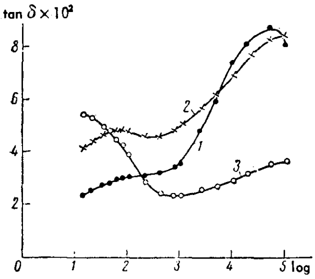


Fig. 2. Plots of $\tan\delta = \varphi(f)$ for MMA–ST copolymers:
1) 90.2% MMA, 125°; 2) 80.5% MMA, 122.5°; 3) 55.5% MMA, 109°.

Figs. 1 and 2 show also that the regions of $\tan\delta_{\max}$ are displaced to lower temperatures (Fig. 1) or to higher frequencies (Fig. 2) as the proportion of the polar MMA in the copolymer is decreased. The latter observation confirms that the relaxation times τ of both processes decrease when the concentration of the polar component is reduced.

Figs. 3 and 4 give plots of $\log f_m = \varphi(T^{-1})$ for a series of copolymers of styrene containing different amounts of methyl methacrylate, f_m being the reciprocal $(2\pi\tau)^{-1}$ and T the absolute temperature. Fig. 3 represents dipole–radical relaxation, and Fig. 4 dipole–elastic relaxation.

Table 1 lists activation energies for dipole–radical processes obtained from the slopes of the straight lines in Fig. 3. It can be seen that the value of $U_{\text{d.r.}}$, the activation energy for dipole–radical relaxation, increases as the percentage of MMA is raised.

It is extremely difficult to obtain an analogous concentration dependence for the activation energies of the dipole–elastic processes, since in many cases the true position of $\tan\delta_{\max}$ for the corresponding losses is distorted by the partial superposition of the region of dipole–radical relaxation. It is quite certain however, that for all polymers the slope of the straight line $\log f_m = \varphi(T^{-1})$ has no physical

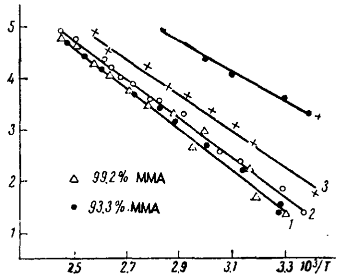


Fig. 3. Plots of $\log f_m = \varphi(T^{-1})$ for dipole–radical losses in MMA–ST copolymers containing different proportions of MMA:
1) 99.2% and 93.3%; 2) 90.2%; 3) 80.5%; 4) 55.5%.

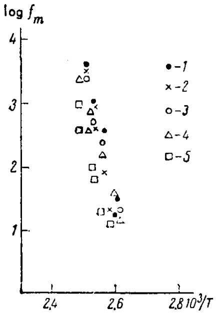


Fig. 4. Plots of $\log f_m = \varphi(T^{-1})$ for the dipole–elastic process in MMA–ST copolymers containing different proportions of MMA: 1) 18%; 2) 24.4%; 3) 40.5%; 4) 55.5%; 5) 80.5%.

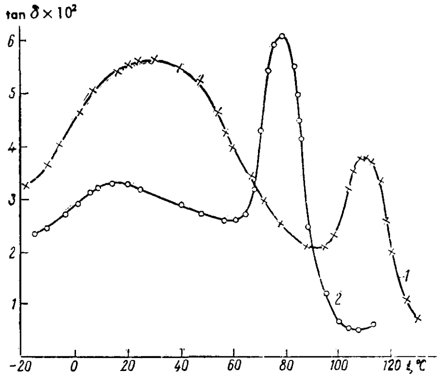


Fig. 5. Plots of tan δ = $\varphi(t°)$ at a frequency of 20 c/s for MMA–MA copolymers having the approximate MMA contents: 1) 80%; 2) 50%.

TABLE 1. Activation energy $U_{d.r.}$ of dipole–radical processes.

% MMA	55.5	80.5	90.2	93.3	99.2
kcal mole^{-1}	13.4	16.2	17.5	17.7	18.3

meaning as regards dipole–elastic losses, since it corresponds to energies of the order of 100 kcal mole^{-1}. Shishkin[21] has shown that the slope of this plot represents not an activation energy but the temperature coefficient of the relaxation frequency. This remark applies also to dipole–radical losses, but the temperature coefficient in this case has not such a high value, and therefore, within the limits of error, the slope of the straight line $\log f_m = \varphi(T^{-1})$ can be taken as the activation energy of the corresponding relaxation process.

On relating the results thus obtained to the structure of the copolymers under investigation, we conclude that, if τ is a measure of the mobility of kinetic units, this mobility increases with increasing concentration of styrene in the copolymers for both relaxation processes. With dipole–elastic losses this effect is less distinct (Fig. 4), since the temperature of vitrification of polystyrene is only 20°–30° lower than that for poly(methyl methacrylate).

A feature of the structure of poly(methyl methacrylate) is the presence of an α-CH_3 group, which causes steric hindrance to the development of relaxation processes. Introduction of styrene links diminishes the concentration of methyl groups in the chain, thereby increasing the mobility of the kinetic units corresponding to both dipole–radical and dipole–elastic relaxation.

This can be proved by results obtained for dielectric losses in MMA–MA copolymers. Fig. 5 shows that, as the concentration of methyl groups decreases, the value of tan δ_{max} for dipole–radical losses falls, and its position is displaced to lower temperatures. The magnitude of tan δ_{max} for dipole–elastic losses increases as the chain becomes increasingly mobile due to the reduction in the proportion of the α-methyl groups. Thus the introduction of styrene links into the PMMA chain and replacement of a proportion of the α-CH_3 groups in this polymer by hydrogen atoms produce qualitatively the same effect.

We suppose that intermolecular interaction is predominant in the case of dipole–radical losses. Increase in the styrene content of the polymer chain loosens the structure of the polymer by weakening steric hindrance due to the presence of methyl groups; this causes a decrease in the relaxation times and in the activation energy (Table 1).

With dipole–elastic losses the relaxing chain segment consists of monomeric styrene and methyl methacrylate links randomly distributed in the copolymer. Study of the effective dipole moments of the monomeric units has shown that intramolecular interaction predominates with dipole–elastic relaxation[22]. As the styrene content of the copolymer chain increases, therefore, this form of molecular interaction will be increasingly determined by the structure of the styrene, not the methyl methacrylate, monomeric unit.

Since the probability of finding styrene units in neighbouring links in the chain and in the space around the segment is greater at low MMA concentrations, the intramolecular interaction of the phenyl radicals is evidently weaker than that of the methyl methacrylate monomeric units.

It can be seen from Fig. 6 that tan δ_{max} for dipole–elastic losses passes through a maximum when the copolymer contains 60% of MMA. The appearance of this maximum can be explained by the action of two opposing factors. The first is the elimination of the steric effect of the α-CH_3, which blocks the movement of the chain. Introduction of styrene links into the macromolecule diminishes the quantity of such retarding units, so that the value of tan δ_{max} increases. Secondly, with decrease in the concentration of methyl methacrylate in the copolymer the number of dipoles per unit volume falls, so that the value of tan δ_{max} also decreases. At MMA contents between 100 and 60 wt.% the decrease in polarity of the polymer chain is masked by the first factor, *i.e.* by the steric effect of CH_3; with further decrease in the number of polar links, the second factor becomes dominant, and tan δ_{max} falls.

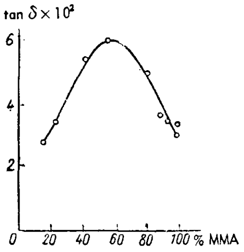


Fig. 6. Values of tan δ_{max} for dipole–elastic losses in MMA–ST copolymers as a function of the MMA content. Frequency 20 c/s.

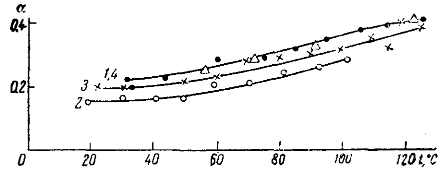


Fig. 7. Dependence of relaxation-time distribution parameter α on temperature for MMA–ST copolymers containing different proportions of MMA:
1) 24.5%; 2) 40.5%; 3) 55.5%; 4) 93.3%.

Recently the hypothesis that polymers are characterised not by a single τ, describing a given relaxation process, but by a set of relaxation times, has been generally recognised. In order to analyse the spectra of τ for molecular relaxation observed in this work, circular diagrams were plotted for the complex dielectric constant[18], and by means of them the distribution parameters α of the relaxation times were calculated.

The value of α defines the width of the spectrum, a value of unity indicating that the process is described by a single relaxation time.

Fig. 7 shows plots of $\alpha = \varphi(t\,°)$, calculated from data for dipole–radical losses, for four copolymers of this type with different compositions. The curves show firstly that the distribution parameter α corresponding to the vitreous state is only about half that for the rubberlike condition. This means that the polymer is more homogeneous in structure in the latter condition. Secondly, α depends on the composition of the copolymer. The higher the concentration of one component, the greater the value of α and the more homogeneous is the structure of the polymer.

Calculations of the distribution parameters α for dipole–elastic losses give a value of the same order as that for dipole–radical losses at temperatures above T_c. It is hard to estimate the variation in the spectrum of relaxation times for dipole–elastic processes because the two relaxation regions overlap at high temperatures. Nevertheless, the basic assumption that the scatter of τ is less and the structure of the polymer is more homogeneous, is confirmed.

Fig. 8 shows plots of $\tan\delta = \varphi(t\,°)$ at a frequency of 1 kc/s for copolymers of MA with three different concentrations of styrene. For this copolymer, two regions of dielectric relaxation losses are also observed in which tan δ passes through a maximum. The right-hand maximum is due to dipole–elastic relaxation, while the losses observed on the left-hand portion must be ascribed to dipole–radical relaxation.

This system is characterised by a different law governing the value of tan δ in the region of the maximum: Fig. 9 shows that for dielectric losses of both types, $\tan\delta_{max}$ increases linearly with the MA concentration within the limits of error of the measurements.

The temperature at which tan δ passes through a maximum does not change with the concentration of the polar

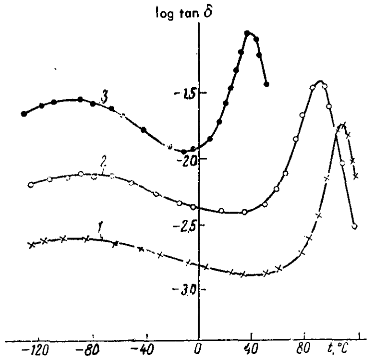


Fig. 8. Plots of log tan δ = $\varphi(t°)$ at a frequency of 1000 c/s for MA–ST copolymers containing different proportions of MA:
1) 14%; 2) 40%; 3) 100%.

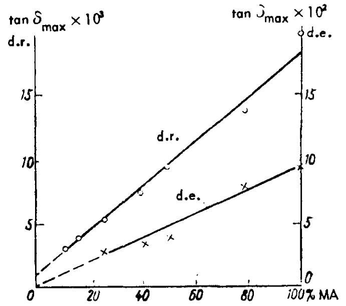


Fig. 9. Values of tan δ_{max} for dipole–radical (d.r.) and dipole–elastic (d.e.) losses in MA–ST copolymers as a function of the MA content. Frequency 1000 c/s.

component in the case of dipole–radical losses, but increases with rise in the styrene content of the chain for dipole–elastic losses.

These results are shown more fully by the plots of $\log f_m = \varphi(T^{-1})$ in Fig. 10. Points representing the dipole–radical process for different compositions of the MA–ST copolymer lie on a single straight line. Consequently the most probable relaxation time τ for this process is independent of the proportion of the polar component. In other words, introduction of styrene does not affect the mobility of the polar group in the side-chain.

Comparison of this result with data for MMA–ST copolymers makes it evident that markedly different effects are produced by the introduction of styrene into MMA and MA chains respectively. In the former case, as already stated, the styrene links open up the structure of the polymer by diminishing the influence of the α-CH_3 groups, and thereby increase the mobility of the side-radical.

Results identical with those for the MA–ST system have been obtained also for the copolymer of methyl vinyl ketone with styrene[20].

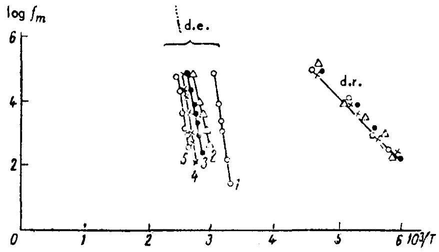


Fig. 10. Plots of $\log f_m = \varphi(T^{-1})$ for dipole–radical (d.r.) and dipole–elastic (d.e.) losses of MA–ST copolymers having different MA contents:
1) 100%; 2) 78%; 3) 49%; 4) 39%; 5) 23%.

2. Comparison of Relaxation Properties of Atactic and Isotactic Polymers

Investigation of molecular relaxation by the dielectric loss method in isotactic poly(methyl methacrylate) and polystyrene has shown that the stereoregularity of the chain has a marked effect on the relaxation properties of polymers[23].

The plots of $\tan \delta = \varphi(t°)$ for atactic and isotactic amorphous PMMA at a frequency of 20 c/s in Fig. 11 show that the stereoregularity of structure of the polymer chain affects both dipole–elastic and dipole–radical relaxation processes. The value of $\tan \delta_{\max}$ for dipole–elastic losses in isotactic PMMA is three times as great as the corresponding value for the atactic polymer, while the observed dipole–radical losses have become somewhat smaller (by a factor of about 1.4). This results in a change in the distribution of dipole losses characteristic of PMMA: in the isotactic polymer, as in other vinyl polymers, the maximum value of the dipole–elastic losses is greater than that of the dipole–radical losses.

The redistribution of dipole losses in the case of the stereoregular polymer is accompanied by a reduction in the most probable relaxation time for the dipole–elastic process, as is indicated by the shift in the corresponding $\tan \delta_{\max}$ region to lower temperatures. From the plots of $\tan f_m = \varphi(T^{-1})$ in Fig. 12, based on temperature and frequency measurements, it is seen that the relaxation time of the dipole–radical process is also somewhat lower in isotactic PMMA than in the atactic polymer.

The activation energy of the dipole–radical process does not change greatly on passing to a polymer having a regular chain, its value being 24 instead of 21 kcal mole^{-1}. As before, the apparent activation energy of the dipole–elastic process remains very high, 138 kcal mole^{-1}, and it can be regarded only as a temperature coefficient of the relaxation time.

Fig. 11 includes also data for a sample of PMMA whose molecules should, from the conditions of polymerisation, have an intermediate degree of regularity. Comparison of plots of $\tan \delta = \varphi(t°)$ obtained at the same frequency readily

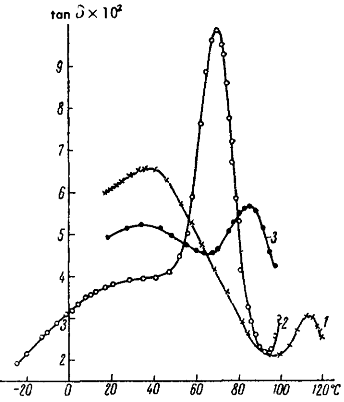


Fig. 11. Plots of $\tan \delta = \varphi(t°)$ at 20 c/s for samples of PMMA having different degrees of stereoregularity:
1) atactic PMMA; 2) with a high degree of regularity (isotactic); 3) with a lower degree of regularity.

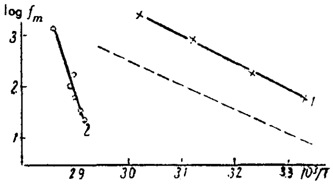


Fig. 12. Plots of $\log f_m = \varphi(T^{-1})$ for isotactic PMMA:
1) dipole–radical losses; 2) dipole–elastic losses. Broken line — analogous relationship for dipole–radical losses in atactic PMMA.

suggests that the dielectric loss method can serve qualitatively as a sensitive indicator of the regularity of a polymer chain.

Examination of the temperature dependence of tan δ for such a non-polar polymer as polystyrene also revealed a difference in the dielectric properties of isotactic and atactic specimens. By comparison with the atactic polymer, partly crystallised isotactic polystyrene has a range of temperatures in which the dipole–elastic losses are extremely diffuse. This diffuseness may, perhaps, be due to the superposition of two or more relaxation processes taking place in the crystalline and the amorphous regions of the polymer.

3. Polyesters

A study of the dipole relaxation of polyesters, especially those containing aromatic nuclei in the chain is of great interest. Some of them possess great thermal stability ($T_c > 200°$), which has attracted attention from the point of view of technical use. We shall consider here the results of an investigation of the temperature–frequency dependence of the dipole losses of polyesters based on "dian" (also called DPP) (bis-2-*p*-hydroxyphenylpropane) and some aliphatic and aromatic acids[24]. The structural formulae and the relative concentration *n* of aromatic nuclei in the chain, which was calculated as the ratio of the number of nuclei to the number of other atoms in the repeating unit of the chain, are set out in Table 2.

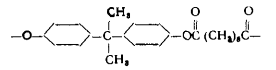
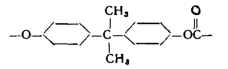
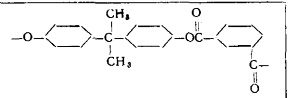
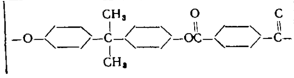
These polyesters (other than PDS) are partly crystalline; this introduces some specific features into the relationships characteristic of dielectric properties, but it does not affect the general validity of the results.

The temperature plots of tan δ for these polyesters at a frequency of 20 kc/s (Fig.13) reveal the occurrence of two relaxation processes in these materials. One is due to segmental movement of the chains (region of dipole–elastic losses), and the other to the mobility of the dipole groups (dipole–radical type of losses).

The temperatures t_{max} corresponding to tan δ_{max} for dipole–elastic losses rise with increase in the relative concentration *n* of aromatic nuclei given in Table 2, and hence the most probable relaxation time for the dipole–elastic process also increases with rise in *n*. However, the number of aromatic nuclei in the chain is not the only factor governing the relaxation time of this process. Account must be taken of the crystallinity of a given specimen, since crystallisation of a polymer is known to entail an increase in the relaxation time of the dipole–elastic process with a simultaneous reduction in the corresponding value of tan δ_{max}.

Comparison of the results in Fig.13 and Table 2 shows that the concentration of aromatic nuclei in the chain does not affect the relaxation times of dipole–radical processes. The value of τ is then determined by the chemical structure of the acid from which the polyester has been synthesised.

TABLE 2. Structural formulae of the polyesters and relative concentration *n* of aromatic nuclei in the chain.

Conventional designation	Repeating unit	Structural formula of repeating unit	*n*
PDS	dian* sebacate		0.154
PDC	dian carbonate		0.500
PDI	dian isophthalate		0.600
PDT	dian terephthalate		0.600

* Bis-2-*p*-hydroxyphenylpropane.

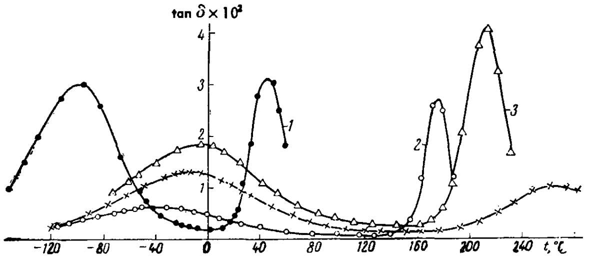


Fig. 13. Plots of tan δ = φ(t°) at a frequency of 20 kc/s for polyesters:
1) PDS; 2) PDC; 3) PDI; 4) PDT.

In PDS, a polyester based on an aliphatic acid, the relaxation time of the dipole–radical process is determined by the mobility of the linear section consisting of eight methylene groups, to which is directly linked a C=O dipole. The temperature–frequency region in which tan δ passes through a maximum corresponds to that in which Willbourn observed the relaxation of linear polymer chains containing ⩾4 CH_2 groups[8].

In PDC, PDI, and PDT, as also in poly(ethylene terephthalate),[25] the region of dipole–radical losses is observed over about the same range of frequencies and temperatures. A common feature of these polyesters is that their synthesis is based on aromatic acids, the carbonyl groups being directly linked to the aromatic nucleus. The roughly identical relaxation times and the similar values for the activation energies (11–13 kcal $mole^{-1}$) compel us to assume that dipole–radical losses are due to the mobility of small sections of the chains, containing COO ester groups.

This conclusion differs from that reached by Reddish in discussing experimental results on the dielectric properties of poly(ethylene terephthalate)[25]. He links the dipole–radical losses with the movement of terminal hydroxyl groups. A control experiment in which such losses are measured for polyesters of different molecular weight also disproves this statement.

In the study of the nature of dipole–radical losses in polyesters with aromatic rings in the chain, the results of an investigation of mixed polyesters are of great interest[26]. These materials are cocondensates synthesised from "dian" (or ethylene glycol) and two different acids – terephthalic and sebacic, or terephthalic and adipic – the relative proportions of the acids being varied.

Fig. 14 shows plots of tan δ = φ(t °) at a frequency of 400 c/s for several cocondensates, the compositions of which are given in Table 3.

The existence of (only) one region of dipole–elastic losses for each of the mixed polyesters is a proof of the random distribution along the chain of components based on the different acids, for example dian sebacate and dian terephthalate.

Fig. 14 shows that mixed polyesters are characterised by the presence of two partly overlapping regions of dipole–radical losses. Comparison of plots of tan δ = φ(t °) for polyesters based on a single acid with those for mixed polyesters, *i.e.* those prepared from two acids, suggests that the occurrence of two processes of dipole–radical relaxation is due to the presence of two types of polar radicals in the chain, one formed from a COO group together with an aliphatic acid radical, and the other from this group combined with an aromatic acid radical. Owing to the difference in mobility of these groups, *i.e.* to the difference in corresponding relaxation times, it is possible to observe both processes of dipole–radical relaxation.

Actually, the rough separation of the tan δ_{max} regions for these processes shows that, according to its temperature–frequency location and its magnitude as well as the concentration of acid radicals of a given type, each can be identified with the corresponding process of dipole–radical relaxation of the single-component polyester.

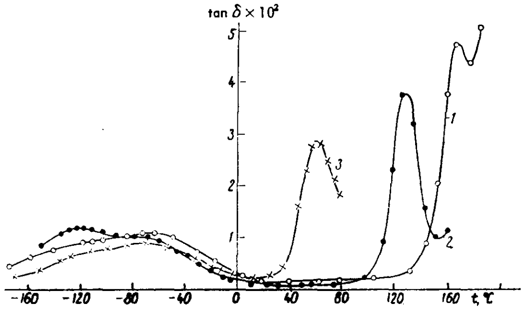


Fig. 14. Plots of tan δ = φ(t°) at 400 c/s for mixed polyesters:
1) TAD-60; 2) TSD-60; 3) TSE-90.

TABLE 3. Composition of mixed polyesters.

Conventional designation	Acid			Alcohol	
	concentration in moles				
	terephthalic	sebacic	adipic	dian	ethylene glycol
TAD-60	0.6	—	0.4	1	—
TSD-60	0.6	0.4	—	1	—
TSE-90	0.9	0.1	—		1

It can thus be regarded as proved that, in both mixed and single-component polyesters, the dipole–radical losses are due to relaxation of the polar COO group, the most probable relaxation time for this process being determined by the mobility of the portion of the chain directly linked to this group.

III. EFFECT OF STRUCTURE OF MONOMER UNIT ON THE MOLECULAR RELAXATION OF POLYMERS

This type of investigation has been carried out with the following polymers – poly(methyl acrylate) PMA, poly(propyl acrylate) PPA, poly-(2-chloroethyl acrylate) PCEA, poly(vinyl acetate) PVA, poly(vinyl butyrate) PVB, and poly-(vinyl β-chloropropionate) PCVP.[27]

The dipole–elastic relaxation of some of these polymers has been investigated also by Fuoss and Mead[28], and the dipole–radical relaxation by Broens and Müller[29]. It has been established that in PVA the dipole losses are due to rotation of acetate groups about the oxygen atom linking them with the main chain of the polymer. Thurn and Wolf[30] carried out similar studies on a very broad basis, and established a link between the relaxation processes observed by mechanical and by dielectric methods. With polymers in the vitreous state these workers discovered several loss regions in which tan δ passes through a maximum. These were most clearly defined in the case of mechanical losses. In particular, with PVA the temperature dependence of the mechanical losses twice passes through a maximum in the region below T_c, while corresponding jumps are observed in the dielectric permittivity ϵ'. They point out that, owing to the superposition of the relaxation processes, it is difficult to determine a relaxation time for each of them. Therefore it also becomes extremely difficult to establish a link between the observed secondary processes (dipole–radical processes in our terminology) and definite groups of atoms.

Hoff *et al.*[13] have studied molecular relaxation in an extremely large number of polymethacrylates by a dynamic mechanical loss method. By varying the structure of radicals substituted in α and β positions, they showed very clearly with what radical or group a given relaxation process was associated. From the temperature shift in the region in which tan δ_{max} occurred, it was possible to assess the changes which had occurred in the structure of the monomer unit, in the flexibility of the polymer chain, in the polarity, and in steric effects. No quantitative comparisons are given in the paper.

The investigations whose results will now be discussed were characterised by an attempt to establish not only with what group of atoms or polar radical of the monomer unit a given relaxation process was associated, but also to make some quantitative comparisons. It was of interest to compare polymers of similar chemical constitution but having side-chains differing in structure, for example PMA and PVA, etc.

The quantities tan δ_{max}, the temperature t_{max}, and the frequency f_m corresponding to tan δ_{max}, and the temperature dependence of these (two) quantities were adopted as the directly observable properties, and activation energies U and the distribution parameter α were calculated from them.

Fig. 15 shows plots of log tan δ at a frequency of 1 kc/s against temperature for the six polymers investigated. Measurements were made also of tan δ as a function of frequency over the range 20–10^5 c/s at several constant temperatures. In the case of PMA the frequency range was extended to 10^{10} c/s. Fig. 15 shows that with each polymer tan δ passes through two maxima, the dielectric losses being of a relaxation type.

With dipole–radical losses the relationship log tan δ = $= \varphi(t\,°)$ is distinguished by the great spread with respect to temperature, which may be an indication of the presence of a broad spectrum of relaxation times for this process. Values of log tan δ in the region of dipole–radical losses are practically identical for PCEA and for PCVP. These polymers are isomers, differing in the mode of linkage of the polar group with the chain. In the region of dipole–elastic losses, on the other hand, the values of tan δ differ markedly. Thus the linking of a polar group through an oxygen atom (in PCVP) considerably increases both $\tan\delta_{\max}$ and the relaxation time of the dipole–elastic process (in comparison with PCEA), without having any effect on the dipole–radical losses.

Fig. 16 shows plots of $\log f_m = \varphi(T^{-1})$, *i.e.* of the relation between relaxation frequency and the reciprocal of the absolute temperature. An important feature is that all the straight line sections for dipole–radical relaxation, when extrapolated to $f_{\max} = 0$, converge to one point, representing a relaxation frequency of the order of 10^{13} c/s. This indicates that this relaxation process can be regarded as a single "act", and is consistent with the well-known views of Debye[31] and of Frenkel'[32] on the passage of a dipole from one equilibrium position to another in the course of thermal motion. This is evidence also of an exponential variation of relaxation time with temperature, of the form $\tau = \tau_0 \exp(U/kT)$, where $\tau_0 = (2\pi f_0)^{-1}$ and U is the activation energy.

The results obtained for PMA deserve special attention. Above 6×10^8 c/s the frequency of both relaxation processes probably varies according to a single exponential law.

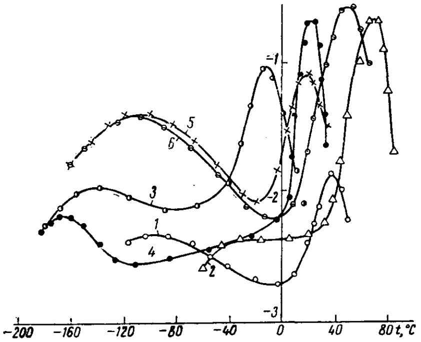


Fig. 15. Plots of log tan δ = $\varphi(t°)$ at 1000 c/s for polymers having isomeric side-chains:
1) PMA; 2) PVA; 3) PPA; 4) PVB; 5) PCEA; 6) PCVP.

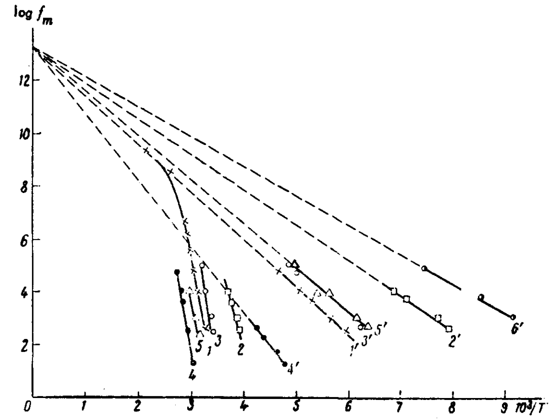


Fig. 16. Plots of $\log f_m = \varphi(T^{-1})$ for dipole–elastic (unprimed numbers) and dipole–radical (primed numbers) losses:
1, 1') PMA; 2, 2') PPA; 3, 3') PCEA; 4, 4') PVA; 5, 5') PCVP; 6') PVB.

Fig. 17 comprises cyclic loci of the complex dielectric constant (ε″ and ε′) for PMA and PVA. The temperatures at which these quantities were measured are indicated on the left of the curves. The diagrams for temperatures of -86° and -35° correspond to dipole–radical relaxation of these polymers, and those at 32° and 58° are plotted from data for dipole–elastic losses. Although measurements were made on the polymer in the rubberlike state, the loss factor ε″ is large at high frequencies, and ε′ at a frequency of 10^{10} c/s is about 30% greater than n^2, the square of the optical refractive index of the material. Such a large discrepancy may be ascribed partly to the superposition of dipole–radical relaxation at high frequencies. However, in the case of cyclic loci plotted from data for dipole–radical losses the value of ϵ_∞ is again greater than n^2. This could be explained by assuming the existence of a third relaxation process.

In summarising this section, let us examine the next two tables.

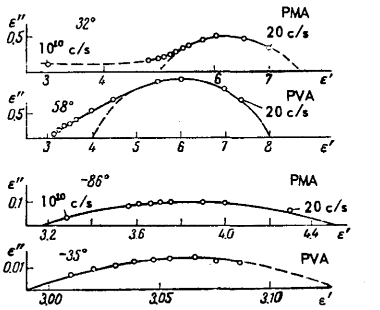


Fig. 17. Cyclic loci of complex dielectric constant for PMA and PVA.

TABLE 4. Comparison of data for dipole–radical losses in isomeric polymers.

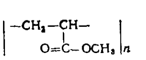
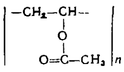
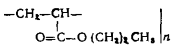
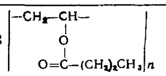
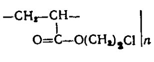
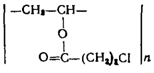
Structural formula of polymer	$f = 1$ kc/s		U, kcal mole^{-1}	α at t_{max}	Structural formula of polymer	$f = 1$ kc/s		U, kcal mole^{-1}	α at t_{max}
	t_{max}, °C	tan $\delta \times 10^2$				t_{max}, °C	tan $\delta \times 10^2$		
PMA  $\left\|-CH_2-\underset{O=C-OCH_3}{\underset{\|}{CH}}-\right\|_n$	−96	2.7	9.6	0.2	PVA  $\left\|-CH_2-\underset{\underset{O=C-CH_3}{\underset{\|}{O}}}{\underset{\|}{CH}}-\right\|_n$	−30	0.40	10.5	0.2
PPA  $\left\|-CH_2-\underset{O=C-O(CH_2)_2CH_3}{\underset{\|}{CH}}-\right\|_n$	−142	1.3	5.7	0.2	PVB  $\left\|-CH_2-\underset{\underset{O=C-(CH_2)_2CH_3}{\underset{\|}{O}}}{\underset{\|}{CH}}-\right\|_n$	−165	0.65	4.8	0.2
PCEA  $\left\|-CH_2-\underset{O=C-O(CH_2)_2Cl}{\underset{\|}{CH}}-\right\|_n$	−110	3.9	8.6	0.2	PCVP  $\left\|-CH_2-\underset{\underset{O=C-(CH_2)_2Cl}{\underset{\|}{O}}}{\underset{\|}{CH}}-\right\|_n$	−109	3.5	8.9	0.2

TABLE 5. Comparison of data for dipole–elastic losses in isomeric polymers.

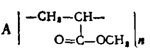
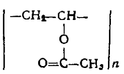
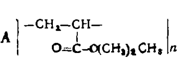
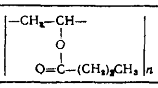
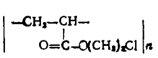
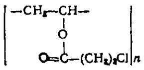
Structural formula of polymer	$f = 1$ kc/s		U, kcal mole^{-1}	α at t_{max}	Structural formula of polymer	$f = 1$ kc/s		U, kcal mole^{-1}	α at t_{max}
	t_{max}, °C	tan $\delta \times 10^2$				t_{max}, °C	tan $\delta \times 10^2$		
PMA  $\left\|-CH_2-\underset{O=C-OCH_3}{\underset{\|}{CH}}-\right\|_n$	33	9.9	42	0.4	PVA  $\left\|-CH_2-\underset{\underset{O=C-CH_3}{\underset{\|}{O}}}{\underset{\|}{CH}}-\right\|_n$	71	25.6	48	0.6
PPA  $\left\|-CH_2-\underset{O=C-O(CH_2)_2CH_3}{\underset{\|}{CH}}-\right\|_n$	−14	9.3	33	0.5	PVB  $\left\|-CH_2-\underset{\underset{O=C-(CH_2)_2CH_3}{\underset{\|}{O}}}{\underset{\|}{CH}}-\right\|_n$	—	21.3	31	0.5
PCEA  $\left\|-CH_2-\underset{O=C-O(CH_2)_2Cl}{\underset{\|}{CH}}-\right\|_n$	17	9.1	39.6	0.4	PCVP  $\left\|-CH_2-\underset{\underset{O=C-(CH_2)_2Cl}{\underset{\|}{O}}}{\underset{\|}{CH}}-\right\|_n$	50	27.8	46.5	0.6

Table 4 sets out the structural formulae of the monomeric units of the polymers, the temperature t_{max} of the maximum in tan δ at a frequency of 1 kc/s, and the magnitude of tan δ_{max} at this frequency, together with activation energies calculated from the results in Fig.15.

Examination of the data for PMA and PVA in the first line of Table 4 shows that apart from U all these quantities differ sharply for these polymers. This difference is especially marked in the case of t_{max} and tan δ_{max} (the former is 60° lower, and the latter is 7 times as great, for PMA). Thus the presence in PVA of an oxygen atom directly linked with the chain lowers the mobility of the polar radical, or in other words increases the relaxation time of the monomer unit of PVA.

The second line of Table 4 gives data for the third representatives of the homologous series of poly(alkyl acrylates) and poly(vinyl esters), namely poly(propyl acrylate) and poly(vinyl butyrate). It is seen that lengthening the side-group by two methylene groups shifts the region of tan δ_{max} to markedly lower temperatures. At the same time the value of tan δ_{max} for PPA has decreased to almost half that for PMA, and the analogous change from PVA to PVB has increased tan δ_{max} by almost 50%. Thus consideration of the values of tan δ_{max} for the third members of these series indicates that they are characterised by having more similar values of the dielectric loss (the values for tan δ_{max} differ only by a factor of 2).

It is also noteworthy that the temperature t_{max} fell more with PVB than with PPA, so that the region of dipole–radical relaxation for the former is now situated at lower temperatures. It is interesting that in the homologous series of poly(alkyl methacrylates) a fundamentally different variation of t_{max} for dipole–radical losses is obtained as the series is ascended. In effect, the work of Mikhailov and Borisova[3] has established that, for the first three members of this series, lengthening the alkyl group in the side-chain has no effect on t_{max} for dipole–radical losses. The same phenomenon, *i.e.* the absence of any effect on the position of the region of dipole–radical relaxation in passing from one homologue to another, was observed by Veselovskii for a series of acetals of poly(vinyl alcohol)[11].

As regards the data for PCEA and PCVP (third row in Table 4), introduction of a chlorine atom has removed the difference between the radical relaxation characteristics of these polymers. The presence of chlorine has raised t_{max} and increased tan δ_{max} for both polymers, which is consistent with our general postulate of the dominant role of intermolecular interaction in dipole–radical relaxation.

The distribution parameter α for relaxation times calculated at t_{max} (*i.e.* at the temperature at which tan δ passes through a maximum at a frequency of 1 kc/s) is, within the limits of error, identical for all the polymers in Table 4, and has a very low value. This indicates a broad spectrum of relaxation times describing dipole–radical processes.

Table 5 is compiled from results for dipole–elastic relaxation in the same polymers. These data introduce nothing fundamentally new, but merely confirm the general principle that elongation of the side-chain by an increase in size of the alkyl group shortens the relaxation time for the dipole–elastic process. This effect can be partly compensated by the introduction of a polar group, *e.g.* a CCl dipole, into the side-chain.

The higher values of tan δ_{max} for PVA and PCVP can be explained by a decrease in dipole correlation within the chain, since the effective dipole moment calculated from values of the dielectric permeability corresponding to the dipole – elastic region of relaxation (according to the cyclic diagrams) is greater for PVA than for PMA.

The value of the distribution parameter α for relaxation times of dipole–elastic processes is considerably higher than analogous values for dipole–radical processes, and may approach unity, as in the case of PVB at 30°. This is common to all polymers, and can be interpreted as evidence that a polymer has a more homogeneous structure in the rubberlike state.

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ELECTRODE PROPERTIES OF ION-EXCHANGE MEMBRANES

E.A.Materova and F.A.Belinskaya

CONTENTS

I. INTRODUCTION

During recent years a large number of papers have appeared both in our own country and abroad on the theory and practical application of membranes made of ion-exchange materials. Such membranes can find wide use as indicator electrodes in potentiometric analysis, as well as in various processes of electrodialysis.

The study of ion-exchange membranes had already begun in the previous century. It was then discovered accidentally that, during the separation of electrolyte solutions by some plant and animal membranes, a potential difference is produced at the membrane–solution boundary. These membranes were termed "semipermeable" or "selective" membranes, since they allowed some substances to pass through and prevented others from doing so. Since then, the electrochemical properties of selective membranes have been studied by biologists and physical chemists[1-10].

Work on the glass electrode has assisted the development of the electrochemistry of semipermeable membranes and their use as electrodes. The study of the electrode and ion-exchange properties of glass membranes and the successful application of the glass electrode to the determination of pH gave an impetus to the production of reversible electrodes made of other ion-exchange materials. For this purpose use was made of various minerals, clays, collodion, cellulose, and other substances capable in various degrees of exchanging ions. Since 1949 ion-exchange resins have come to be used for the preparation of selective membranes, and of electrodes which are reversible with respect to a large number of cations and anions.

The present review discusses work on the theory of membrane potentials and the use of ion-exchange membranes made of mineral and organic exchangers as reversible electrodes with special emphasis on membranes made of ion-exchange resins, which are the most promising for practical application.

II. THEORIES OF MEMBRANE POTENTIALS

The first serious attempt at a theory of membrane processes was made by Michaelis[9,10] who visualised a membrane as a capillary structure penetrated by pores of various diameters. Owing to the unequal sizes of pores, molecules, and ions, the membrane acts as a sieve, stopping some ions and molecules and allowing others to pass through. The smaller the pores the greater is the part played by fields of force due to electrical charge, adhesion, and surface tension at the pore surfaces. The most important is the field due to the electric charge produced by the adsorption of ions on the pore walls, forming an electrical double layer which affects the mobility of the ions in the pores of the membrane.

The magnitude of the e.m.f. arising at the boundary between two electrolyte solutions separated by a membrane is expressed by Michaelis by an equation analogous to that deduced by Nernst for the diffusion potential between two electrolyte solutions

$$E=\frac{U_c-U_a}{U_c+U_a}\,\frac{RT}{ZF}\ln\frac{C_1}{C_2}\,, \qquad (1)$$

$$E=\frac{RT}{ZF}\ln\frac{U_{c_1}+U_a}{U_{c_2}+U_a}\,. \qquad (2)$$

Eqn. (1) relates to the case in which the membrane separates solutions of the same electrolyte at concentrations C_1 and C_2. Eqn. (2) is valid for the case in which the membrane separates solutions of different electrolytes at the same concentration (the electrolytes have the same anions but different cations).

In Eqns. (1) and (2) the symbols U_c and U_a denote the mobilities of cation and anion in the membrane, which are assumed to be independent of the concentration. From Eqn. (1) the ratio of the mobilities of cation and anion in the membrane can be calculated, and from Eqn. (2) the mobility ratio for two cations in the membrane if the mobility of the anion is put equal to zero.

The Michaelis theory played an important part in the electrochemistry of membrane phenomena. However, its fundamental equations (1) and (2) are approximate and the theory takes no account of interaction between solutes and the membrane material. The main concept of this theory – the link between the capillary and the electrical properties of membranes – has been further developed in papers by foreign and especially by Soviet scientists. The school of I. I. Zhukov at Leningrad University has carried out a large programme of work on the electrochemical properties of capillary systems, mainly membranes used in electrodialysis[11].

An important contribution to the electrochemistry of membrane processes taking into account their ion-exchange nature was made by the theory of fixed charges put forward independently by Teorell[12,13] and by Meyer and Sievers[14,15]. This theory is based on the view that organic membranes contain a number of dissociating ion-exchange groups, for example carboxyl or amino groups, which are strongly bound to the macromolecule. The immobile, fixed charges resulting from dissociation of these groups are balanced by an equivalent quantity of free, mobile ions of opposite sign. At the membrane–solution interface a Donnan equilibrium is established corresponding to the condition:

$$y(y+A)=C^2\,, \qquad (3)$$

where y is the concentration of electrolyte which has penetrated into the membrane, and is equal to the concentration of ions of the electrolyte having the same sign as the fixed ions; A is the concentration of fixed ions in the membrane, expressed as the number of ionised groups per unit volume of water contained in the pores of the membrane; C is the concentration of electrolyte in the external solution; and $(y + A)$ is the concentration in the membrane of ions of opposite charge to the fixed ions.

The Donnan equilibrium results in the establishment at the membrane–solution interface of a potential termed the "Donnan potential":

$$E_{\mathrm{Don}}=\frac{RT}{F}\ln\frac{C}{y+A}\,. \qquad (4)$$

The authors of the theory of fixed charges deduced an equation for the potential of a membrane separating two solutions of a uni-univalent electrolyte at concentrations C_1 and C_2. They assumed the electrolyte solution to be completely dissociated and ideal both inside and outside the membrane, and the concentration of fixed ions in the membrane to be constant. They regard the potential of the membrane as the sum of two Donnan potentials at the membrane–solution interfaces and a diffusion potential within the membrane. Expressing this last potential by means of the Henderson equation, they give the following expression for the concentration membrane potential:

$$E=E_{1\mathrm{Don}}-E_{2\mathrm{Don}}+E_{\mathrm{diff}}=\frac{RT}{F}\left[u\ln\frac{x_2+Au}{x_1+Au}+{}^1\!/_2\ln\frac{(x_1+A)(x_2-A)}{(x_1-A)(x_2+A)}\right],$$
$$u=\frac{U_c-U_a}{U_c+U_a}\,,\qquad x=\sqrt{4C^2+A^2}\,. \qquad (5)$$

The subscripts 1 and 2 relate here to two solutions having concentrations C_1 and C_2. From the point of view of the theory of fixed charges, the main characteristics of the membranes are the quantity A, which the authors term the "selectivity constant", and the ratio of the mobilities of cation and anion in the membrane (U_c/U_a). Both characteristics are assumed to be independent of the concentration of the solutions. Meyer and Sievers[14,15] suggested a graphical method for calculating A and (U_c/U_a) from the dependence of the membrane potential on the concentration of the solution. If the selectivity constant or the concentration of fixed ions $A \ll C_1$ and C_2, it can be neglected in Eqn. (5), which simplifies to

$$E=\frac{U_c-U_a}{U_c+U_a}\,\frac{RT}{F}\ln\frac{C_2}{C_1}\,. \qquad (6)$$

Eqn. (6) is the equation for the diffusion potential. If $A \gg C_1$ and C_2, Eqn. (5) yields the usual Nernst expression for the e.m.f. of a concentration cell:

$$E=\frac{RT}{F}\ln\frac{C_2}{C_1}\,. \qquad (7)$$

This last equation corresponds to the case in which the membrane is permeable only to ions of one sign, and can be regarded as an electrode which is reversible with respect to these ions.

Thus the concentration of fixed ions is important when it is comparable with the concentration of the external solution. When $C \gg A$, the potential is determined by the ratio of the external concentrations and the ratio of the ionic mobilities in the membrane; when $C \ll A$, only the ratio of external concentrations is significant.

The theory of fixed charges constituted a major advance in understanding the nature of membrane phenomena. It indicated a method for preparing membranes of high electrochemical activity, by showing that the selectivity of the membrane with respect to ions of a given sign is determined primarily by the concentration of dissociated ion-exchange groups in the membrane. However, this theory is approximate in character, and can represent real processes only in the few cases in which A and U_c/U_a remain constant.

Even in the early papers in which the theory of fixed charges was analysed and criticised, it was concluded[16-19] that the theory gives only the qualitative dependence of membrane potentials on concentration. A weakness of the theory is the neglect of the interaction of ions in solution and in the membrane. Meyer and Bernfeld[15] attempted to allow for this interaction by replacing A by the quotient $A/(l_a + l_c)^{\frac{1}{2}}$, where l_a and l_c are the partition coefficients of anions and cations between solution and ion exchanger, *i.e.* the actual ratio of the ionic activity coefficients in the external solution and in the membrane.

Marshall[20] replaced ionic concentrations in Eqn. (5) by activities in the external solutions and in the membrane. Instead of the quantity A he used the concept of the mean activity of the mobile ions inside the membrane, the charge on which was balanced by that on the fixed ions in the membrane. Manecke and Bonhoeffer[21,22] also employed the concept of a mean activity coefficient of the mobile ions in the membrane ($f_\pm$), and expressed the Donnan equilibrium by the equation

$$a^2 = C_+C_-f_\pm^2 = C_-(C_- - A) \times f_\pm^2 \,, \tag{8}$$

where a is the mean activity of the electrolyte in the solution, C_+ and C_- are the concentrations of mobile ions in the membrane, and A is the concentration of fixed ions.

The development of synthetic ion-exchange resins provided ample opportunities for the preparation of ion-exchange membranes having a high concentration of fixed ions (with a large exchange capacity). Such membranes were used to test the Teorell–Meyer–Sievers theory more rigorously. This test could be carried out by comparing values of A and U_c/U_a given by the Meyer–Sievers graphical method with the same quantities determined by other methods (A analytically, U_c/U_a by a radioactive tracer method).

Bonhoeffer *et al.*[23,24] tested the applicability of the theory of fixed charges to resins of different acid strengths. They showed that the theory is consistent with the behaviour of a strongly acid cation exchanger, but in the cases of a weakly acidic cation exchanger and a weakly basic anion exchanger, one of the chief premises of the theory – the constancy of A – is not satisfied. These workers considered that this was due to the change in swelling properties and in the number of dissociated groups in the membrane with variation in the pH.

Helfferich[25] studied the variation of A with concentration for a strongly basic anion exchanger, and concluded that this quantity cannot be regarded as constant even after the introduction of corrections ($f_\pm$ or l), especially at high concentrations. Direct determinations of ionic mobilities in the membrane showed that these vary little with concentration, so that the divergence between theory and experiment can be explained primarily by different types of complicated ionic interactions within the membrane, which depend substantially on concentration.

Summarising the discussion of the theory of fixed charges, we can say that this theory is only qualitatively or, in a few cases, semi-quantitatively consistent with experiment. In spite of all the corrections and refinements which several workers have tried to introduce into the equation for membrane potentials, no rigorous calculation can be made of the e.m.f. of cells containing different types of membranes and different electrolytes. Membrane processes are in general very complicated. A theoretical consideration of these processes must take account of the transfer of solvent (the swelling properties of the exchanger), interaction between ions in solution and with the material of the membrane, and also kinetic factors in the exchange and transport of ions.

The fundamental assumptions of the theory of fixed charges were developed and refined during 1951–1953 by Teorell[26-28] in his extended theory of fixed charges. He tried to consider the various properties of charged and neutral membranes, with and without a current passing through them, from a single viewpoint. Great attention was paid to mass transfer through membranes and to related processes. Teorell analysed these phenomena by applying to such processes the Nernst–Planck equation describing the distribution of ions in the case of free diffusion of univalent ions:

$$\Phi' = -U'C'\left(\frac{RT}{C'}\frac{dC'}{dx} \pm F\frac{d\varphi}{dx}\right) \,, \tag{9}$$

where Φ' is the flux, *i.e.* the quantity of ions of a given type entering the membrane through unit surface in unit time, U' is the mobility of cation or anion, C' is the concentration of ions of the given type within the membrane, x is a space co-ordinate in the direction of motion of the ions through the membrane, φ is a potential depending on x, R is the gas constant, F the Faraday (positive for cations, negative for anions), and T the absolute temperature. By applying Eqn. (9) to various membrane processes, Teorell deduced a series of equations for calculating the conductivity, the spatial distribution of ions in the membrane, the potential, etc. In the generalised theory too, he considered the membrane potential to be the sum of two Donnan potentials and a diffusion potential, this last being calculated on the basis of a Planck distribution.

Teorell's generalised equation for membrane potential, like any equation containing a diffusion potential, can be approximately solved only for particular cases – when the membrane separates (1) two solutions of the same electrolyte at different activities, and (2) solutions of two different electrolytes of the same activity. The generalisation made by Teorell describes complex membrane phenomena and their interplay, and is therefore a fruitful approach. However, the value of his general equations is limited by the fact that they can be solved only in the simplest cases.

A theoretical examination of membrane phenomena has been made also in a series of papers by Schlögl and his collaborators[29-35]. In these, membrane processes are regarded as non-equilibrium or, under certain conditions, as steady-state processes. Schlögl's work is mainly devoted to an investigation of charged membranes carrying a current, the diffusion of ions through a membrane, and the determination of membrane potentials and ionic mobilities in a membrane. Like Toerell, he uses the Nernst–Planck equation (9) for the ionic flux to calculate the diffusion potential within the membrane.

According to Schlögl, the membrane potential is the sum of a diffusion potential within the membrane and two Donnan potentials at the two phase boundaries:

$$E=\frac{RT}{F}\int_{\mathrm{I}}^{\mathrm{II}}\frac{U_-C_- - U_+C_+}{U_-C_- + U_+C_+}\,d\ln a+\frac{RT}{2F}\ln\frac{f_-^{\mathrm{I}}\,f_+^{\mathrm{II}}}{f_+^{\mathrm{I}}\,f_-^{\mathrm{II}}}\quad, \tag{10}$$

where U and C are the mobilities and concentrations respectively of ions inside the membrane, a is the activity of the external electrolyte solution, and f_+ and f_- are the ionic activity coefficients of the external solution.

The last term in Eqn. (10) contains the activity coefficients of individual ions, which cannot be determined experimentally. However, in combination with appropriate terms which must appear in a real cell owing to the auxiliary electrodes, the last term does give measurable quantities. Eqn. (10) is based on the same Teorell–Meyer–Sievers ideas, but it takes account of the interaction between the ions and with the material of the membrane. In order to integrate Eqn. (10) the dependence of U_+C_+ and U_-C_- on the external concentrations must be known. In some cases this dependence can be evaluated experimentally, for example by a radioactive tracer method[29].

Membrane potentials are considered from rather different standpoints in papers by the Japanese investigators Nagasawa and Kobatake[36,37], in which the potentials of collodion, regenerated cellulose film, and parchment membranes, and of the glass electrode are discussed on the basis of Eyring's theory of reaction rates. The equation derived by Kobatake and Nagasawa for the membrane potential is

$$E=\frac{RT}{F}\left[d\ln\left(\frac{c_1}{c_2}\right)-\alpha\ln\left(\frac{c_1+\beta}{c_2+\beta}\right)+\left(\frac{U_+-U_-}{U_++U_-}\right)\ln\frac{c_1+\beta}{c_2+\beta}\right], \tag{11}$$

where c_1 and c_2 are the concentrations of the electrolyte solutions separated by the membrane, α and β are constants depending on the nature of the membrane and the ionic mobilities, and U_+ and U_- are respectively the mobilities of cation and anion in the membrane.

With a small charge on the membrane and in concentrated solutions Eqn. (11) simplifies to the usual equation for the diffusion potential, analogous to Eqn. (6). In dilute solutions and for dense membranes Eqn. (11) can be written in the form

$$E=\alpha\frac{RT}{F}\ln\frac{c_1}{c_2}\,, \tag{12}$$

where α is a function of the charge and the ionic mobilities in the membrane. For a glass electrode and membranes of ideal selectivity, $\alpha = 1$.

In 1953 Scatchard[38] published a paper in which membrane potentials were regarded from the viewpoint of the general thermodynamic relationships for the e.m.f.'s of voltaic cells with transport. His equation for the e.m.f. of a voltaic cell containing a membrane is

$$E\left(\frac{F}{RT}\right)=E_{0\alpha}\frac{F}{RT}-\sum_i \nu_{i\alpha}\,d\ln a_{i\alpha}-\int_{\alpha}^{\omega}\sum t_{i\alpha}\,d\ln a_i- \tag{13}$$

$$-\sum_i \nu_{i\omega}\ln a_{i\omega}-E_{0\omega}\frac{F}{RT}\,,$$

where $E_{0\alpha}$ and $E_{0\omega}$ are the standard potentials of the two electrodes, $\nu_{i\alpha}$ and $\nu_{i\omega}$ are the numbers of moles of the i-th species formed at the corresponding electrodes by the passage of one Faraday, a_i is the activity of the i-th species, and t_i is the number of moles of substance i transported in the direction of the positive current by the passage of one Faraday.

The integral contains various transport numbers (t_i) of ions and neutral molecules, in particular of solvent molecules. Scatchard applies the general thermodynamic equation (13) to several cases, and makes careful allowance for the transport of solvent, which, like that of anions through a cation-exchange membrane, may lead to departures of the membrane from ideal behaviour. He examines the influence of hydrolysis (*i.e.* partial replacement of cations in a cation exchanger by hydrogen ions, and of anions in an anion exchanger by hydroxyl ions), diffusion, and other processes on the e.m.f. of a voltaic cell containing a membrane. He considers from the same viewpoint the bi-ionic potential, *i.e.* the potential difference obtained by separating solutions of two different electrolytes by means of an ion-exchange membrane. Scatchard comments that the Teorell–Meyer–Sievers method – division of the potential into two Donnan potentials and a diffusion potential – provides no opportunity for separating the main terms from the correction terms in the expression for the e.m.f. of a cell with a membrane, and that neglect of the transport of water, which in several cases is of considerable importance, is a shortcoming of previous theories. The transport of water was allowed for also in papers by Stewart and Graydon[39,40]. The equation which they derived for the membrane potential can be obtained by integrating Eqn. (13) under simplifying conditions.

A completely different approach to the electrical properties of semipermeable membranes was made by Staverman and Overbeek[41-44], who showed that in general membrane processes not far from thermodynamic equilibrium can be described by non-equilibrium thermodynamics, which is based on two principles – a linear law for the rate of approach of the system to a state of equilibrium, and Onsager's reciprocal relation. Investigations in which non-equilibrium thermodynamics is employed to explain membrane phenomena are still few[44-47], but definite progress may be expected from theories based on these ideas.

Work carried out in the Department of Physical Chemistry of Leningrad University on the electrode properties of ion-exchange membranes in pure and in mixed electrolyte solutions has used the ideas of Nikol'skii's ion-exchange theory of the glass electrode[48]. According to this theory, the electrode behaviour of a glass, as well as of an ion-exchange resin, which is selective to ions of one sign, depends on the composition of the solution and on the strength of bonding of the ions with the solid phase. This effect is determined by the magnitude of the equilibrium constant (exchange constant K) for the exchange of A^+ and B^+ ions between the solid phase (s) and the solution (l):

$$B_l^+ + A_s^+ \rightleftarrows A_l^+ + B_s^+ , \tag{14}$$

$$K = \frac{a_{A+l} \times a_{B+s}}{a_{A+s} \times a_{B+l}} .$$

The magnitude of the exchange constant defines the selectivity of the ion-exchange electrode with respect to one of the exchangeable ions. According to the ion-exchange theory, the electrode potential relative to a reference, *e.g.* calomel, electrode can be represented by the equation:

$$E = E^\circ + \frac{2.3RT}{ZF}\log(a_{A^+} + Ka_{B^+}) , \tag{15}$$

where a_{A^+} and a_{B^+} are the activities of A^+ and B^+ ions respectively in the solution. Belinskaya and Materova[49,50] have shown that, in spite of their substantial difference in physical and chemical properties, glass and organic ion-exchange resins possess similar electrode properties, since their electrode behaviour is governed by the exchange of ions between solid phase and solution. Thus it has been shown for resins of different acid strengths that the ability of the acidic group to undergo dissociation determines the selectivity towards hydrogen ions of electrodes made of these ion exchangers. The same is observed also with glasses having different exchange constants for hydrogen and metal ions[48]. This similarity confirms the applicability of the ideas of the ion-exchange theory of the glass electrode to resin membrane electrodes having ideal selectivity.

III. ELECTRODE PROPERTIES OF ION-EXCHANGE MEMBRANES

1. Mineral Membranes

In this section we shall discuss mineral membranes, which, like glass electrodes, may possess various electrode functions. The early workers in this field used various aluminosilicate minerals capable of ion exchange. Thus, for example, Tendeloo[51-53] chose the minerals muscovite and fluorite, and Marshall[54] selected apophyllite and chabazite. Such an electrode was prepared by attaching a polished plate of the mineral to a glass tube and soaking it in a solution of an appropriate electrolyte ($CaCl_2$, $BaCl_2$, KCl, etc.). These mineral membrane electrodes proved unsatisfactory. They had high resistances, and only roughly responded to a change in concentration of the corresponding cation. The use of clay materials for the preparation of electrodes seemed more promising. In 1941 Marshall and Bergman[20] worked out a method for preparing membranes from the colloidal fraction of electrodialysed clays (montmorillonite, beidellite). A suspension of the clay was poured on to a smooth surface and dried. The resulting film was attached to a glass tube, and an electrolyte solution of known concentration was poured over it. Such electrodes were investigated by measuring the e.m.f. of the following cell:

$$\mathrm{Hg} \mid \mathrm{Hg_2Cl_2},\ \ \mathrm{KCl\,(sat.)} \mid \mathrm{soln.} \mid \mathrm{membrane} \mid \mathrm{soln.} \mid \mathrm{KCl\,(sat.)},\ \ \mathrm{Hg_2Cl_2} \mid \mathrm{Hg} .$$

The measured value was compared with the e.m.f. calculated from the Nernst equation, in which concentrations had been replaced by the activities of the cations in the two solutions†:

$$E = \frac{RT}{ZF}\ln\frac{a'_+}{a''_+} . \tag{16}$$

Marshall and his coworkers, and later Bose *et al.*, showed that clay mineral electrodes can be used to determine the activities of the following ions in pure dilute electrolyte solutions – K^+,[20,55] NH_4^+,[56] Na^+,[56,57] Mg^{2+},[55,58] Ca^{2+},[59,60] Mn^{2+},[61] Co^{2+},[61] Cu^{2+},[61] and Zn^{2+}.[61]

These workers applied to the experimental results the fundamental principles of the Teorell–Meyer–Sievers theory of fixed charges as modified by Marshall[62] to allow for the peculiarities of clay films.

Marshall's work showed that the electrode properties of clay membranes depend on the temperature to which the membranes have been heated, the nature of the clay, and the exchange cation. Heat-treatment (400°–600°) improves the mechanical properties of membranes, makes them more compact, and increases the charge per unit volume[57,63,64]. With the hydrogen form of montmorillonite, heat-treatment changes the selective properties of the membranes. Thus membranes heated above 450° are selective only towards singly charged ions, which enables the activity of such ions to be determined in the presence of ions carrying a double charge. The hydrogen form of montmorillonite heated at a lower temperature (up to 350°) is selective towards both types of ions. Membranes prepared from the potassium or the calcium form of montmorillonite are sensitive to both univalent and bivalent ions independently of the temperature of heat-treatment. Beidellite membranes react to a change in concentration of ions bearing one, two, or three charges.

Marshall proposed a method for determining ionic activities in mixed solutions based on the selective properties discovered in clay membranes[57-60,65-67]. The technique worked out for determining the activities of various ions was applied to the investigation of colloidal solutions and to obtaining titration curves for various clays[68-76].

Mineral electrodes possess several substantial defects, which limit their practical application. They have a high electrical resistance and low chemical and mechanical stability, and they act as reversible electrodes only within a very narrow range of concentrations, usually from 0.1–0.01 to 0.0001 N solutions for univalent cations, and from 0.01 to 0.0001 N for bivalent cations.

In 1948 Wyllie[77] was able to prepare membrane electrodes from fragments of shales. Such electrodes extended the range over which the electrode e.m.f. follows the change in sodium ion concentration roughly to 1 M NaCl.

2. Membranes Based on Some Organic Substances

Organic substances such as collodion, cellulose, proteins, etc. all possess weakly acidic or weakly basic properties and are able to exchange ions.

Collodion membranes were first studied in detail by Michaelis[9,10]. The so-called dried collodion membranes which he prepared, when placed between two different

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† Activity coefficients of the individual ions were calculated on the assumption that $f_{K^+} = f_{Cl^-}$.

electrolyte solutions, give potentials close to the theoretical values, *i.e.* to those calculated from the Nernst equation for the potential of a reversible electrode.

A great deal of knowledge on the various properties of collodion and protamine membranes has been obtained by Sollner and his coworkers[78-80]. They have described methods for the preparation of the membranes[81-86], membrane potentials in various electrolyte solutions[87-90], the resistance of the membranes[91-93], and the Donnan membrane equilibrium[18,78,94,95].

Sollner's work has shown that oxidised collodion can yield membranes possessing a low resistance (from a few down to one hundredth ohm cm^{-2}) and giving potentials in dilute solutions (< 0.1 M) which are close to the theoretical values. According to his results[80], the selectivity of collodion membranes is maintained in K_2SO_4 solutions up to a concentration (on the two sides of the membrane) of $0.2/0.1\,N$, while in KCl this limit is at $0.04/0.02\,N$, in LiCl $0.02/0.01\,N$, and in HCl $0.004/0.01\,N$. In more concentrated solutions the membranes begin to lose their selectivity towards the cation and allow anions to pass through in considerable quantities.

Collodion membranes impregnated with protamine possess anion-exchange properties. Their selectivity towards anions is somewhat less than that of oxidised collodion membranes towards cations.

Sollner ascribes the appearance of potentials on collodion membranes to the presence in the matrix of the membrane of active groups capable of dissociating, *e.g.* carboxyl groups[78,80,96]. In his opinion the electrochemical activity is determined by the exchange capacity of the membrane. Collodion differs from substances which are normally called ion exchangers only in the small number of groups capable of dissociation.

Sollner and his coworkers were the first to suggest the use of collodion membranes as electrodes for measuring the activity of cations – K^+, Li^+,[93,97,98] Na^+, NH_4^+, Mg^{2+},[93,97] Ca^{2+}, Rb^+, Cs^+.[78,80] In Sollner's opinion, protamine membranes can be used as electrodes reversible with respect to anions – BO_3^-, I^-;[93] R^-, Cl^-, ClO_3^-, ClO_4^-, NO_3^-, IO_3^-; and $CH_3.COO^-$.[95-98]

Collodion membranes were successfully used by Carr[99-101] to determine the activity of calcium, sodium, and chloride ions in protein solutions. In 1953 Shafershtein and Bulgakova[102] reported the use of oxidised collodion membranes to determine the activity of potassium and sodium ions in protein solutions. They concluded that the membranes could not be used at pH < 4.5. They suppose that at low pH values the dissociation of carboxyl groups is suppressed and the surface charge on the membrane is thereby decreased, the membrane itself becoming permeable to anions. The pH value of 4.5 mentioned by Shafershtein and Bulgakova can apparently be regarded, by analogy with the behaviour of resins having feebly acid groups[49], as a limit down to which hydrogen ions do not affect the potential of a membrane functioning as a metal.

Hirsch[103-105] has studied the effect of pH on the potentials of membranes made of oxidised cellulose film and of cellulose with a constant ratio of the salt concentration on the two sides of the membrane (0.03/0.003 M KCl or NaCl). Hirsch correctly attempts to find a link between the rise in potential with increase in pH and the exchange properties of the membrane material. However, the method proposed for calculating the dissociation constant of the acidic groups of the membranes from the curves relating membrane potential and pH cannot be regarded as correct, since the membrane potential is determined not only by the pH but also by the activity of the metallic ions.

3. Membranes Made of Ion-Exchange Resins

Ion-exchange membranes can be of two types depending on the methods of preparation – (1) homogeneous, consisting solely of the ion-exchange material, and (2) heterogeneous, which contain an inert binder in addition to the ion exchanger.

Homogeneous membranes are usually obtained in the synthesis of the resin, by completing resinification in special moulds. To confer mechanical strength on them, the membranes are sometimes poured on to various supports, networks of non-conducting inert materials. Homogeneous membranes have been prepared from strongly acid cation exchangers[106-113], weakly acid cation exchangers[114-116], strongly basic anion exchangers[21,25,116,117], and weakly basic anion exchangers[118].

Heterogeneous membranes can in principle be prepared from any resins by varying the nature of the binder and the resin content of the membrane. Among substances which can be employed as binders are polystyrene, poly(methyl methacrylate), polyethylene, poly(vinyl chloride), paraffin wax, collodion, rubber, various cements, etc.

Several methods exist for preparing heterogeneous membranes: (1) compressing[118] a mixture of the finely powdered resin and binder under pressure[110,119-131]; (2) milling an inert binder with the powdered resin[110,132-135]; (3) casting the membranes from solution or from a melt of the binder containing the powdered ion-exchange resin[49,128,136-141] or a polyelectrolyte type of material[80,137,142]; (4) treatment of inert membranes with the aim of conferring ion-exchange properties on them by adsorption, *e.g.* of dissolved sulphonated polystyrene with collodion[80,137,142], the sulphonation of polystyrene[135,143], etc.‡; (5) binding the swollen resin with Portland cement[119]. Descriptions of the methods for preparing various homogeneous and heterogeneous membranes can be found also in several review papers[144,145] and monographs[146-149].

Homogeneous membranes will obviously possess a lower resistance than non-homogeneous membranes prepared from the same resin. On the other hand, the mechanical strength of the latter is greater, since a wide selection of binders of great strength is available for their preparation, and the resin content of the membrane can be varied. Extensive information on the physical properties of membranes, mainly used in electrodialysis, is given in papers by Winger *et al.*[150], Trostyanskaya[133], Spiegler[110], and Osborn[149].

The first papers on the electrode properties of ion-exchange resin membranes appeared during 1949–1950. Kressman and Kitchener[120,151], Juda and McRae[152], and Wyllie and Patnode[121] described methods for making resin membranes and discussed the possibility of using such membranes as reversible electrodes for activity measurements in electrolyte solutions.

The materials chosen for investigation were cation exchangers possessing a considerable exchange cpacity or

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‡ Membranes obtained by this method may be regarded as either homogeneous or non-homogeneous.

a high concentration of fixed ions. These resins should, according to the Teorell–Meyer–Sievers theory, ensure that the membranes are highly selective towards cations. Wyllie and Patnode[121] made a detailed study of the electrode properties of Amberlite IR-1, Zeocarb, and Amberlite IR-100 membranes in NaCl solutions (the membranes were prepared by pressing a mixture of the powdered resin and polystyrene or methyl methacrylate). Although these workers measured the membrane potentials by means of voltaic cells with transport, for which no exact calculation can be made of the theoretical e.m.f. values, the measured membrane potentials confirmed the high selectivity of the membranes, which was maintained up to a comparatively high concentration of NaCl. Such results have not been obtained with any of the mineral or clay membranes studied up to the present. The simplicity of preparation, high electrochemical activity (selectivity towards anions or cations), comparatively low resistance, and the mechanical strength of resin electrodes have attracted the attention of many investigators.

During recent years resin membranes have been used as reversible electrodes to determine the activity of various electrolytes. Papers in which ion-exchange resin electrodes have been studied are listed, for convenience of classification, in the Table.

TABLE. Papers on the electrode properties of ion-exchange resin membranes.

Electrode function	Electrolyte	Reference	Electrode function	Electrolyte	Reference
H^+	HCl	42.121,124.128.137 142.143,154–157	NH_4^+	NH_4OH NH_4Cl $(NH_4)_2SO_4$	163 154 154
	H_2SO_4 H_3PO_4	154,155,156	Li^+	LiCl	124,126,156
	HNO_3	155	Ag^+	$AgNO_3$	156
	β-naphthol-sulphonic acid	154	Ca^{2+}	$CaCl_2$	126,156
			Mg^{2+}	$MgCl_2$	126
Na^+	NaCl	42,109,111,121.123, 124,128,153,154.156, 158,159,160	Ba^{2+}	$BaCl_2$	111,124,131,153,162
			Zn^{2+}	$ZnSO_4$	164
	Na_2SO_4	123,156,158	Cd^{2+}	$CdCl_2$ $CdSO_4$	124 164
	$NaNO_3$ Na_2SO_4 CH_3COONa $C_7H_5O_3Na$	156	Cu^{2+}	$CuSO_4$	124
			Mn^{2+}	$MnSO_4$	164
			Cl^-	NaCl	122.127.155.156
	sodium poly (vinyl sulphate)	158		KCl HCl	127.141,165.128,155
	sodium polyacrylate	161		$BaCl_2$ $MgCl_2$	155 127
K^+	KCl	21.111.115.123, 137,139,140,142.154, 156,157.162	Br^-	KBr	129
			NO_3^-	KNO_3	129
			CH_3COO^-	CH_3COONa	155
	K_2SO_4 $K_4Fe(CN)_6$	154 154	SO_4^{2-}	H_2SO_4 Na_2SO_4	128 122,127
	potassium polyacrylate	161		K_2SO_4 $MgSO_4$	127 127
			PO_4^{3-}	$NaHPO_4$ H_3PO_4	127 127

Special mention must be made of the work of Bergin and Heyn[163], which showed that cation-exchange membranes can be used to measure the activity of (NH_4^+) cations in alcoholic and aqueous–alcoholic solutions. In addition, measurements of membrane potentials have been made in several researches having quite different aims – determination of ionic transport numbers through the membrane from the e.m.f. of a voltaic cell[108,116–168], determination of concentration of fixed ions by the Meyer–Sievers graphical method[23,24], and determination of the selectivity characteristics of membranes[120,138,150,167]. Information about the electrode properties of membranes can be obtained also from the results in these papers.

The following methods are used to measure the activity or concentration in pure electrolyte solutions by means of membrane electrodes:

a) **Calculation from theoretical equation.** For this purpose we set up a voltaic cell without transport, of the type

$$\mathrm{Ag}\,|\,\mathrm{AgCl},\ \ \underset{a_1}{MCl_n}\,|\text{ membrane }|\,\underset{a_2}{MCl_n},\ \ \mathrm{AgCl}\,|\,\mathrm{Ag}, \tag{I}$$

where $n = 1, 2, \ldots$; or a cell with transport

$$\mathrm{Hg}\,|\,\mathrm{Hg_2Cl_2},\mathrm{KCl\,(saturated)}\,|\,M_mX_n\,|\text{ membrane }|\,M_mX_n\,|\,\mathrm{KCl\,(saturated)},\mathrm{Hg_2Cl_2}\,|\,\mathrm{Hg}. \tag{II}$$

From the measured e.m.f. and the known activity of one of the solutions, the unknown activity is calculated using the equation for the appropriate voltaic cell:

$$E_{\mathrm{I}} = \frac{\nu RT}{ZF}\,2.3\log\frac{a_{\pm}^{(2)}}{a_{\pm}^{(1)}}\,, \tag{17}$$

or

$$E_{\mathrm{II}} = E_{\mathrm{II}}^{0} + \frac{RT}{ZF}\,2.3\log a_i \approx E_{\mathrm{II}}^{0} + \frac{RT}{ZF}\,2.3\log a_{\pm}\,, \tag{18}$$

where E_{II}^{0} is a constant term in the e.m.f. of the voltaic cell, ν the number of ions into which a molecule of the electrolyte dissociates, Z the valency of the cation with respect to which the membrane is reversible, $a_{\pm}$ the mean activity of the electrolyte, and a_i the activity of the ion with respect to which the membrane is reversible.

The use of voltaic cells without transport enables the determination of activity to be thermodynamically more rigorous than that of cells with transport.

b) **Calculation from calibration curve.** If the electrode behaviour of the membrane is not theoretical, activities can be determined by means of a calibration curve obtained with solutions of known activity, as is done, for example, in work with glass electrodes.

c) **Titration to zero membrane potential.** In a voltaic cell of type I or II (having two identical auxiliary electrodes) the membrane is used to separate the electrolyte solution of unknown concentration from a definite quantity of water (or of a dilute solution of the electrolyte of known concentration). To the water is then added a standard, more concentrated solution of the same electrolyte until the e.m.f. becomes zero. The unknown concentration can be calculated from the volume of the standard solution used in the titration.

d) **Potentiometric titration.** This can be an acid–base or a precipitation titration, the ion-exchange resin electrodes serving as indicator electrodes reversible with respect to cations or to anions.

Such indicator electrodes have been widely used by Sinha[122,130] and later by Parsons[169] for the titration of hydrochloric acid with caustic soda, of sodium chloride with silver nitrate, potassium sulphate with barium chloride and barium acetate[122,130], and sodium sulphate and sulphuric acid with barium acetate[169].

In the first method the activity can be calculated only with membranes whose electrode behaviour is theoretical. Such membranes have been obtained from many strongly acidic resins[21,42,121,142,153,154,156,157,165] and from some feebly acidic resins containing carboxyl groups[42,123,156]. The other three methods are applicable both to electrodes which behave theoretically and those whose behaviour diverges somewhat from the theoretical.

The range of concentrations over which membrane electrodes can be used in pure electrolyte solutions depends on the nature of the membrane and of the electrolyte. At very low and high electrolyte concentrations there are departures from the linear relation between the potential of the membrane electrode and the logarithm of the mean electrolyte activity. According to the data of Schindewolf and Bonhoeffer[153] and of Kressman[154] deviations in dilute solutions begin at concentrations of $5 \times 10^{-4} - 10^{-5}$ M, and are explained by the chemical instability of the material of the vessels used for the potential measurements. In concentrated solutions the potential differs from the theoretical value for all membranes[109,114,137,153,154,156]. The electrode behaviour of cation-exchange resin membranes is maintained up to higher concentrations in solutions of acids than in salt solutions – HCl up to 1–4 M, [153-156] H_2SO_4 up to pH = 0 [154] and 4.48 M, [156] and H_3PO_4 up to pH = 0.[156] With electrodes reversible with respect to doubly charged ions the range within which a linear relationship between E and log $a_{\pm}$ is obeyed is smaller in uni-bivalent electrolytes[126,131,153] than in uni-univalent electrolytes.

The anionic behaviour of resin membranes has been less thoroughly studied than their cationic behaviour. Available results indicate that the membranes function as electrodes up to higher concentrations in solutions of uni-bivalent electrolytes than in those of uni-univalent electrolytes.

Deviations of the membrane potential from the theoretical value corresponding to the equation for the e.m.f. of a concentration cell with reversible electrodes may be primarily determined, at high electrolyte concentrations, by diffusion of the ion of the same sign as the membrane (Donnan sorption) and by transport of the solvent.

The behaviour of membrane electrodes in mixed electrolyte solutions is of great interest, but there are few papers on this topic, and they are almost all concerned with electrodes made of strongly acidic resins. Thus Manecke[21] investigated the behaviour of membranes made of a phenolsulphonic cation-exchange resin in mixed solutions of sodium and potassium chlorides, and concluded that such membranes are not specific with respect to the individual cations, their use requiring preliminary calibration of the electrodes in mixed solutions of known concentration.

Schindewolf and Bonhoeffer[153] have shown that the potentials of sodium electrodes based on a phenolsulphonic cation-exchange resin, with sodium chloride concentrations on the two sides of the membrane of $10^{-2}\,N/10^{-3}\,N$, are independent of pH only within the pH range 5–8. In a study of the electrode behaviour of sodium membranes from a sulphonated cation-exchange resin, Kressman[154], found the membrane potentials in 0.01 M sodium chloride solution to be independent of the hydrogen-ion concentration over the range pH 4–10. In the case of hydrogen membrane electrodes he showed[154] that the potassium ion affects the membrane potential when its concentration exceeds that of the hydrogen ions by a factor of 2.5. Kressman is inclined to explain the observed slight selectivity of sulphonated cation-exchange resin membranes towards the hydrogen ion by the greater mobility of the latter in the membrane as compared with the potassium and sodium ions.

Kahlweit[157] used membrane electrodes made of a phenolsulphonic resin to study the effect of additions of various acids on the activity coefficients of hydrochloric acid, and of additions of salts on those of potassium chloride. In isolated cases he obtained results close to published values, *e.g.* for the $HCl-HClO_4$ system.

Thus sulphonated resin electrodes exhibit no appreciable selectivity towards any cations. To obtain specific electrodes it was of interest to investigate the electrode behaviour of membranes made of selective resins.

Woerman *et al.*[138] studied the electrode properties of a resin which was selective towards potassium ions, owing to the presence in the resin of groups able to form a sparingly soluble compound with such ions. Electrodes made of this resin did not, however, exhibit the expected selectivity towards potassium ions. This was explained by the stable bonding of these ions making it possible for other ions to diffuse into the membrane. This conclusion was supported by independent measurements of the mobilities of potassium and sodium ions in the membrane. Since these results were obtained with only one resin, and no data were given for the behaviour of the membrane in pure solutions, the conclusions in this paper cannot be generalised to other possible cases of selective membrane electrodes.

More positive results are given in papers on the electrode properties of membranes made of resins containing active groups of different acid strengths[49,50]. Membranes from weakly acidic resins were shown to possess considerable selectivity towards hydrogen ions compared with sodium ions. Within certain limits, electrodes made of these resins enable pH measurements to be made in solutions of complicated composition. The ion-exchange character of membrane electrodes and their analogy with glass electrodes suggest that, with a correct choice of resin, electrodes might be obtained having the same high selectivity towards individual ions as that possessed, for example, by the glass electrode. The problem of increasing the selectivity of resin electrodes is bound up with the synthesis of special resins and with a detailed study of ionic mobilities in the resin phase. The production of selective electrodes will permit the solution of many practical problems of potentiometric pH control and of the determination of ionic activities in mixed electrolyte solutions.

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ORGANOSILICON COMPOUNDS OF FLUORINE

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CONTENTS

I. INTRODUCTION

The first compound of silicon and fluorine, silicon tetrafluoride, was prepared by Scheele in 1771.[1] However, organic derivatives of silicon fluorides were prepared only recently. In the last 10 to 15 years, owing to advances in the chemistry of organosilicon and organofluorine compounds, a great deal of research has been devoted to organosilicon compounds containing fluorine, in connection with attempts to combine the valuable properties of organosilicon and organofluorine materials and to obtain new polymers. A critical review of research in this field is therefore needed.

II. PHYSICAL PROPERTIES OF ORGANOSILICON FLUORINE COMPOUNDS

Fluorine is the most electronegative element of the Periodic System, and has the smallest covalent radius of the halogens. It forms a very stable bond with silicon. The difference between the Si–F and the C–F bond is a result of the properties of the silicon atom (Table 1). The electronegativity of silicon is considerably lower than that of carbon, and its covalent radius considerably larger. In contrast to carbon, silicon is able to use its 3*d* orbital to form bonds. Its co-ordination number is six.

The energy of the Si–F bond is, on average, 134 kcal × × mole^{-1}, considerably higher than the energies of bonds of silicon with other elements[2-5]. The average Si–F bond length is 1.56 Å,[6-20] similar only to silicon-hydrogen (1.49 Å) and silicon-oxygen (1.61 Å) bond lengths. The bonds with chlorine, bromine, and iodine are considerably longer, 2.02, 2.19, and 2.49 Å respectively. The Si–F bond length depends on the other atoms and groups linked to the silicon. Usually, the higher their electronegativity, the shorter is the Si–F bond.

Electron diffraction[6,9] and microwave spectroscopy[10-21], which is more precise, are used to determine the internal rotation barrier[19] and dipole moments of organosilicon

TABLE 1.

Element	Physical properties of atoms				Bond energy kcal mole^{-1}		Bond length, Å		Bond refraction, ml mole^{-1}	
	nuclear charge	electronic configuration	relative electro-negativity	co-ordination number	C	Si	C	Si	C	Si
C	6	$1s^22s^22p^2$	2.5	4	84.9	75.0	1.54	1.93	1.25	2.56
Si	14	$1s^22s^22p^6$ $3s^23p^2$	1.8	6	75.0	51.0	1.93	2.34	2.56	5.65
F	9	$1s^22s^22p^5$	4.0	—	102.0	134.0	1.36	1.54	1.72	1.50

compounds[11,19,20]. From microwave spectra Laurie[20] obtained the following Si–F bond lengths for a series of fluorosilanes:

	H_2SiF	H_2SiF_2	$HSiF_3$	SiF_4
Si–F bond length (Å)	1.595	1.577	1.565	1.54

Others have noted a similar change of Si–F bond length[16,19]. As the number of fluorine atoms attached to silicon increases, the bond lengths for other atoms attached to silicon change considerably, as a rule, becoming shorter. For the Si–F bond this shortening is illustrated by the following[21]:

	$(CH_3)_2SiHF$	CH_3SiHF_2	H_2SiF_2	$HSiF_3$
Si–F bond length (Å)	1.473	1.474	1.471	1.455

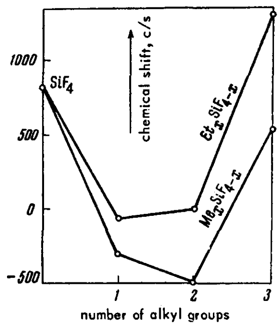
Vibration frequencies of the Si–F bond. The valency vibrations of the Si–F bond in fluorosilanes are in the 850–920 cm^{-1} region of the infra-red[22-24] and Raman spectra[22-28]. The frequency obviously depends on the radicals attached to silicon. According to Ebsworth *et al.*[22], it is 858 cm^{-1} in CH_3SiH_2F, and 916 cm^{-1} in $(CH_3)_3SiF$. The fluorine atoms, therefore, affect the vibration frequencies of the other bonds considerably, generally increasing them. Thus, the vibration frequency of the Si–H bond increases as more fluorine atoms are attached to silicon[21]. Moreover, the introduction of fluorine atoms into organic radicals, increasing their electronegativity, also increases the vibration frequency of the Si–H bond. Ponomarenko *et al.*[29,30] suggested a simple empirical relationship between the vibration frequencies (ν) of the Si–H and Si–D bonds and the effective electronegativity of silyl groups containing fluorine and other halogens:

$$\nu = AX_c,$$

where A is a constant, equal to 1011 for hydrides and 734 for deuterides of silicon, and X_c is the effective electronegativity of the silyl group. This relationship is obeyed by many silicon and germanium hydrides and deuterides.

Chemical shift in nuclear magnetic resonance spectra. This effect of an atom or radical bound to silicon on the properties of the Si–F bond is also exhibited in nuclear magnetic resonance spectra. The atoms or groups attached to silicon may strengthen or weaken the shielding of the fluorine atom by changing the character of the electron shell of silicon. This is manifested in nuclear magnetic resonance as the ^{19}F chemical shift. The Figure shows the change of chemical shift in methyl- and ethyl--silyl fluorides on gradual replacement of fluorine in SiF_4 by methyl or ethyl radicals[31,32]. The similar changes of chemical shift are explained by the superposition of two effects, namely shielding of ^{19}F owing to d_π-p_π bonding, and the inductive effect of the methyl and ethyl groups. Gradual replacement of methyl or ethyl groups by fluorine causes the chemical shift of the hydrogen atoms in the remaining groups to decrease[32].

Refraction of the Si–F bond. Warrick's value of 1.50 ml $mole^{-1}$ for the refraction of the Si–F bond is now generally adopted[33,34], though some workers accept the higher value, 1.95 ml $mole^{-1}$.[35] This discrepancy possibly arises because the refraction of the Si–F bond depends on the atoms and groups bound to silicon. Ponomarenko and Snegova[36] noticed that the discrepancy between the calculated and experimental values for molecular refraction increases with the number of fluorine atoms attached to silicon. Group refractions have been proposed for certain fluorine-containing organic radicals bound to silicon[37].



Dependence of the ^{19}F chemical shift on the number of fluorine atoms and alkyl groups attached to silicon.

The above properties of the Si–F bond have a considerable effect on the physical and chemical properties of organosilicon fluorine compounds.

Dipole moments of organosilicon fluorine compounds. Because of the large difference in the electronegativities between silicon and fluorine, the Si–F bond is polar, producing dipole moments in silicon fluorides (Table 2).

TABLE 2.

Compound	Dipole moment, D	Ref.	Compound	Dipole moment, D	Ref.
H_3SiF	1.27	20	$(C_2H_5)_2SiF_2$	2,23	38
H_2SiF_2	1.54	20	$C_2H_5SiF_3$	2 77	38
$HSiF_3$	1.268	2,20	$(C_6H_5)_2SiF_2$	2.57	38
CH_3SiHF_2	2.11	19	$(C_6H_5)_3SiF$	1,84	38
$(C_2H_5)_3SiF$	1.72	38			

Silicon fluoride complexes. The basic difference between silicon and carbon is in the ability of the former to use its 3*d* orbital to form complexes in which it is penta- or hexa-co-ordinated. Owing to the small covalent radius and high electronegativity of fluorine, silicon fluorides form complexes with amines, amides, alcohols, and other electron donors more readily than other silicon halides. The complexes known include: $SiF_4.2NH_3$,[39,40] $SiF_4.N(CH_3)_2CHO$,[40] $SiF_4.2[N(CH_3)_2CHO]$,[40] $SiF_4.[H_2NCH_2.CH_2NH_2]$,[41] $SiF_4.(CH_3OH)_6$,[42] $SiF_4.(CH_3OH)_8$,[42] and $SiF_2.(OR)_4$.[42] Inorganic complexes known are H_2SiF_6 and its salts[1,2,43]. This pronounced capacity for complex-formation will later be shown to reveal itself in their chemical properties.

Compounds of fluorine with bivalent silicon are also known[44].

III. PREPARATION AND CHEMICAL PROPERTIES OF ORGANOSILICON FLUORINE COMPOUNDS IN WHICH FLUORINE IS BOUND TO SILICON

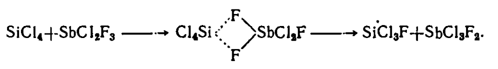
1. Methods of Preparation

Methods at present known for preparing organosilicon fluorine compounds with a fluorine atom bound to silicon are: a) replacement of halogen in the Si–X bond by F (where X = Cl, Br, I); b) replacement of oxygen in the Si–O bond by F; c) replacement of nitrogen in the Si–N bond by F; d) rupture of a Si–C bond, with formation of a Si–F bond; e) replacement of hydrogen in the Si–H bond by F; f) rupture of a Si–Si bond, with formation of a Si–F bond.

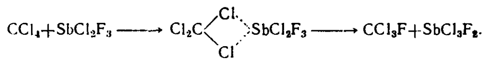
Replacement of halogen in the Si–X bond by F. Of these methods for forming a Si–F bond the first has been most studied. In 1905 Ruff and Albert[45] found that the reaction of trichlorosilane with SbF_3 or AsF_3 yields exclusively SiF_4, but with SnF_4 and TiF_4 partially fluorinated products are produced. The applicability of the Swarts reaction to organosilicon compounds was thus established. It was shown later that stepwise fluorination may yield mono-, di-, and tri-substituted derivatives of $HSiCl_3$ in good yield[46]. $HSiF_3$ was found to decompose even at low temperatures according to the equation:

$$4HSiF_3 \longrightarrow SiH_4+3SiF_4.$$

Booth *et al.*[47,48] applied the Swarts reaction to $SiCl_4$, and prepared all the products of stepwise replacement of chlorine in $SiCl_4$ by fluorine. The Swarts reaction proceeds readily at low temperatures with such compounds as $SiCl_4$, $HSiCl_3$, and $GeCl_4$, which can form co-ordination compounds with antimony fluorides:


$$SiCl_4+SbCl_2F_3 \longrightarrow Cl_4Si{<}\overset{F}{\underset{F}{\,}}{>}SbCl_2F \longrightarrow SiCl_3F+SbCl_3F_2.$$

Replacement of the chlorine atoms attached to silicon by fluorine renders such co-ordination easier and favours complete fluorination. Polyhalogen compounds of carbon behave quite differently in this respect:


$$CCl_4+SbCl_2F_3 \longrightarrow Cl_2C{<}\overset{Cl}{\underset{Cl}{\,}}{>}SbCl_2F_3 \longrightarrow CCl_3F+SbCl_3F_2.$$

The Swarts reaction can be successfully used to prepare various mixed fluorochlorobromosilanes[49], fluorosilanes[50,51], fluorodisiloxanes , and fluorodisilanes[53]. In contrast to SiH_2I_2 and $SiHI_3$, monoiodosilane does not form the corresponding fluorosilane H_3SiF in the reaction with HgF_2 or AgF.

Various compounds can be used as fluorinating agents. Hill and coworkers[54,55] obtained mixed fluorochlorosilanes by passing a mixture of SiF_4 and $SiCl_4$ through a glass tube packed with small pieces of porous material and heated to 600°. Anderson[56], with different reaction conditions (empty glass tube, 700°), obtained mixtures of silicon fluorobromides, fluoroiodides, and fluoroisocyanates. Replacement of halogens by fluorine proceeds readily with silicon halides containing organic radicals. In 1946 Booth and coworkers[57–62] found that fluorination of alkyltrichlorosilanes by the Swarts method gave mono-, di-, and tri-fluoro derivatives. Ethoxychlorosilanes are also readily fluorinated[63]. The resulting trifluoro- and difluoro-ethoxysilanes, in contrast to triethoxyfluorosilane, have a tendency to disproportionation. The Swarts reaction is convenient for the fluorination of phenylchlorosilanes[64–66], mixed alkylarylchlorosilanes[36,67,68], and alkylsilicon hydrides[38,69,70]. In the last case the Si–H bond could not be disrupted by antimony fluoride. Trichlorosilane is an exception in this respect[45].

In 1944 Emeléus and Wilkins used zinc fluoride for the first time to fluorinate alkyl- and phenyl-chlorosilanes[71]. It proved to be a very efficient fluorinating agent, which could be used to separate the azeotropic mixture of trimethylchlorosilane and tetrachlorosilane, since it fluorinates almost exclusively trimethylchlorosilane[72,73]. Zinc fluoride has subsequently been widely used for fluorinating various alkyl(aryl)chlorosilanes[74,75] and alkylalkoxychlorosilanes[76]. The yield of alkylalkoxyfluorosilanes did not exceed 22% owing to side reactions. Schnell[77] used a mixture of metallic zinc and zinc fluoride to prepare vinyltrifluorosilane from vinyltrichlorosilane, in 75% yield. Ammonium fluoride is a milder fluorinating agent for alkylchlorosilanes than zinc fluoride[78,70]. In fluorination of alkoxychlorosilanes with ammonium fluoride, the alkoxy group is not replaced[78]. Payne[80] showed that in fluorination of monomethyl-, diethyl-, triethyl-, and dimethyl-chlorodisiloxanes with ammonium fluoride the silicon-oxygen bond is broken, while under similar conditions tetraethyl- and pentaethyl-chlorodisiloxanes are fluorinated without this side reaction, forming tetraethyldifluorodisiloxane and pentaethylfluorodisiloxane, respectively.

Pearson and Brice[81] suggested an interesting method for fluorinating alkyl(aryl)chlorosilanes using anhydrous HF at low or room temperatures. It is a good fluorinating agent[82,83] which does not disrupt the Si–C bond under these conditions.

Boron trifluoride can also be used as a fluorinating agent. In the high-temperature condensation of benzene with trichlorosilane in the presence of boron trifluoride at high pressure, small amounts of phenylfluorodichlorosilane and phenyldifluorochlorosilane were obtained in addition to phenyltrichlorosilane[84,85].

Replacement of oxygen in the Si–O bond by F. In 1933 Flood[86] developed a convenient method for the preparation of triethylfluoro(chloro, bromo)silane in almost quantitative yield by the reaction of hexaethyldisiloxane with sodium or ammonium fluorides (chlorides, bromides) in the presence of concentrated sulphuric acid at low temperatures. Sommer and coworkers[87–89] used this reaction for the preparation of other trialkylfluorosilanes, in particular trimethylfluorosilane and trimethylchlorosilane of high purity. It was later shown that calcium fluoride can also be used[90].

In a patent[91] alkylalkoxysilanes were fluorinated with alkali metal bifluorides. For instance, on boiling pentyltriethoxysilane for 15 min with sodium bifluoride pentyltrifluorosilane was obtained in 89% yield. To fluorinate hexa-alkyldisiloxanes Voronkov[92] used potassium and ammonium bifluorides in the presence of concentrated sulphuric acid:

$$R_3Si{-}O{-}SiR_3+KHF_2+H_2SO_4 \longrightarrow 2R_3SiF+KHSO_4+H_2O$$

The yield of fluorination products reached 88% .

Since 1944 [71] hydrogen fluoride has been extensively used in the preparation of fluorinated organosilicon compounds from alkylsiloxanes and alkylalkoxysilanes. To avoid side reactions, all reactions with hydrogen fluoride are carried out at about 0°. In spite of the low temperature, the rate of reaction is sufficiently high and the reaction is practically complete in 15 to 45 min. For the preparation of alkylfluorosilanes from alkylsiloxanes, anhydrous hydrogen fluoride is usually used in the presence of concentrated sulphuric acid[82,93,94], which is not, however, indispensable[80,95]. Booth and Freedman[95] used HF in their study of the structure of siloxanes. The reaction of siloxanes with HF results in cleavage of the Si–O bond only, giving a quantitative yield of alkylsilyl fluorides:

Anhydrous hydrogen fluoride reacts with alkylalkoxysilanes[75,91,96,97] forming alkylsilyl fluorides. To separate phenyltrichlorosilane from phenylmethyldichlorosilane, they are fluorinated by an alcoholic HF solution[75,97], or by passing HF through their solution in absolute alcohol[96]. The resulting fluorides are easily separated by rectification.

Marans, Sommer, and Whitmore[98] found a 48% aqueous solution of hydrogen fluoride to be a good fluorinating agent for alkylalkoxysilanes. This was corroborated by Anderson[35] and Sommer[99]. To prepare alkylsilyl fluorides from various organosilicon compounds Eaborn[100] used aqueous-alcoholic HF solution. The importance of this is that dilute HF solutions can be used without reducing the yield of fluorinated products, and the reaction can be carried out in glass apparatus.

Peppard, Brown, and Johnson[101] investigated the possibility of preparing alkylsilyl fluorides from alkylalkoxysilanes by the action of SbF_3 on them in the presence of $SbCl_5$. They found the course of the reaction to depend considerably on the alkyl and alkoxy groups bound to silicon. For instance, while $(C_2H_5O)_4Si$ is readily fluorinated giving $(C_2H_5O)_3SiF$ and $(C_2H_5O)_2SiF_2$, tetra-allyloxysilane and triallyloxysilane do not react with SbF_3 at all, even in the presence of $SbCl_5$. Heal[63] showed that SbF_3 does not remove the ethoxy group in the absence of $SbCl_5$, but instead vigorously substitutes fluorine for chlorine in ethoxysilanes, the most stable of the three ethoxyfluorosilanes being $(C_2H_5O)_3SiF$. Trifluoroethoxy- and difluoroethoxy-silanes formed in the reaction undergo disproportionation even at low temperatures according to:

$$2C_2H_5OSiF_3 \longrightarrow SiF_4 + (C_2H_5O)_2SiF_2,$$

$$3(C_2H_5O)_2SiF_2 \longrightarrow SiF_4 + 2(C_2H_5O)_3SiF.$$

BF_3 is also a good fluorinating agent[102]. It reacts vigorously with methylmethoxysilanes, completely or partially replacing methoxy groups by fluorine to give methylfluorosilanes. Hexamethyldisiloxane reacts with excess BF_3 giving trimethylfluorosilane and B_2O_3. Sommer and Ansul[103,104] extended these studies using alcoholic BF_3 solution as fluorinating agent at 50° to 60°. The yields of fluorinated products reached 95%.

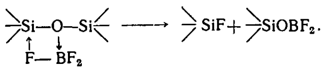
Emeléus and Onyszchuk[105] found that the reaction of 1,3-dimethyldisiloxane and 1,3,3,3-tetramethyldisiloxane with BF_3 proceeds in two stages:

$$2(CH_3SiH_2)_2O + BF_3 \longrightarrow CH_3SiH_2OBF_2 + CH_3SiH_2F.$$

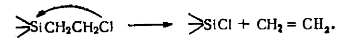
The resulting $CH_3SiH_2OBF_2$ begins to decompose even at -78°. At room temperature this process is quickly completed:

$$3CH_3SiH_2OBF_2 \longrightarrow 3CH_3SiH_2F + BF_3 + B_2O_3.$$

The authors suggested the following mechanism for this reaction:



This is the most probable mechanism, if one considers the complex-forming capabilities of boron and silicon atoms. The decomposition of the intermediate complex and the intermediate products recalls the well-known β-decomposition of β-halogenoalkylsilanes:



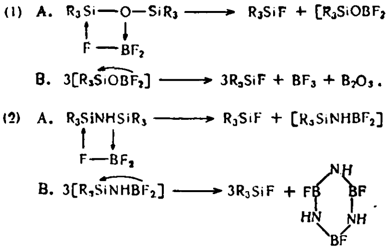
This will be discussed later.

Fluorosulphonic acid[106] and acetyl fluoride[107] can also be used to replace the alkoxy group in alkylalkoxysilanes by fluorine.

Replacement of nitrogen in the Si–N bond by F. According to Burg and Kuljian[108] trisilylamine and boron trifluoride, in a 1:1 ratio, react at -78° to -40° to form unstable adducts which decompose irreversibly at a higher temperature to form H_2SiF_2, $HSiF_3$, and other compounds. A detailed study of the reactions of BF_3 with $(H_3Si)_3N$, $(H_3Si)_2NCH_3$, and $H_3SiN(CH_3)_2$ showed[109] that the white solid adducts formed at -80° decompose slowly forming H_3SiF and $(H_3Si)_2NBF_2$, $H_3SiN(CH_3)BF_2$ and $(CH_3)_2NBF_2$ respectively. The silyldifluoroaminoboranes are in their turn unstable and on increasing the temperature decompose further to derivatives of borazole and H_3SiF. Thus, $H_3SiN(CH_3)BF_2$ gives *N,N′,N″*-trimethyl-*B,B′,B″*-trifluoroborazole and H_3SiF, and $(H_3Si)_2NBF_2$ gives *N,N′,N″*-trisilyl-*B,B′,B″*-trifluoroborazole and H_3SiF.

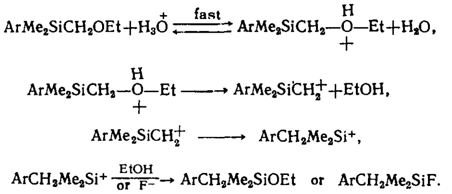
Tris(methylsilyl)amine, dimethyl(methylsilyl)amine, and dimethyl(trimethylsilyl)amine[110] react with BF_3 at -78° forming crystalline adducts, which decompose in the presence of BF_3 to give respectively methylfluorosilane and *N,N*-bis(methylsilyl)-*B,B*-difluoroaminoborane, methylfluorosilane and *N,N*-dimethyl-*B,B*-difluoroaminoborane, and trimethylfluorosilane and *N,N*-dimethyl-*B,B*-difluoroaminoborane. Like silylamines, hexamethyldisilazane forms with BF_3 a complex $[(CH_3)_3Si]_2NH.BF_3$ which decomposes on heating into $(CH_3)_3SiF$ and $(CH_3)_3SiNHBF_2$ [102].

A thorough study of the reactions of silylamines and siloxanes with BF_3 reveals similarities between their mechanisms:



Bailey, Sommer, and Whitmore[111] found that by the action of concentrated HF on trialkylaminosilane the nitrogen in the Si–N bond can be replaced by fluorine, to form trialkylfluorosilanes in up to 89% yield. Nitrogen in the Si–N bond of tetraisocyanosilane is easily replaced by fluorine by using SbF_3.[112] SiF_4 can also cause isocyanate groups to be replaced by fluorine. For example, all three possible fluoroisocyanosilanes are formed[56] by passing an equimolar mixture of SiF_4 and $Si(NCO)_4$ through a glass tube at 700°.

Rupture of a Si–C bond with formation of a Si–F bond. Several cases are known of replacement of carbon in the Si–C bond by fluorine. Eaborn and Jeffery[113] found that the reactions of *p*-$ClC_6H_4(CH_3)_2SiCH_2OC_2H_5$ and *p*-$CH_3C_6H_4(CH_3)_2SiCH_2OC_2H_5$ with aqueous-alcoholic solutions of HF proceeded as follows:



$$ArMe_2SiCH_2OEt+H_3\overset{+}{O} \underset{}{\overset{\text{fast}}{\rightleftharpoons}} ArMe_2SiCH_2{-}\underset{+}{\overset{H}{O}}{-}Et+H_2O,$$

$$ArMe_2SiCH_2{-}\underset{+}{\overset{H}{O}}{-}Et \longrightarrow ArMe_2SiCH_2^{+}+EtOH,$$

$$ArMe_2SiCH_2^{+} \longrightarrow ArCH_2Me_2Si^{+},$$

$$ArCH_2Me_2Si^{+} \xrightarrow[\text{or } F^{-}]{EtOH} ArCH_2Me_2SiOEt \text{ or } ArCH_2Me_2SiF.$$

Under these conditions only the Si–C(arom.) bond in *p*-$CH_3OC_6H_4(CH_3)_2SiCH_2OC_2H_5$ is broken, anisole and $(CH_3)_2\cdot$ $\cdot(C_2H_5OCH_2)SiF$ being formed.

In his study of the action of various reagents on triethylsilane Anderson[114] discovered that silver fluoride was capable of fluorinating not only the Si–H bond, but also one of the Si–C bonds forming triethylfluorosilane and diethylfluorosilane. Eaborn[5] discovered a number of transformations of the Si–C bond in studying transformations of various organosilicon compounds under the action of silver and other metal halides.

Alkylfluorosilanes can be obtained by the reaction between R_4Si and SiF_4.[115] For instance, heating $(C_2H_5)_4Si$ and SiF_4 in a 1 : 1 ratio for three hours in an autoclave at 300° to 350° and 13 to 14 atm gave 22% $C_2H_5SiF_3$, 46.6% $(C_2H_5)_2\cdot$ $\cdot SiF_2$, 23.7% $(C_2H_5)_3SiF$ and 7.5% unreacted $(C_2H_5)_4Si$.

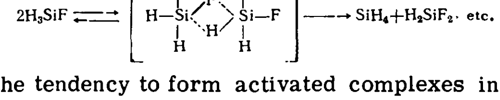
None of these methods for replacing the Si–C bond by Si–F have as yet more than limited preparative value.

Replacement of hydrogen in the Si–H bond by F. In 1905, in an effort to prepare mixed fluorides from trichlorosilane and SbF_3 or AsF_3, Ruff and Albert[45] found SiF_4 to be the only reaction product. They established that $HSiF_3$ is very unstable decomposing at high temperatures according to:

$$4HSiF_3 \longrightarrow 2H_2+3SiF_4+Si.$$

This was in fact the first observation of disproportionation in fluorosilanes.

Disproportionation of halogenosilanes[116] presumably depends on their ability to use the 3*d* orbital of silicon to form activated complexes, which decompose into new products according to the scheme:



Since the tendency to form activated complexes increases with the electronegativity of the halogen atoms bound to silicon, the tendency to disproportionation also increases on passing from iodosilanes to fluorosilanes.

Replacement of the Si–H bond by Si–F occurs not only by the action of SbF_3, AsF_3, or by disproportionation, but also, as mentioned above, by the action of silver fluoride[114].

Rupture of a Si–Si bond with formation of a Si–F bond. We conclude this survey by quoting two preparative methods using compounds containing a Si–Si bond. In one, mixed fluorochlorosilanes were prepared by Schumb and coworkers[117,118] by the action of chlorine or bromine on hexafluorodisilane. The main reaction products were SiF_4, $SiClF_3$, $SiCl_2F_2$, and $SiBrF_3$, $SiBr_2F_2$, and $SiBr_3F$.

In the other method[80] fluorochlorosilanes can be obtained by boiling hexachlorodisilane with NH_4F.

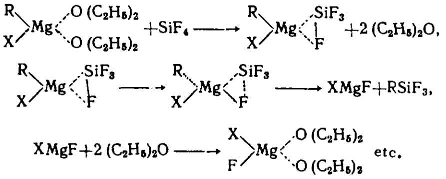
2. Chemical Properties

All known reactions of silicon fluorides may be divided into the following principal types: replacement of fluorine in the Si–F bond by (a) group IV elements; (b) group V elements; (c) group VI elements; (d) group VII elements and hydrogen; and (e) reactions in which the Si–F bond remains intact.

Replacement of fluorine in the Si–F bond by group IV elements. This type of substitution covers all reactions of organic and inorganic silicon fluorides with organic compounds of magnesium, sodium, lithium, and aluminium, and other alkylating agents.

In 1936, in their study of the reaction of ethylmagnesium chloride and bromide with silicon tetrafluoride, Gierut, Sowa, and Nieuwland observed that fluorine can be replaced by organic radicals giving triethylfluorosilane[39]. The same results were obtained with propyl-, butyl-, and pentylmagnesium halides. Ethylmagnesium bromide also gave 5% tetraethylsilane. Compared with alkylmagnesium bromides, alkylmagnesium chlorides give better yields of trialkylfluorosilanes.

The formation of trialkylfluorosilanes in these reactions is connected mainly with steric effects of organic radicals. In tributyl- and tripentyl-fluorosilanes the Si–F bond is so protected that it can react neither with the Grignard reagent, nor even with sodium in liquid ammonia. The same results were obtained by Medoks and Kotelkov[120] in the reaction of phenylmagnesium bromide with SiF_4 in ether solution at room temperature, where triphenylfluorosilane was the main product. From a thorough investigation Medoks[121] suggested this scheme for the reaction of the Grignard reagent with SiF_4 in ether solution:



The $RSiF_3$ produced reacts with another molecule of RMgX in like manner. Given the strongly pronounced tendency of SiF_4 to form complexes, the author assumes that reaction of SiF_4 with XMgF etherate takes place simultaneously with the above reaction, according to:

$$2MgClF\,[(C_2H_5)_2O]_2+SiF_4 \longrightarrow MgSiF_6+MgX_2\,[(C_2H_5)_2O]_2+2\,(C_2H_5)_2O.$$

This assumption is fully justified since $MgSiF_6$ is in fact found among the reaction products. Soschestvenskaya [122,123] found incidentally that even salts of fluorosilicic acid (*e.g.* Na_2SiF_6) can react with Grignard reagents at 160° to 170° to give tetra-alkyl(aryl)silanes. Under these conditions $MgSiF_6$ decomposes to SiF_4.

As already remarked, steric hindrance has a considerable effect on the course of the reaction of SiF_4 with RMgX. In his study of the reaction of isopropylmagnesium chloride with SiF_4 Eaborn [124,125] obtained mainly di-isopropyldifluorosilane. Even greater steric hindrance was found with the α-naphthyl radical. According to Petrov and Chernysheva [126–129], the reaction of α-naphthylmagnesium bromide with SiF_4 results in two products, α-naphthyltrifluorosilane and di-α-naphthyldifluorosilane. Tri-α-naphthylfluorosilane is formed only on heating. The authors showed that in the synthesis of tetrasubstituted silanes, by using RLi instead of RMgX and SiF_4 instead of SiX_4 considerable steric hindrance could be overcome, since the R–Li and Si–F bonds are more ionic than the R–MgX and Si–X bonds (where X = Cl, Br, I). These conclusions were subsequently confirmed by the synthesis of triphenyl(vinylethynyl)silane [130] and triphenylvinylsilane [131].

Steric hindrance can also be overcome by using excess of the Grignard reagent, increasing the reaction temperature, using solvents other than ether [132,133], and in a number of other ways. When the reaction is not limited by steric hindrance, in order to obtain silicon fluorides R_2SiF_2 (R = phenyl, benzyl) the temperature should be kept below 0°, and the addition of SiF_4 to the Grignard reagent speeded up [134–136]. SiF_4 and Na_2SiF_6 can also be alkylated by other than organolithium or organomagnesium reagents. Several patents appeared recently on the use of the etherate of $(C_2H_5)_3Al$ [137–139] at 200°–250° and a mixture of CH_3AlCl_2 with $(CH_3)_2AlCl$ [140] at 200°–220° as alkylating agents. Ethylfluorosilanes [115] can also be obtained by the reaction of equimolar quantities of $(C_2H_5)_4Si$ and SiF_4 in an autoclave at 300°–350°, and methyltrifluorosilane [141] by passing a mixture of CH_3Cl and SiF_4 through a mixture of silicon and reduced copper heated to 300°.

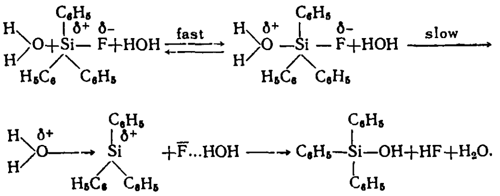
Since SiF_4 and Na_2SiF_6 are manufactured industrially, all these methods for the replacement of fluorine in them are of commercial as well as preparative importance.

Replacement of fluorine in the Si–F bond by group V elements. Only two short papers have appeared [56,142] dealing with replacement of fluorine in the Si–F bond by nitrogen or nitrogen-containing groups. We have already discussed one of them [56]. In the other, Chugunov used the reaction of triphenylfluorosilane with diphenylamine in boiling toluene solution in the presence of lithium. A 20% yield of triphenylsilyldiphenylamine, a crystalline product, m.p. 224°–225°, was obtained.

Replacement of fluorine in the Si–F bond by group VI elements. These reactions include alcoholysis, hydrolysis, and certain others. The rate of alcoholysis depends to a considerable extent on the structure of the silicon fluoride and the alcohol. The first investigation in this field [39] had already shown that while methyl and ethyl alcohols reacted quantitatively with SiF_4, propyl, isopropyl, and isobutyl alcohols underwent only 20 to 60% reaction. Moreover, compounds containing both fluorine and ethoxy groups not only undergo disproportionation readily [63,78], but also enter into exchange reactions with alcohols of higher molecular weight (*e.g.* $CH_2{=}CHCH_2OH$, $n\text{-}C_4H_9OH$) to form, in all cases, trialkoxyfluorosilanes [101].

The reaction of phenyltrifluorosilane with ethanol also yields only phenyldiethoxyfluorosilane, the third fluorine atom being completely inactive [64]. The same is true of the reaction of water with phenyltrifluorosilane [143] at 70°, when also one Si–F bond remains intact. On boiling in anhydrous ethanol, triphenylfluorosilane undergoes only 80% alcoholysis [100].

The reaction of alkyl(alkoxy)fluorosilanes and SiF_4 with alcohols, phenols, and *o*-, *m*-, and *p*-cresol can sometimes be accelerated by the addition of aluminium ethoxide [144] or ammonia [145]. Under the action of alkali all alkyl(aryl, alkoxy)fluorosilanes readily undergo hydrolysis [76,87,88,136]. In 1949 Swain and coworkers [146] made a thorough study of the kinetics of triphenylfluorosilane hydrolysis and suggested the following reaction mechanism:



This hydrolysis mechanism is also valid† for other organic and inorganic silicon halides. It is based on the assumption that silicon is capable of forming stable or unstable bonds involving its 3*d* orbitals.

The action of sulphuric acid upon alkyl-, aryl-, and benzyl-fluorosilanes is more complex, since rupture of the Si–C bond often occurs as well as hydrolysis [147]. Szmant and coworkers maintain that in this case there is nucleophilic attack of the sulphate anion on the silicon. However, one cannot exclude the possibility of the reaction also proceeding according to the scheme:

$$R_3Si{-}F \ldots H{-}OSO_3H \longrightarrow \overset{\delta+}{R_3Si} \ldots F{-}H \ldots \overset{\delta-}{OSO_3H}.$$

The nature of the radicals bound to silicon has a substantial effect on the behaviour of silicon fluorides in chemical reactions. Sommer and coworkers [87,148] studied the stability of organosilicon compounds containing α- and β-halogen atoms towards various reagents; they found that those containing a β-halogen are unstable, decomposing with rupture of the Si–C bond under the action of alkalis, water, potassium acetate, CH_3MgBr, etc. The compound $(CH_2ClCH_2).(C_2H_5)_2SiF$ decomposes more rapidly than the compound $(CH_2ClCH_2)(C_2H_5)_3Si$.

Replacement of fluorine in the Si–F bond by oxygen-containing groups is possible in reactions other than alcoholysis or hydrolysis. Anderson [149] observed that hexaethyldistannoxane reacts with diphenyldifluorosilane in the following way:

$$n\,[(C_6H_5)_2SiF_2]+n\,[(C_2H_5)_3Sn]_2O \longrightarrow [(C_6H_5)_2SiO]_n+2n\,[(C_2H_5)_3SnF].$$

Replacement of fluorine in the Si–F bond by group VII elements and hydrogen. Schumb and coworkers [150] studied the action of anhydrous aluminium, magnesium, iron, calcium, boron, and barium chlorides

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† Compare, however, Eaborn, "Organosilicon Compounds", 1st Edn., pp. 103–113 and 177–183 (Ed. of Translation).

on various fluorine-containing compounds, including SiF_4 and alkylfluorosilanes. They showed SiF_4 to react at atmospheric pressure with all these chlorides except $BaCl_2$ to form $SiCl_4$ (as main product) and all the intermediate fluorochlorosilanes. Chlorination of SiF_4 with aluminium chloride at 8–9 atm and 195°–250° gave only $SiCl_4$, which was explained by disproportionation of the intermediate fluorochlorosilanes into $SiCl_4$ and SiF_4 under these conditions.

Alkylfluorosilanes are also readily chlorinated by anhydrous aluminium chloride. This reaction was extended by Eaborn[124,151] who established that anhydrous aluminium bromide, chloride, and iodide are efficient reagents for replacement of fluorine in alkyl-, aryl-, and alkylaryl-fluorosilanes. Simultaneous replacement of the fluorine in the Si–F bond by chlorine and hydrogen is achieved by passing a 1 : 1 or 3 : 1 HCl–SiF_4 mixture through ground silicon or silicon-containing material at 385°–525°.[152] $HSiClF_2$ and $HSiCl_2F$ are the main reaction products. Alkylsilicon hydrides containing more than one Si–H bond are obtained by heating a mixture of 80% diethylaluminium hydride and 20% triethylaluminium with SiF_4 in an autoclave at 260°.[153] Besides SiF_4, $SiCl_4$, and $Si(OR)_4$ can be used in this reaction.

Reactions in which the Si–F bond remains intact. The extraordinary stability of the Si–F bond is the reason why, in contrast to bonds of silicon with other halogens or other atoms, it can remain intact in a number of chemical reactions. In 1933 Flood and coworkers[86,154] found that the Si–F bond in triethylfluorosilane is not hydrolysed in the presence of water nor is fluorine exchanged for bromine or iodine when this compound is acted upon by these halogens. In the latter cases one ethyl group is easily lost, diethylbromo(iodo)fluorosilane and ethyl bromide (iodide) being formed:

$$R_3SiF+X_2 \longrightarrow R_2SiXF+RX.$$

It was further shown that in phenylfluoro-, phenylchlorofluoro-, alkylphenylfluoro-, and alkylchlorofluoro-silanes[64] one Si–F bond is very stable and does not react with water or alcohol. The high stability of this Si–F bond has permitted the preparation of alkyl- and phenyl-polysiloxanes containing an Si–F bond[143,155].

Reference has been made[156] to the very high stability of the Si–F bond in diethyldifluorosilane to the action of 100% H_2O_2 in ether solution at -20° to -35°. Only the Si–C bond was oxidised to a small extent (21–23%) to form $C_2H_5.(C_2H_5O)SiF_2$ and $(C_2H_5O)_2SiF_2$. In the action of n-butyl and allyl alcohols on triethoxyfluorosilane only the ethoxy groups are replaced by n-butoxy and alloxy[101], the fluorine atoms remaining:

$$(C_2H_5O)_3SiF+3n\text{-}C_4H_9OH \longrightarrow (n\text{-}C_4H_9O)_3SiF+3C_2H_5OH.$$

In mixed fluorobromo- and fluoroiodo-silanes also chlorine replaces only bromine and iodine, and not fluorine[49], while in alkyl(aryl)fluorosilanes only the alkyl and aryl radicals are replaced[83]. Ponomarenko and Snegova found recently[65] that in chlorination, and more so in bromination, of phenyltrifluorosilane in the presence of powdered iron, rupture of the Si–C bond took place, but the Si–F bond remained intact. The behaviour of $C_6H_5SiF_3$ in these reactions differs sharply from the behaviour of $C_6H_5.SiCl_3$. This is explained by the greater electrophilic character of the Si atom in $C_6H_5SiF_3$ and the smaller size of fluorine compared with chlorine. From a systematic study of the orienting capacity of fluorosilyl groups in radical or electrophilic chlorination and bromination of ethyl- and phenyl-silyl chlorides, Ponomarenko and Snegova[36,65] were able to show that stepwise replacement of alkyl radicals by fluorine results in a sharp increase of the orienting capacity of these groups. In the photochemical chlorination of ethylsilyl fluorides this is evident from the formation of a larger proportion of β-isomers than in chlorination of the corresponding ethylsilyl chlorides. The $-SiF_3$ group in $C_6H_5SiF_3$ has a strong meta-orienting tendency. Fluorosilyl groups also have a considerable stabilising effect on the C–Cl bonds in alkyl radicals in dehydrochlorination by means of quinoline, so that α- and β-chlorides behave differently.

Alkali metal mercaptides, organomagnesium compounds, and alcohols react at -78° with dichlorodifluorosilane, replacing selectively the chlorine atoms only[157,158]. These reactions are often the most suitable for the preparation of compounds of type R_2SiF_2, $(RS)_2SiF_2$, and $(RO)_2SiF_2$.

According to Yakubovich and Ginsburg[159], $SiCl_4$, and $SiBr_4$ react vigorously with 2.5–3% solutions of diazomethane in ether at -45° to -55°:

$$SiCl_4+CH_2N_2 \longrightarrow ClCH_2SiCl_3+N_2,$$
$$ClCH_2SiCl_3+CH_2N_2 \longrightarrow (ClCH_2)_2SiCl_2+N_2, \text{ etc.}$$

SiF_4, on the other hand, does not react with diazomethane to form organosilicon fluorine compounds. In the authors' opinion this is because of the high activation energy for methylation of the Si–F bond.

It follows from the chemical reactions of organic and inorganic silicon fluorides that fluorine bound to silicon has a number of specific features, compared to the other halogens, which are consistent with the physical properties of the Si–F bond discussed in section II.

Although a considerable number of organosilicon compounds containing fluorine attached to silicon have so far been obtained, and their physical and chemical properties studied to some extent, very little is known about their application in industry. Organosilicon compounds containing fluorine in an organic radical are more promising in this respect.

IV. PREPARATION AND CHEMICAL PROPERTIES OF FLUORO-ORGANOSILICON COMPOUNDS WHERE FLUORINE IS IN THE ORGANIC RADICAL

1. Methods of Preparation

At present the following methods are known for the preparation of fluoro-organosilicon compounds with fluorine in the organic radical: (a) organometallic method; (b) replacement of hydrogen in the Si–H bond by organic radicals; (c) the Swarts reaction; (d) direct synthesis; (e) reactions of alkenylsilanes; (f) other reactions.

Organometallic method. The first fluoro-organosilicon compound was prepared by this method in 1949 by Roberts and coworkers[160] from p-FC_6H_4MgBr and $(CH_3)_3SiCl$. This method is interesting because it can be used to prepare relatively easily fluorine-containing organosilicon monomers which are very important for research. $(m\text{-}CF_3C_6H_4)_3SiF$ and $(m\text{-}CF_3C_6H_4)_4Si$ were thus prepared from m-$CF_3C_6H_4MgBr$ and SiF_4,[161] $(p\text{-}CF_3C_6H_4)_3SiH$ from p-$CF_3C_6H_4MgBr$ and $HSiCl_3$,[162] and p-$FC_6H_4SiCl_3$ and

$(p\text{-}FC_6H_4)_2SiCl_2$ from $p\text{-}FC_6H_4MgBr$ and $SiCl_4$.[163,164] An especially large number of derivatives was prepared from trifluoromethylphenylmagnesium bromide and $SiCl_4$,[165-168] CH_3SiCl_3,[169-171] $ClCH_2SiCl_3$,[171] $CH_2{=}CHSiCl_3$,[172] or $(C_2H_5O)_4Si$.[66] Gilman, Brook, and Miller[173] obtained $(C_6H_5)_3(m\text{-}CF_3C_6H_4)Si$ from $(C_6H_5)_3SiCl$ and $m\text{-}CF_3C_6H_4Li$. Mindlin and Andrianov[174] prepared $m\text{-}CF_3C_6H_4(CH_3)Si.(OC_2H_5)_2$ and $m\text{-}CF_3C_6H_4Si(OC_2H_5)_3$, in one stage, in 30% yield, from $m\text{-}CF_3C_6H_4MgBr$ with $CH_3Si(OC_2H_5)_3$ and $(C_2H_5O)_4Si$, respectively.

Reactions of tetrachlorosilane and alkylchlorosilanes with more complex Grignard reagents, namely $3,5\text{-}(CF_3)_2.C_6H_3MgBr$, $2,5\text{-}(CF_3)_2C_6H_3MgBr$,[166,167] and $4\text{-}Cl\text{-}3\text{-}CF_3C_6H_3.MgBr$[175] have also been used. They all give good yields of the corresponding organosilicon fluorine compounds.

Lithium can also be used in the reaction of aromatic fluorine-containing compounds with chlorosilanes. Fluorinated organolithium compounds react with $SiCl_4$[176] and alkyl-(aryl)chlorosilanes[177,178], to form $(m\text{-}CF_3C_6H_4)_4Si$, $(CF_3)_2.C_6H_3Si(Cl_2)CH_3$, $(C_6H_5)_2Si(C_6H_3CF_3\text{-}m)_2$, and other fluorine-containing arylsilanes. Although by using lithium instead of magnesium the reaction can be carried out at lower temperatures and higher yields of the products are obtained, organolithium compounds are still not widely used for the synthesis of organosilicon fluorine compounds.

Organosilicon monomers have also been prepared from aliphatic fluoro-compounds capable of forming Grignard reagents. In 1951 Henne and Francis[179] described the preparation of a Grignard reagent from heptafluoroiodopropane in ether solution at -80° in a dry nitrogen atmosphere. Haszeldine subsequently published[180-182] the preparation of perfluoromethylchlorosilanes from CF_3MgI and $SiCl_4$. McBee and coworkers[183-185] and others[186,187] extended this to the preparation of various organosilicon fluorine compounds, *e.g.* $[(C_3F_7)CH_2CH_2]_4Si$, $[(C_3F_7)CH_2CH_2]_3SiCl$, $[(C_3F_7)CH_2CH_2]_2Si(OC_2H_5)_2$, $[(C_3F_7)CH_2CH_2](CH_3)Si(OC_2H_5)_2$, $(C_3F_7)Si(C_2H_2)_2$, $(CF_3CH_2CH_2)_2Si(OCH_3)_2$, from Grignard reagents or from fluoro-organolithium compounds.

Not only aromatic and aliphatic fluoro-organosilicon compounds may be obtained from organomagnesium compounds. Unsaturated polyfluorides can also react with chlorosilanes under Grignard conditions. Knunyants and coworkers found recently[188] that $CF_2{=}CFMgI$ reacts with tetrachlorosilane to form $(CF_2{=}CF)_4Si$ as the only reaction product. They were not, however, successful in causing perfluorovinylmagnesium iodide to react with CH_3SiCl_3, $CH_3(C_6H_5)SiCl_2$, and $C_6H_5SiCl_3$. They explained this by a change in the electron density of the silicon atom under the influence of the atoms or groups bound to it. In their opinion the reaction proceeds most readily with those compounds in which the central atom has the lowest electron density. Of the silicon halides, therefore, only $SiCl_4$ reacts with $CF_2{=}CFMgI$. Replacement of one chlorine atom in $SiCl_4$ by a perfluorovinyl group lowers the electron density of the silicon even more, rendering the subsequent substitution easier.

Replacement of hydrogen in the Si–H bond by organic radicals. The possibility of addition of silicon hydrides to unsaturated fluorine-containing compounds using heterogeneous catalysts was first discovered by Wagner[189], and by Mackenzie, Spialter, and Schoffmann[190] in 1954. $HSiCl_3$ was added to $CH_2{=}CF_2$ and $CF_2{=}CF_2$, admittedly with very low yields. In 1956 Ponomarenko, Sokolov, and Petrov[191] described the preparation of a series of organosilicon fluorine compounds from CH_3SiHCl_2 and $C_2H_5SiHCl_2$, $CF_2{=}CFCl$, and $CF_2{=}CF_2$ in the presence of 1% platinised charcoal, yields up to 23% being obtained. Under these conditions CH_3SiHCl_2 and $C_2H_5SiHCl_2$ gave both α- and β-chlorides in the reaction with $CF_2{=}CFCl$. The above silicon hydrides gave with $CF_2{=}CFCl$ and $CF_2{=}CF_2$ not only addition products but also telomerisation products[192].

Tarrant and coworkers[193] used 5% platinised charcoal in the synthesis of fluorinated organosilicon monomers. The structure of the fluoro-olefine was found to affect the yield of the addition product considerably. While, for example, $CF_3CH{=}CH_2$ and $C_2F_5CH{=}CH_2$ give a good product yield (up to 72%) with $HSiCl_3$ and CH_3SiHCl_2 in the presence of 5% platinised charcoal at 250°, other olefines, *e.g.* $CF_2{=}CFCl$, react much less with these silicon hydrides (up to 25%). Under these conditions the reaction with $CF_3CF{=}CF_2$ is very explosive. CH_3SiHCl_2 and $HSiCl_3$ react with fluoro-olefines of type $CH_2{=}CHR_F$ according to:

$$CH_3SiHCl_2 + CH_2{=}CHR_F \longrightarrow (CH_3)Cl_2\ SiCH_2CH_2R_F,$$

where $R_F = CF_3$, C_2F_5, C_3H_7, etc. $(CH_3)Cl_2SiCH_2CHF_2$, $(CH_3)Cl_2SiCH_2CH_2C_2F_5$, $(CH_3)Cl_2SiCH_2CH_2CF_3$, and many similar compounds have been prepared using platinised charcoal[194-196].

The most active initiator of addition based on platinum is chloroplatinic acid, whose catalytic properties were first discovered by Speier *et al.*[197] Ponomarenko *et al.*[198] first used H_2PtCl_6 for the synthesis of fluorinated organosilicon monomers. In the presence of 10% Pt/SiO_2 after heating CH_3SiHCl_2 with $CH_2{=}CF_2$ at 160° for 11 h only an 11% yield of product is obtained, while in the presence of a 0.1 M $H_2PtCl_6.6H_2O$ solution in iso-propanol heating for one hour under the same conditions gives a 34% yield. The yield obtained in the presence of H_2PtCl_6 also depends to a considerable extent on the structure of the fluoro-olefine. The rate of addition of silicon hydrides to fluoro-olefines decreases as the number of fluorine atoms at the double bond increases:

$$CH_2{=}CH_2 > CH_2{=}CF_2 > CF_2{=}CClF > CF_2{=}CF_2.$$

Telomerisation products are also obtained in additions of silicon hydrides to olefines which are initiated by chloroplatinic acid. The high catalytic activity of H_2PtCl_6 has been confirmed for a number of cases[199].

Petrov *et al.*[200-204] showed that the rate of addition in the presence of platinised charcoal and chloroplatinic acid is affected by the structure of the silicon hydride. For instance, the yields obtained from the fluoroethylallyl ethers $CH_2{=}CHCH_2OCF_2CFClH$ and $CH_2{=}CHCH_2OCF_2CF_2H$ in the presence of 1% platinised charcoal at 160° decrease in the following order:

$$RSiHCl_2 > Cl_3SiH \gg R_2SiHCl \gg R_3SiH.$$

With simultaneous addition of pairs of silicon hydrides to the same ethers a different order of decreasing relative activity is found,

$$\underset{(1.9-2.5)}{R_3SiH} > \underset{(1.2-1.4)}{R_2SiHCl} > \underset{(1)}{RSiHCl_2} > \underset{(0.8-1)}{Cl_3SiH},$$

which corresponds to the order of increasing electronegativity of the silyl groups.

These peculiarities of the addition of silicon hydrides to unsaturated compounds in the presence of platinised charcoal led Petrov *et al.* to conclude, despite wide acceptance of the heterolytic character of these reactions[197,205-207], that they are specific homolytic reactions[208]. Their specificity arises from their proceeding on the surface of a heterogeneous catalyst. Differences in the rates of normal and simultaneous addition are caused by the adsorbability of the silicon hydrides on the catalyst surface, and by the rate of formation and activity of the silyl radicals. The latter depends on inductive and steric effects of the substituents bound to silicon. Proof of the homolytic nature of the process lies in the fact that at the temperature at which the reaction starts platinised charcoal considerably facilitates the homolytic hydrogenation of diphenylpicrylhydrazyl:

$$(1)\ \geqslant\text{Si—H} \xrightarrow{\text{Pt/C}} \geqslant\dot{\text{Si}}+\dot{\text{H}},$$

$$(2)\ \dot{\text{H}}+(C_6H_5)_2N\dot{N}[C_6H_2(NO_2)_3] \longrightarrow (C_6H_5)NNH[C_6H_2(NO_2)_3].$$

Deuterium exchange at the reaction temperature in the presence of platinised charcoal provides further evidence for this reaction scheme:

$$C_2H_5SiHCl_2+CH_3(C_2H_5)_2SiD \xrightarrow{\text{Pt/C}} C_2H_5SiDCl_2+CH_3(C_2H_5)_2SiH.$$

Petrov *et al.* synthesised a series of fluorinated organosilicon monomers, *e.g.* $C_6H_5SiCl_2CH_2CH_2CF_3$, p-$FC_6H_4SiCl_2$.$CH_2CH_2CF_3$, $(CH_3)Cl_2SiCH_2CH_2CH_2OCF_2CFClH$, $(CH_3)Cl_2$.$SiCH_2CH_2CH_2OCF_2CF_2H$, $C_6H_5SiCl_2CH_2CH_2CH_2OCF_2CF_2H$, $Cl_2Si(CH_2CH_2CF_3)_2$.

Addition in the presence of H_2PtCl_6 is complicated because, during the reaction, H_2PtCl_6 may be reduced to Pt. Even in this case, however, the homolytic mechanism provides a better explanation for the experimental facts than the heterolytic.

Besides platinum, ultra-violet light is widely used to initiate addition of silicon hydrides to fluoro-olefines. Haszeldine and coworkers[209-211] found that under ultra-violet irradiation $HSiCl_3$ and CH_3SiHCl_2 combined almost quantitatively with $CF_2=CF_2$ in 60 to 110 h. Haszeldine considers the reaction to proceed by a radical-chain mechanism:

$$HSiCl_3 \xrightarrow{h\nu} Cl_3\dot{S}i+\dot{H}$$

$$Cl_3\dot{S}i+CF_2=CF_2 \longrightarrow Cl_3SiCF_2\dot{C}F_2$$

$$Cl_3SiCF_2\dot{C}F_2+CF_2=CF_2 \longrightarrow Cl_3SiCF_2CF_2CF_2\dot{C}F_2 \text{ etc.}$$

$$Cl_3Si(CF_2CF_2)_n+HSiCl_3 \longrightarrow Cl_3Si(CF_2CF_2)_nH+Cl_3\dot{S}i \text{ etc.}$$

The chain length n can be regulated by altering the reagent proportions. The absence of even traces of hydrogen from the reaction products can be explained by the following parallel reactions:

$$\dot{H}+CF_2=CF_2 \longrightarrow CF_2H\dot{C}F_2,$$

$$CF_2H\dot{C}F+HSiCl_3 \longrightarrow CF_2HCF_2H+Cl_3\dot{S}i \text{ etc.}$$

With silicon hydrides R_2SiH_2 and $RSiH_3$ the reaction proceeds in stages, one hydrogen atom reacting at a time[211,212].

Under the action of ultra-violet light $CF_3CH=CH_2$, CF_3.$CF_2CH_2CH=CH_2$, and $CF_3(CH_3)C=CH_2$ react in high yield with $HSiCl_3$ and H_2SiCl_2 without forming telomers[213]. Dichlorosilane gave good yields for replacement of either one or both hydrogen atoms.

In a number of cases peroxides are good initiators for addition of silicon hydrides to fluoro-olefines. In their study of the comparative activity of t-butyl peroxide and ultra-violet light in initiating addition of silicon hydrides to unsaturated fluorine derivatives, McBee *et al.*[214] observed that often the peroxide was the more active initiator. For example, the reaction of methyldichlorosilane with $CF_3CH=CH_2$ yields, on irradiation for 90 h, only 3.6% CH_3Cl_2.$SiCH_2CH_2CF_3$, but in the presence of t-butyl peroxide 69.5% is obtained in a shorter time.

5% and 10% solutions of ozone in CCl_3F are also good initiators for addition of $HSiCl_3$ to $CF_2=CF_2$ and $CF_2=CFCl$.[215,216] The yields reached 40%, whereas using platinised charcoal the maximum yield of the same products did not exceed 23%.[191]

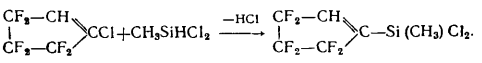
In 1958 El-Abbady and Anderson[217] showed that γ-rays could be used as initiators for addition of silicon hydrides to fluoro-olefines: 3 kcurie of ^{60}Co was used as source. The yield of addition product depended on the structure of the fluoro-olefine and often reached 52%. $C_2F_5CH_2CH_2SiCl_3$, $C_3F_7CH_2CH_2SiCl_3$, $C_2F_5(CH_3)CHCH_2SiCl_2(CH_3)$, and $C_3F_7CH_2$.$CH_2SiCl_2(CH_3)$ were prepared in this way.

Under the action of γ-rays, ultra-violet light, peroxides, and ozone, addition proceeds by a free-radical mechanism, according to the above scheme[209-217]. The similarity of the addition mechanisms is confirmed by the reaction order being the same for all the initiators (the Farmer rule is applicable), the identical effect of the silicon hydride structure on yields of addition product (Cl_3SiH gives better yields than CH_3SiHCl_2), and other analogies.

Addition of silicon hydrides to fluoro-olefines is one of the most convenient methods for the preparation of fluoro-organosilicon compounds in the laboratory and on an industrial scale.

Another method for replacement of hydrogen in the Si–H bond by organic radicals containing fluorine is high-temperature condensation. CH_3SiHCl_2 reacts with C_6H_5F in the presence of H_3BO_3 or B_2O_3 in an autoclave at 232°–260° to form a mixture of isomeric (fluorophenyl)methyldichlorosilanes in yields up to 18%.[218,219] This reaction can also proceed without catalysts. For example, on prolonged heating of $HSiCl_3$ and CH_3SiHCl_2 with $CF_2=CF_2$, $CF_2=CFCl$, $CF_2=CFCF=CF_2$, and other fluoro-olefines at 200°–250° without any catalyst[220,221] substitution takes place to give $CF_2=CFSiCl_3$, $CFCl=CFSiCl_3$, $(CF_2=CF)(CH_3)SiCl_2$, etc. Addition also occurs, yielding $HCF_2CF_2SiCl_3$ and $HCF(Cl)$.CF_2SiCl_3.

High-temperature condensation of silicon hydrides with fluoro-olefines containing chlorine atoms at the double bond, at atmospheric pressure, is of considerable theoretical and practical interest. This reaction proceeds at 350°–600°. Mironov *et al.*[222] carried out such a reaction using CH_3SiHCl_2 and $CF_2=CFCl$ in an empty tube at 500° and obtained a small yield of $(CH_3)Cl_2SiCF=CF_2$. Other more complex unsaturated fluorine-containing compounds can react in the same way[223] at 350°–600°, for example:



This method for the preparation of fluorinated organosilicon monomers has not yet been fully developed.

The Swarts reaction is a convenient method for the synthesis of organosilicon compounds containing fluorine bound to silicon. It can, however, also be used to prepare such compounds containing fluorine in the organic radical. In 1954 Frost[66] showed that good yields of *m*- and *p*-$CF_3C_6H_4SiF_3$ can be obtained by the reaction of *m*- and *p*-$CCl_3C_6H_4SiCl_3$ with a mixture of SbF_3 and $SbCl_3$. Subsequently, with a view to reducing the consumption of SbF_3 and $SbCl_5$, he suggested the following general scheme for the synthesis of *o*-, *m*-, and *p*-(trifluoromethylphenyl)trifluorosilanes[83]:

$$CH_3C_6H_4MgBr + SiCl_4 \longrightarrow CH_3C_6H_4SiCl_3 + MgClBr,$$

$$CH_3C_6H_4SiCl_3 \xrightarrow{+HF} CH_3C_6H_4SiF_3 \xrightarrow{+Cl_2} CCl_3C_6H_4SiF_3,$$

$$CCl_3C_6H_4SiF_3 \xrightarrow{SbF_3+SbCl_5} CF_3C_6H_4SiF_3.$$

Motsarev and Yakubovich[224] later prepared *p*-$CF_3C_6H_4SiF_3$ by this method. The Swarts reaction has also been applied to halogenated aliphatic organosilicon compounds. In the reaction of a SbF_3–$SbCl_5$ mixture with $CCl_3CH_2CHBrSiCl_2 \cdot (CH_3)$ and $CBr_3CBr_2CH_2CHBrSiCl_2(C_6H_5)$ at 120°–130°, in both compounds all the halogen atoms, except the α-bromine atoms, are replaced by fluorine[67,68].

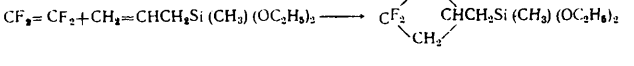
The potentialities of the Swarts reaction for the preparation of fluorinated organosilicon compounds have not yet been sufficiently studied.

Direct synthesis. In 1951 Izard and Kwolek[226] attempted to obtain fluoro-organosilicon compounds directly from CF_3Cl and silicon–copper alloy or pure silicon at 360°–700° by the Rochow method[225], but failed. In the same year Haszeldine[181] obtained the first fluorinated organosilicon monomers to be prepared by this method, using CF_3I instead of CF_3Cl.

The direct synthesis was later carried out using the perfluoroalkyl bromides CF_3Br and C_2F_5Br [227,228] and the perfluoroalkyl chlorides CF_3Cl, C_2F_5Cl, and C_3F_7Cl.[229] It is interesting that, in spite of the assertions of Izard and Kwolek[226] that fluoro-organosilicon compounds could not be obtained by direct synthesis starting from CF_3Cl, the authors of a patent[229] succeeded in obtaining a series of perfluoroalkylsilicon compounds, *e.g.* $(CF_3)_2Si_2Cl_2$, $(C_2F_5)_2SiCl_2$, and $(C_3F_7)_2SiCl_2$, by passing these perfluoroalkyl chlorides over silicon–copper alloy (in a ratio between 90 : 10 and 99 : 1) at 400° – 500°. One of the most serious shortcomings of the direct method for the preparation of fluoro-organosilicon compounds is the low yield of the desired products.

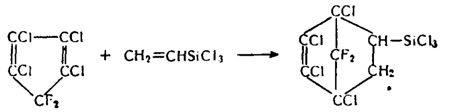
Reactions of alkenylsilanes. Reactions of alkenylsilanes yielding fluorine-containing organosilicon compounds which are known at present are: copolymerisation of alkenylsilanes with perfluoro-olefines, the Diels–Alder reaction, and addition of perfluorobromo(iodo)alkanes.

In 1953 Frost[230] showed that alkenylsilanes react with perfluoro- and perfluorochloro-olefines when heated in an autoclave at 100° either in the presence of organic peroxides and ozonides or in their absence.



This reaction has been studied using $(CH_2{=}CHCH_2)_2Si(OC_2H_5)_2$, $CH_2{=}CHSiCl_3$, $CH_2{=}CHSiCl_2(CH_3)$, and other alkenylsilanes, and the following perfluoro-olefines: $CF_2{=}CFCl$, $CF_2{=}CF_2$, $CF_3CF{=}CF_2$, and $C_2F_5CF{=}CF_2$.[230-232]

A logical extension of this work is the synthesis of fluoro-organosilicon compounds by the Diels–Alder reaction[37,233]. Ponomarenko and Snegova[37] showed 5,5-difluorotetrachlorocyclopentadiene to enter more readily than hexachlorocyclopentadiene into diene synthesis with vinyl- and allyl-silanes:



Fairly high yields (up to 60%) and experimental simplicity render the Diels–Alder reaction a convenient method for the preparation of fluoro-organosilicon compounds.

In the presence of radical initiators alkenylsilanes react with perfluoroalkyl bromides and iodides[213,234]. Haszeldine and coworkers[213] carried out addition of CF_3I, CF_3Br, $CF_2ClCFClI$, and CCl_3Br to $CH_2{=}CHSiCl_3$ and $CH_2{=}CHSiCl_2(CH_3)$. The reaction mechanism is:

$$CF_3I \xrightarrow{h\nu} \dot{C}F_3 + \dot{I}$$

$$\dot{C}F_3 + CH_2{=}CHSiCl_3 \longrightarrow CF_3CH_2\dot{C}HSiCl_3$$

$$CF_3CH_2\dot{C}HSiCl_3 + CF_3I \longrightarrow CF_3CH_2CHISiCl_3 + \dot{C}F_3 \text{ etc.}$$

The methods of synthesis discussed in this section may also have practical importance.

Other reactions. Anderson and coworkers[235,236] developed a convenient method for the preparation of various complex fluoro-organosilicon esters starting from alkyl(aryl)chlorosilanes and the silver salts of perfluoro-organic acids:

$$R_{4-n}SiCl_n + nR'COOAg \longrightarrow R_{4-n}Si(OCOR')_n + nAgCl,$$

where $n = 1, 2, 3$; $R = CH_3$, C_2H_5, C_6H_5, etc.; $R' = CHF_2$, CF_3, C_2F_5, C_3F_7.

Fluoro-organosilicon ethers are formed in the reaction of halogenosilanes with fluorine-containing alcohols or salts[237,238]. For example, the reaction of $CF_3CF_2CH_2OH$ with $(Cl_3Si)_2O$ yields $(CF_3CF_2CH_2O)_4Si$, $[(CF_3CF_2CH_2O)_3Si]_2O$ and $[(CF_3CF_2CH_2O)_3SiO]_2Si(CH_2CF_2CF_3)_2$. The formation of the last compound is rather difficult to explain. According to Voronkov and Dolgov[238] β-fluoroethoxysilanes can easily be prepared by the exchange reaction:

$$>SiOCH_3 + HOCH_2CH_2F \longrightarrow >SiOCH_2CH_2F + CH_3OH,$$

or by the reaction of silicon hydrides with $HOCH_2CH_2F$:

$$R_3SiH + HOCH_2CH_2F \xrightarrow{CH_2FCH_2OK} R_3SiOCH_2CH_2F + H_2.$$

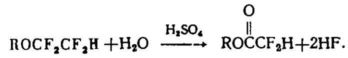
Finally, according to a patent[228] fluoro-organosilicon compounds can be prepared by passing a F_2–SiF_4 mixture over CaC_2 at high temperatures. $C_4F_9SiF_3$ and other fluoro-organosilicon compounds were isolated from the resulting complex mixture of perfluoroalkylsilicon fluorides.

Petrov *et al.*[201,204] found that organosilicon alcohols, just like ordinary alcohols, react easily with tetrafluoroethylene under the influence of sodium alcoholates:

$$(CH_3)_3Si(CH_2)_nOH + CF_2{=}CF_2 \xrightarrow{Na} (CH_3)_3Si(CH_2)_nOCF_2CF_2H,$$

where n = 1, 2, or 3.

Silicon-containing ethers do not rearrange in the presence of 96% H_2SO_4; *cf.* ethers of the type $ROCF_2CF_2H$:

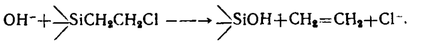


$$ROCF_2CF_2H + H_2O \xrightarrow{H_2SO_4} RO\overset{\overset{O}{\|}}{C}CF_2H + 2HF.$$

2. Chemical Properties

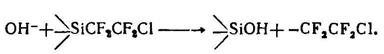
The known reactions of fluoro-organosilicon compounds may be divided into: (a) reactions involving rupture of the Si–C bond; (b) the action of acids or alkalis on fluoropolysiloxanes; (c) reactions of fluoro-organosilicon hydrides; and (d) reactions of fluoro-organosilicon halides.

Reactions involving rupture of the Si–C bond. In the presence of various electrophilic or nucleophilic reagents or on heating, a number of β-halogenated organosilicon compounds containing Si–F bonds decompose with rupture of the Si–C bond according to[87,148]:



$$OH^- + \rangle SiCH_2CH_2Cl \longrightarrow \rangle SiOH + CH_2{=}CH_2 + Cl^-.$$

Fluoro-organosilicon compounds containing β-chlorine atoms also decompose in the presence of nucleophilic reagents. Haszeldine and coworkers showed[209,211], however, that the decomposition products are different in this case:



$$OH^- + \rangle SiCF_2CF_2Cl \longrightarrow \rangle SiOH + {-}CF_2CF_2Cl.$$

The fluorine atoms have a stabilising effect on the chlorine atoms, preventing formation of a chloride anion in aqueous solution. At the same time the perfluoroalkyl group, which behaves like a pseudohalogen, increases the susceptibility of the silicon atom to nucleophilic attack. According to Knunyants and coworkers[188], under the action of aqueous alkali solutions, all the Si–C bonds in tetraperfluorovinylsilane $Si(CF{=}CF_2)_4$ are broken, $CF_2{=}CFH$ being formed quantitatively. Although ordinary β-chloro-derivatives are unstable towards nucleophilic attack, *e.g.* to a Grignard reagent, these β-fluorine atoms in $CF_3CF_2CF_2CH_2SiCl_3$ do not react even with an excess of Grignard reagent[214].

At temperatures above 200° perfluoroalkylchlorosilanes such as $Cl_3SiCF_2CF_2H$, $Cl_3SiCF_2CF_2Cl$, and $(CH_3)Cl_2SiCF_2.CF_2H$ begin to decompose according to:

$$Cl_3SiCF_2CF_2H \longrightarrow Cl_3SiF + CF_2{=}CFH,$$

i.e. they undergo β-decomposition. Polysiloxanes obtained from these monomers, *e.g.* $[CF_2HCF_2SiO_{1.5}]_n$, are more stable[209,211].

Ponomarenko *et al.*[198] found that in the catalytic addition of CH_3SiHCl_2 to $CH_2{=}CF_2$ in the presence of 10% Pt/SiO_2 at 160°, in addition to the main reaction

$$CH_3SiHCl_2 + CH_2{=}CF_2 \longrightarrow (CH_3)Cl_2SiCH_2CF_2H,$$

the by-products CH_3SiCl_2F, CH_3SiCl_3, $(CH_3)Cl_2SiCH_2CH_3$, and a complex mixture of telomers are also formed. These products (especially CH_3SiCl_2F) can be explained only by β-decomposition of the addition product.

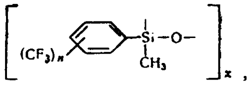
The stability of fluoro-organosilicon compounds towards aqueous alkali solutions is higher the further away the fluorine atoms are from the silicon atoms. Alkylsilicon fluorides, such as $CF_3CH_2CH_2SiCl_3$ and $CF_3CH_2CH_2SiCl_2.(CH_3)$, which contain fluorine atoms in the γ-position and beyond, are stable in the presence of alkali[214]. Polysiloxanes obtained from alkylsilicon fluorides, such as $(CF_3CH_2.CH_2SiO_{1.5})_n$, $[(CF_3CH_2CH_2)(CH_3)SiO]_n$, and $[(CF_3CH_2CH_2)_2.SiO]_n$, are very resistant to heat; they do not decompose on prolonged heating at 250°.[213]

In arylsilicon fluorides containing a fluorine atom in the *para*-position, *e.g.* p-$FC_6H_4Si(CH_3)_3$, the $Si{-}C_{arom}$ bond is ruptured under the action of an aqueous-methanol solution of HOCl much slower than in other substituted arylsilanes, except for the chloro and bromo derivatives[239]. Under the action of nitric acid p-(fluorophenyl)alkylchlorosilanes undergo quantitative rupture of the $Si{-}C_{arom}$ bond[163,164].

According to Motsarev and Yakubovich[224], the trifluoromethyl group in the *para*-position strongly inactivates the aromatic ring and stabilises the $Si{-}C_{arom}$ bond. This is shown by the fact that, on prolonged action of chlorine in the presence of $FeCl_3$, p-$CF_3C_6H_4SiF_3$ is not chlorinated nor is the $Si{-}C_{arom}$ bond ruptured, while under the same conditions p-$CH_3C_6H_4SiCl_3$ and p-$CCl_3C_6H_4SiCl_3$ are not only chlorinated but also undergo partial rupture of the $Si{-}C_{arom}$ bond.

Action of acids and alkalis on fluorine-containing polysiloxanes. The action of acids and alkalis on fluorine-containing polysiloxanes has already been discussed. Their stability to acids, alkalis, and other reagents depends to a great extent on the structure of the fluoroalkyl and fluoroaryl radicals bound to silicon. For example, polysiloxanes obtained from $CF_3CH_2CH_2SiCl_3$, $(CF_3CH_2CH_2)_2SiCl_2$, and $(CF_3CH_2CH_2)_3SiCl$ are resistant to heat and acids, and do not decompose on prolonged heating with 10% KOH.[187] On the other hand, polysiloxanes obtained from $HCF_2CF_2SiCl_3$ and $ClCF_2CF_2SiCl_3$ are decomposed readily by alkali solutions, even without heating[209].

The most resistant to heat and chemical reagents are polysiloxanes derived from arylsilicon fluorides with the general formula:



where n is not higher than 3, and x = 3–10. These polysiloxanes do not decompose even on prolonged boiling with fuming sulphuric or nitric acids[167,170].

In fluorine-containing cyclic polysiloxanes $[R_FCH_2CH_2.(CH_3)SiO]_{3-4}$, where R_F = CF_3, C_2F_5, or C_3F_7, the ring is opened on heating with solid alkali and there is further polymerisation to form polyfluoroalkylsiloxanes $[R_FCH_2CH_2.(CH_3)SiO]_n$, where n = 5000–6000.[240]

Reactions of fluoro-organosilicon hydrides. It is obvious from the above that the trifluoromethyl group has a considerable effect on the properties of fluoro-organosilicon compounds in which it occurs, its position in the molecule with respect to silicon being of decisive importance. Steward and Pierce[186] proved this especially clearly in their comparative study of hydrolysis of the Si–H bond in a series of fluoro-organosilicon hydrides. They established that the relative rate of hydrolysis of the Si–H bond in $CF_3CH_2CH_2(CH_3)_2SiH$ is 59 times higher, and in $CF_3CH_2CH_2CH_2(CH_3)_2SiH$ 8.3 times higher, than in $CH_3.CH_2CH_2(CH_3)_2SiH$. The rate of hydrolysis increases several times if the silicon atom is bound to two organic radicals containing CF_3 groups. For instance, it is 2100 times higher in $(CF_3CH_2CH_2)_2(CH_3)SiH$ than in $CH_3CH_2CH_2.(CH_3)_2SiH$.[186] The increased hydrolysis rate is connected with the higher susceptibility of the silicon atom to nucleophilic attack under the influence of the CF_3 group.

It may be that it is owing to the inductive, rather than the steric, effect of the CF_3 group that the compound $(m\text{-}CF_3C_6H_4)_3SiH$ does not react with organolithium compounds[178].

Reactions of fluoro-organosilicon halides. Like the ordinary alkyl(aryl)halogenosilanes, fluoroalkyl(aryl)halogenosilanes yield polysiloxanes on hydrolysis. The most widely used method for the preparation of polyfluoro-organosiloxanes is by aqueous or acid hydrolysis of fluoro-organosilicon monomers containing chlorine attached to silicon and by subsequent polycondensation of the hydrolysis products. The Si–Cl bond in the fluoroalkylsilicon chlorides $HCF_2CF_2SiCl_3$, $CF_3CH_2CH_2SiCl_3$, and $CF_3.CH_2CH_2(CH_3)SiCl_2$ [181,187,195,209,211,213,221], in the fluoroarylsilicon chlorides $CF_3C_6H_4SiCl_3$, $CF_3C_6H_4(CH_3)SiCl_2$, $(CF_3C_6H_4)_2SiCl_2$, and $[3,5\text{-}(CF_3)_2C_6H_3]_2SiCl_2$,[165,166,170,175] and in other fluoro-organosilicon monomers[231–233,241] readily undergoes hydrolysis. Although hydrolysis of these monomers proceeds relatively easily, the polycondensation of the products of hydrolysis, even unifunctional ones, containing simple fluoroalkyl radicals, is more difficult. For example, even at high temperatures $[3,5\text{-}(CF_3)_2C_6H_3]_3SiOH$ does not dimerise, but melts instead[167].

Polyfluoro-organosiloxanes can also be obtained by hydrolysis of the ethoxy derivatives of fluoro-organosilicon compounds, *e.g.* $\overline{CF_2CF_2CH_2CH}CH_2Si(CH_3)(OC_2H_5)_2$, $(\overline{CF_2CF_2CH_2CH}CH_2)_2Si(OC_2H_5)_2$.[230] This method, however, has no advantages over those discussed above.

Fluoro-organosilicon monomers can be converted to polysiloxanes without resorting to hydrolysis. One patent[242] claims the preparation of polyfluoro-organosiloxanes by boiling fluoro-organosilicon compounds containing Si–Cl bonds with metal oxides (Pb, Ca, Mg, or Zn) in the presence of organic nitriles. This reaction is considerably accelerated by addition of $CaCl_2$ or $HgCl_2$.

V. APPLICATIONS OF FLUORO-ORGANOSILICON COMPOUNDS

The development of the chemistry of fluoro-organosilicon compounds in the last decade has been mainly determined by practical demands of attempting to combine the invaluable properties of fluorocarbon polymers with those of organosilicon polymers in order to obtain polymers with new properties such as greater resistance to oils and fuels, thermal stability, lubricating properties, adhesion, etc. This is evident from the existence of innumerable patents on this subject, and the commercial availability of new fluoro-organosilicon polymers.

The use of fluoropolyorganosiloxanes has been recommended for the preparation of heat-resistant rubbers and resins[187,195,232,243–246], heat-resistant lubricants and hydraulic fluids[91,143,165,230–234,247,248] and dielectrics and insulating materials[133,175,224,242]. An example[244] is the new fluorosilicone rubber "Silastic LS-53" which the American firm "Dow-Corning" put on the market in 1957. The properties of the resin based on this new rubber are given in Table 3, together with the properties of the resin obtained from ordinary polydimethylsilicone rubber. This fluorosilicone rubber has brittle point -68°, glass point -61°, and remains practically unchanged on aging for 16 weeks at 200°, and is resistant to fuels, oils, and hydraulic fluids. The resin from it is used in the manufacture of aeroplane gaskets. "Silastic LS-53" is a copolymer of dimethyldichlorosilane with methyl(trifluoropropyl)dichlorosilane[249].

Fluorosilicone oils obtained from $\overline{CF_2CF_2CH_2CH}CH_2Si.(OC_2H_5)_2CH_3$ have a high heat-resistance, and are good lubricants, their friction coefficient being (steel on steel) 0.167.[230] Good lubricating properties are also exhibited by fluorosilicone oils of the general formula:

$$[m\text{-}CF_3C_6H_4Si(CH_3)O]_n{}^{247} \text{ and } \{[3,5\text{-}(CF_3)_2C_6H_3]_2SiO\}_n{}^{165}.$$

Non-hydrolysable trialkyl(aryl)fluorosilanes containing fluorine attached to silicon have been suggested as additives for high-temperature oils[91] and resins[250,251].

Compounds R_3SiF, where R is an alkyl radical with 4 to 18 carbon atoms a cyclic radical with 5 to 8 carbon atoms, or a phenyl, phenylethyl, or benzyl radical, are recommended as lubricants or hydraulic fluids. They are chemically inert, have a high viscosity index, low friction coefficient, and satisfactory lubricating properties[252,253]. Tripentylfluorosilane $(C_5H_{11})_3SiF$ is recommended for filling gun recoil shock absorbers[253].

Monomers such as $C_2H_5SiCl_2F$, $CH_3(C_6H_5)SiF_2$, $C_6H_5Si.Cl_2F$, $(C_6H_5)_2SiClF$, whose one Si–F bond remains intact on hydrolysis, have been proposed as insecticides[64].

Complex organosilicon fluorine compounds of the type $[(C_6H_5)_2NH]_2SiF_6$ can be used to prepare certain herbicides[254].

The physical properties (b.p., m.p., density, and refractive index) of all organosilicon fluorine compounds at present known are collected in Table 4.

TABLE 3.

Physical and mechanical indices	Polydimethylsilicone resin	Polyfluorosilicone resin
Tensile strength, kg cm^{-2}	49	56
Tear-resistance	moderate	satisfactory
Permanent set at 150°, %	20	7
Brittle point, °C	– 60	– 65
Swelling after 4 days, %, in		
kerosene	> 100 (at 100°)	18 (at 150°)
ether lubricant	10 (at 100°)	7 (at 150°)
mineral oil	5 (at 100°)	0 (at 150°)

TABLE 4. Physical properties of organosilicon fluorine compounds.

Empirical formula	Structural formula	B.p., °C	M.p., °C	d_4^{20}	n_D^{20}	Reference
$HSiClF_2$	$HSiClF_2$	—50	—144	—	—	46
$HSiCl_2F$	$HSiCl_2F$	—18.4	—149.5	—	—	46
$HSiF_3$	$HSiF_3$	—97.5	—131.2	—	—	45,46,51
H_2SiF_2	H_2SiF_2	—77.5	—119.1	—	—	50,51
H_3SiF	H_3SiF	—88.1	—	—	—	109,51
$SiClBr_2F$	$SiClBr_2F$	59.5	—99.3	—	—	49
$SiClF_3$	$SiClF_3$	—70	—142	—	—	48,55,117
$SiCl_2BrF$	$SiCl_2BrF$	35.4	—112.3	—	—	49
$SiCl_2F_2$	$SiCl_2F_2$	—32.2	—139.7	—	—	48,55,117
$SiCl_3F$	$SiCl_3F$	12.2	—120.8	—	—	47,48,55,79
SiF_4	SiF_4	—95.7	—	—	—	1,2,45,48
$SiBrF_3$	$SiBrF_3$	—41.7	—70.5	—	—	118
$SiBr_2F_2$	$SiBr_2F_2$	—13.7	66.9	—	—	118
$SiBr_3F$	$SiBr_3F$	83.8	—82.5	—	—	118
$SiFI_3$	$SiFI_3$	188(752)	—	3.164^{30}	—	56
SiF_2I_2	SiF_2I_2	84—85(756)	—	2.41^{25}	—	56
SiF_3I	SiF_3I	—24	—	—	—	56
$CSiF_3NO$	$SiF_3(NCO)$	—6	—	—	—	112
$CSiBrF_5$	CF_3SiBrF_2	12—13	—	—	—	227
$CSiF_6$	CF_3SiF_3	—42	—	—	—	227
CH_3SiClF_2	CH_3SiClF_2	— 0.5	—110	—	—	59
CH_3SiCl_2F	CH_3SiCl_2F	29.5	—98.7	—	—	59,198
CH_3SiF_3	CH_3SiF_3	—30.2	—72.8	—	—	59, 72,74,81,95
CH_4SiClF	$CH_3SiHClF$	1.2	—	—	—	170
CH_4SiF_2	CH_3SiHF_2	—35.6	—	—	—	69
CH_5SiF	CH_3SiH_2F	—44	—	—	—	105
$C_2SiCl_3F_3$	$CF_2=CFSiCl_3$	74—76(746)	—	—	—	221
$C_2SiCl_4F_2$	$CFCl=CFSiCl_3$	116—117(746)	—	—	—	221
$C_2SiCl_4F_4$	$CF_2ClCF_2SiCl_3$	102	—	—	—	209
$C_2SiF_2N_2O_2$	$(OCN)_2SiF_2$	68.6	—75	1.437	1.3536	112
$C_2HSiCl_3F_4$	$CF_2HCF_2SiCl_3$	84.2	—	—	1.367	209,215,216,220
$C_2HSiCl_4F_3$	$C_2HClF_3SiCl_3$	123	—	—	—	214,215,216
$C_2H_3SiCl_2F_3$	$C_2H_3Cl_2SiF_3$	91.7—92(749)	—	1.5007	1.3750	36
$C_2H_3SiCl_3F_2$	$CF_2HCH_2SiCl_3$	104—105.5	—	1.43	1.4050	189
$C_2H_3SiF_3$	$CH_2=CHSiF_3$	—25	—	—	—	77
$C_2H_4SiClF_3$	$CH_3CHClSiF_3$	39—39.5(749)	—	1.2606	1.3180	36
$C_2H_4SiClF_3$	$CH_2ClCH_2SiF_3$	68.5(749)	—	1.3661	1.3418	36
$C_2H_5SiClF_2$	$C_2H_5SiClF_2$	27.2	—	1.103	—	57,64
$C_2H_5SiCl_2F$	$C_2H_5SiCl_2F$	62.2	—	1.151	—	57,64
$C_2H_5SiF_3$	$C_2H_5SiF_3$	— 4.4	—105	—	—	36,57,64,71,107
$C_2H_5SiF_3O$	$C_2H_5OSiF_3$	— 7	—122	—	—	63,78
C_2H_6SiClF	$(CH_3)_2SiClF$	36.4	—85.1	—	—	60
$C_2H_6SiF_2$	$(CH_3)_2SiF_2$	2.7	—87.5	—	—	60,72,74,81
C_2H_7SiF	$(CH_3)_2SiHF$	— 9	—115	—	—	105
$C_3SiCl_5F_3$	$CCl_2=C(CF_3)SiCl_3$	77.5—78.5(35)	—	—	—	214
$C_3SiCl_7F_3$	$CCl_3CCl(CF_3)SiCl_3$	118—120(8.5)	—	—	—	214
$C_3SiFN_3O_3$	$(OCN)_3SiF$	134.3	—29.2	1.456	1.4161	112
$C_3HSiCl_6F_3$	$CHCl_2CCl(CF_3)SiCl_3$	78—78.5(3.8)	—	—	—	214
$C_3H_3SiCl_2F_3$	$CH_3(CF_2=CF)SiCl_2$	97—100	—	1.3311	1.3904	221,222
$C_3H_3SiCl_2F_3$	$CH_3(CClF=CF)SiClF$	94(740)	—	—	—	221
$C_3H_3SiCl_3F_2$	$CH_3(CClF=CF)SiCl_2$	121(741)	—	—	—	221
$C_3H_3SiCl_3F_3I$	$CF_3CH_2CHISiCl_3$	79(25)	—	—	—	213
$C_3H_4SiCl_2F_4$	$CH_3(CHF_2CF_2)SiCl_2$	96	—	1.3879	1.3689	191,211
$C_3H_4SiCl_3F_3$	$CH_3(CHF_2CClF)SiCl_2$	124.5(734)	—	1.4211	1.4000	191,193
$C_3H_4SiCl_3F_3$	$CF_3CH_2CH_2SiCl_3$	114	—	1.3951^{28}	1.3845^{28}	187,193,213,214
$C_3H_5SiCl_2F_3$	$CF_3CH_2CH_2SiHCl_2$	90—91	—	—	—	213
$C_3H_6SiCl_2F_2$	$CH_3(CHF_2CH_2)SiCl_2$	113—113.5(743)	—	1.2790	1.3941	198
$C_3H_6SiCl_3F$	$CH_3CHFCH_2SiCl_3$	123—124	—	$1.1924^{21,5}$	$1.4348^{21,5}$	193
$C_3H_7SiClF_2$	n-$C_3H_7SiClF_2$	55—57(745)	—	—	—	58
$C_3H_7SiClF_2$	iso-$C_3H_7SiClF_2$	48.8	—	—	—	61
$C_3H_7SiCl_2F$	iso-$C_3H_7SiCl_2F$	84	—	—	—	61
$C_3H_7SiF_3$	n-$C_3H_7SiF_3$	24.9	—	—	—	58
$C_3H_7SiF_3$	iso-$C_3H_7SiF_3$	24.9	—127.6	—	—	61
C_3H_9SiF	$(CH_3)_3SiF$	16,4	—74.3	—	—	60,72,74,89,92,95,98,99
$C_4HSiCl_3F_5$	$CF_2=CFCHFCF_2SiCl_3$	146	—	—	—	221
$C_4HSiCl_3F_8$	$CHF_2CF_2CF_2CF_2SiCl_3$	90(195)	—	—	—	209
$C_4H_3SiCl_3F_6$	$CF_3CF_2CHF\ CH_2SiCl_3$	127—127.8(758)	—	—	—	214
$C_4H_3SiCl_4F_3$	$CH_3[CCl_2=C(CF_3)]SiCl_2$	76—76.5(32)	—	—	—	214
$C_4H_3SiCl_5F_3I$	$CClF_2CClFCH_2CHISiCl_3$	124(1)	—	—	—	213
$C_4H_4SiCl_3F_5$	$CF_3CF_2CH_2CH_2SiCl_3$	120	—	—	1.3705^{25}	217
$C_4H_6SiClBrF_4$	$CH_3(CClF_2CH_2CHBr)SiF_2$	67.5—68(50)	—	1.631^{25}	1.4000^{25}	67,68
$C_4H_6SiCl_2F_4$	$C_2H_5(CHF_2CF_2)SiCl_2$	119.7(748)	—	1.3527	1.3819	191
$C_4H_6SiCl_3F_3$	$C_2H_5(CHF_2CClF)SiCl_2$	154(754)	—	1.4170	1.4120	191
$C_4H_6SiBrF_5$	$CH_3(CF_3CH_2CHBr)SiF_2$	114—115(736)	—	1.579^{25}	1.3680^{25}	67,68
$C_4H_7SiCl_2F_3$	$CH_3(CF_3CH_2CH_2)SiCl_2$	122	—	1.2611	1.3946	186,193,195,213,214
$C_4H_8SiClF_3$	$CH_3(CF_3CH_2CH_2)SiHCl$	96.5(746)	—	1.1565	1.3651	203
$C_4H_8SiCl_2F_2$	$C_2H_5(C_2H_3Cl_2)SiF_2$	148.2(751)	—	1.3099	1.4207	36
$C_4H_8SiF_2$	$C_2H_5(CH_2=CH)SiF_2$	56(742)	—	0.9578	1.3346	36
$C_4H_8SiF_4$	$(CH_3)_2(CHF_2CF_2)SiH$	62,3	—	—	—	212
$C_4H_9SiClF_2$	n-$C_4H_9SiClF_2$	84,5	—	—	—	62
$C_4H_9SiClF_2$	$C_2H_5(CH_3CHCl)SiF_2$	103.2(753)	—	1.1155	1.3790	36
$C_4H_9SiClF_2$	$C_2H_5(CH_2ClCH_2)SiF_2$	125.5(751)	—	1.1467	1.3900	36
$C_4H_9SiCl_2F$	n-$C_4H_9SiCl_2F$	116.1	—	—	—	62
$C_4H_9SiF_3$	n-$C_4H_9SiF_3$	52.4	—96.9	$1.006^{26,5}$	—	63,81,106
$C_4H_9SiF_3$	$CH_3(CF_3CH_2CH_2)SiH_2$	58.2(759)	—	0.9802	1.3408	30
$C_4H_{10}SiClF$	$(C_2H_5)SiClF$	96—97(758)	—	—	—	79
$C_4H_{10}SiF_2$	$(C_2H_5)_2SiF_2$	61—62	—	0.9289^{27}	1.3393^{23}	5,36,38,71,79,94,100,93, 106,107
$C_4H_{10}SiF_2O_2$	$(C_2H_5O)_2SiF_2$	83—83.5	—	—	—	101
$C_4H_{10}SiF_2S_2$	$(C_2H_5S)_2SiF_2$	163—164	—	—	—	157,158
$C_4H_{11}SiF$	$(CH_3)_2(C_2H_5)SiF$	51	—	—	1.3570^{15}	100,124
$C_5H_4SiCl_2F_8$	$CH_3(CHF_2CF_2CF_2CF_2)SiCl_2$	138(753)	—	1.5119	1.3570	192,211
$C_5H_4SiCl_3F_7$	$CF_3CF_2CF_2CH_2CH_2SiCl_3$	62—64(49)	—	—	1.3626^{25}	217
$C_5H_6SiCl_2F_6$	$CH_3(CF_3CF_2CHFCH_2)SiCl_2$	128—129.1(746)	—	—	—	214
$C_5H_6SiCl_3F_5$	$CF_3CF_2CH(CH_3)CH_2SiCl_3$	64—65(28)	—	—	1.3812^{25}	217
$C_5H_6SiCl_4F_3I$	$CH_3(CClF_2CClFCH_2CHI)SiCl_2$	116.5(33)	—	1.846^{25}	1.4895^{25}	68,213,234
$C_5H_7SiCl_2F_5$	$CH_3(CF_3CF_2CH_2CH_2)SiCl_2$	131	—	1.3136^{26}	1.3691^{25}	193,195
$C_5H_7SiCl_3F_4O$	$CHF_2CF_2OCH_2CH_2CH_2SiCl_3$	186(751)	—	1.4335	1.3994	201
$C_5H_7SiCl_4F_3O$	$CHClFCF_2OCH_2CH_2CH_2SiCl_3$	213(753)	—	1.4563	1.4230	200
$C_5H_8SiCl_2F_4O$	$CHF_2CF_2OCH_2CH_2CH\ SiHCl_2$	165.2(742)	—	1.3693	1.4001	204
$C_5H_8SiCl_3F_3O$	$CHClFCF_2OCH_2CH_2CH_2SiHCl_2$	188(746)	—	1.3886	1.4171	202

TABLE 4 (contd.)

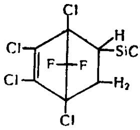
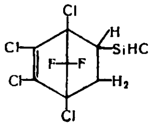
Empirical formula	Structural formula	B.p., °C	M.p., °C	d_4^{20}	n_D^{20}	Reference
$C_5H_9SiCl_2F_3$	$CH_3[CH_3CH(CF_3)CH_2]SiCl_2$	139	—	1.2322^{26}	1.3936	193,213,248
$C_5H_9SiF_3O_2$	$(CH_3)_3SiOCOCF_3$	90.2	—	1.077	1.338	235
$C_5H_{10}SiClF_3$	$(CH_3)_2(CF_3CH_2CH_2)SiCl$	118	—	1.113^{25}	1.3727^{25}	186
$C_5H_{10}SiClF_3$	$(CH_3)_3(C_2HClF_3)Si$	43—44(43)	—	1,134	1.3887^{22}	214
$C_5H_{10}SiF_4O_3$	$CHF_2CF_2Si(OCH_3)_3$	98(190)	—	—	—	209
$C_5H_{11}SiF_3$	n-$C_5H_{11}SiF_3$	77	—	$1.0023^{26,5}$	—	81,91,106
$C_5H_{11}SiF_3$	$(CH_3)_2(CF_3CH_2CH_2)SiH$	80(748)	—	0.954^{25}	1.3485^{25}	186
$C_5H_{13}SiF$	$CH_3(C_2H_5)_2SiF$	80—82(754)	—	—	1.3820^{17}	124
$C_5H_{13}SiFO$	$(CH_3)_2(C_2H_5OCH_2)SiF$	88—89	—	—	1.3710	113
$C_6HSiCl_3F_{12}$	$CHF_2CF_2CF_2CF_2CF_2CF_2SiCl_3$	128(205)	—	—	—	209
$C_6H_3SiCl_3F_6$	$CH_3(CF_2CF_2CF_2CCl{=}C)SiCl_2$	161(740)	—	—	—	221
$C_6H_4SiClF_3$	o-$ClC_6H_4SiF_3$	150—150.5(747)	—	1.3856	1.4460	65
$C_6H_4SiClF_3$	m-$ClC_6H_4SiF_3$	139.5—140.4(759)	—	1.3684	1.4430	65
$C_6H_4SiCl_2F_6$	$CH_3(CF_2CF_2CF_2CH{=}C)SiCl_2$	144(740)	—	1.481^{25}	—	221
$C_6H_4SiCl_3F$	p-$FC_6H_4SiCl_3$	194.5(738)	—	—	—	163,164
$C_6H_4SiF_6$	$CF_3C_6H_4SiF_3$	116.5—117(747)	—	1.400^{25}	1.3778	67
$C_6H_5SiClF_2$	$C_6H_5SiClF_2$	130—135	—	1.200^{27}	—	64,85
$C_6H_5SiCl_2F$	$C_6H_5SiCl_2F$	163—166	—	1.274^{26}	—	64,85
$C_6H_5SiCl_2F$	p-$FC_6H_4SiHCl_2$	177(747)	—	1.2936	1.5030	202
$C_6H_5SiCl_2F_7$	$CH_3(CF_3CF_2CF_2CH{=}CH)SiCl_2$	144	—	1.481	—	223
$C_6H_5SiF_3$	$C_6H_5SiF_3$	102	—18	1.2169	1.4110	38,64,65,71,75,81,91
$C_6H_6SiCl_3F_7$	$CF_3CF_2CF_2CH(CH_3)CH_2SiCl_3$	53—54(24)	—	—	1.3722^{25}	217
$C_6H_6SiF_6O_4$	$(CH_3)_2Si(OCOCF_3)_2$	128.2	—	1.361	1.331	235
$C_6H_7SiCl_2F_7$	$CH_3(CF_3CF_2CF_2CH_2CH_2)SiCl_2$	147	—	1.3707	1.3136	193,195,213,217
$C_6H_8SiCl_2F_6$	$(CF_3CH_2CH_2)_2SiCl_2$	162—163	—	1.3843	1.3810	187,202,213
$C_6H_8SiF_8$	$(CH_3)_2(CHF_2CF_2)_2Si$	120	—	—	—	212
$C_6H_9SiCl_2F_3$	$(CH_3)_3[CCl_2{=}C(CF_3)]Si$	157(756)	—	1.243	1.4322	214
$C_6H_9SiCl_2F_5$	$CH_3[CF_3CF_2CH(CH_3)CH_2]SiCl_2$	65(52)	—	—	1.3884^{25}	217
$C_6H_{10}SiClF_5$	$(CH_3)_2(CF_3CF_2CH_2CH_2)SiCl$	129(750)	—	1.199^{25}	1.3608^{25}	186
$C_6H_{10}SiCl_2F_4O$	$CH_3(CHF_2CF_2OCH_2CH_2CH_2)SiCl_2$	190.1(750)	—	1.3140	1.3960	201
$C_6H_{10}SiCl_3F_3O$	$CH_3(CHClFCF_2OCH_2CH_2CH_2)SiCl_2$	215(753)	—	1.3395	1.4160	200
$C_6H_{10}SiF_2$	$(CH_2{=}CHCH_2)_2SiF_2$	46.5(20)	—	—	—	134
$C_6H_{10}SiF_6$	$(CF_3CH_2CH_2)_2SiH_2$	45.5(33)	—	1.1928	1.3446	30
$C_6H_{11}SiBrF_2$	$(CH_3)_3(CBrF_2CH{=}CH)Si$	66—68(52)	—	—	—	213
$C_6H_{11}SiF_3$	$C_6H_{11}SiF_3$	105.3	—	1.113	1.3717	35,106
$C_6H_{11}SiF_5$	$(CH_3)_2(CF_3CF_2CH_2CH_2)SiH$	94(743)	—	1.078^{25}	1.3387^{25}	186
$C_6H_{12}SiClF_3$	$CH_3(C_2H_5)(CF_3CH_2CH_2)SiCl$	140(758)	—	1.1044	1.3871	203
$C_6H_{12}SiClF_3O$	$(CH_3)_3(CHClFCF_2OCH_2)Si$	141(751)	—	1.0966	1.3810	204
$C_6H_{12}SiBr_2F_2$	$(CH_3)_3(CBrF_2CH_2CHBr)Si$	95(25)	—	—	—	213
$C_6H_{12}SiF_3I$	$(CH_3)_3(CF_3CH_2CHI)Si$	72(20)	—	—	—	213
$C_6H_{13}SiF$	$C_6H_{11}SiH_2F$	118.1	—	0.925	1.4207	35
$C_6H_{13}SiF_3$	$(CH_3)_2(CF_3CH_2CH_2CH_2)SiH$	105(756)	—	0.950^{25}	1.3612^{25}	186
$C_6H_{13}SiF_3$	$(CH_3)_3(CF_3CH_2CH_2)Si$	94.3—95.1(750)	—	0.896	1.3576	214
$C_6H_{13}SiF_3O_2$	$CH_3(CF_3CH_2CH_2)Si(OCH_3)_2$	96.5—96.8(751)	—	1.0954	1.3576	185,213
$C_6H_{13}SiF_3O_3$	$CF_3CH_2CH_2Si(OCH_3)_3$	144	—	1.137	1.3547	185,213,214
$C_6H_{14}SiClF$	$(n\text{-}C_3H_7)_2SiClF$	140—144	—	—	—	158
$C_6H_{14}SiClF$	$(C_2H_5)_2(CH_3CHCl)SiF$	152	—	0.9955	1.4208	87,111
$C_6H_{14}SiClF$	$(C_2H_5)_2(CH_2ClCH_2)SiF$	171	—	1.0100	1.4277	87
$C_6H_{14}SiF_2$	$(n\text{-}C_3H_7)_2SiF_2$	111—113	—	0.9113	—	98,158
$C_6H_{14}SiF_2$	$(iso\text{-}C_3H_7)_2SiF_2$	102	—	—	1.3663	100.124
$C_6H_{14}SiF_2O_2$	$(CH_3CH_2CH_2O)_2SiF_2$	35(16)	—	0.8692	1.3830	42
$C_6H_{15}SiF$	$(C_2H_5)_3SiF$	109—110	—	0.8360	1.3900	5,27,38,86,92,98,100,111,119,124,238
$C_6H_{15}SiFO_3$	$(C_2H_5)_3SiF$	133—133.5	—	—	—	63,78,101
$C_6H_{15}SiFS_3$	$(C_2H_5S)_3SiF$	114—115(10)	—	—	—	157,158
$C_7H_8SiCl_7F_2$		130(10)	—	1.7010	1.5141	37
$C_7H_4SiCl_3F_3$	o-$CCl_3C_6H_4SiF_3$	229	—9	1.562^{25}	1.4997^{25}	83
$C_7H_4SiCl_3F_3$	m-$CF_3C_6H_4SiCl_3$	108(47.4)	—	—	1.4678^{25}	66,166,167
$C_7H_4SiCl_3F_3$	p-$CCl_3C_6H_4SiF_3$	212.2	5—5,5	1.510^{25}	1.4833^{25}	83
$C_7H_4SiCl_6F_2$		88(16)	—	1,4474	1,4326	37
$C_7H_4SiF_6$	o-$CF_3C_6H_4SiF_3$	138	—36	1.435^{25}	1.3876^{25}	83
$C_7H_4SiF_6$	m-$CF_3C_6H_4SiF_3$	118.2	—34	1.3985^{25}	1.3783^{25}	66
$C_7H_4SiF_6$	p-$CF_3C_6H_4SiF_3$	118.6	—3	1.399^{25}	1.3783^{25}	66,83,224
$C_7H_7SiF_3$	o-$CH_3C_6H_4SiF_3$	130.8	—78	1.190^{25}	1.4278^{25}	83
$C_7H_8SiF_2$	$CH_3(C_6H_5)SiF_2$	141—142	—	1.0993	—	64,75,96—99
$C_7H_9SiCl_2F_7$	$CH_3[CF_3CF_2CF_2CH(CH_3)CH_2]SiCl_2$	65(26)	—	—	1.3748^{25}	217
$C_7H_{11}SiClF_6$	$CH_3(CF_3CH_2CH_2)_2SiCl$	45.5—47(6)	—	1.2791	1.3699	186,203
$C_7H_{11}SiCl_2F_3$	$(CH_3)_3(CClF_2CClFCH{=}CH)Si$	57—59(15)	—	—	—	213
$C_7H_{11}SiF_3$	$(CH_3)_3(CF_2{=}CFCH{=}CH)Si$	25(25)	—	—	—	213
$C_7H_{12}SiCl_2F_4O$	$C_2H_5(CHF_2CF_2OCH_2CH_2CH_2)SiCl_2$	207.2(749)	—	1.2837	1.4033	201
$C_7H_{12}SiCl_2F_3I$	$(CH_3)_3(CClF_2CClFCH_2CHI)Si$	99—100(9)	—	—	—	213
$C_7H_{12}SiCl_3F_3O$	$C_2H_5(CHClFCF_2OCH_2CH_2CH_2)SiCl_2$	231.5(751)	—	1.3155	1.4249	200
$C_7H_{12}SiF_6$	$(CH_3)_3(CF_3CF_2CHFCH_2)Si$	109,8—111.5(747)	—	1.133	1.3441	214
$C_7H_{12}SiF_6$	$CH_3(CF_3CH_2CH_2)_2SiH$	64(40)	—	1.163^{25}	1.3500^{25}	186
$C_7H_{13}SiF_5$	$(CH_3)_3(CF_3CF_2CH_2CH_2)Si$	100—101	—	—	1.3000	217

TABLE 4 (contd.)

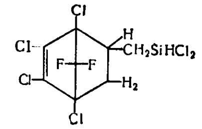
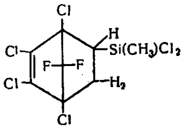
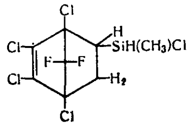
Empirical formula	Structural formula	B.p., °C	M.p., °C	d_4^{20}	n_D^{20}	Reference
$C_7H_{14}SiF_4O$	$(CH_3)_3(CHF_2CF_2OCH_2CH_2)Si$	137(746)	—	1,0550	1.3670	204
$C_7H_{15}SiF_3$	n-$C_7H_{15}SiF_3$	127	—	0,983	1.3606	70
$C_7H_{16}SiF_2$	n-$C_7H_{15}SiHF_2$	132.6	—	0.916	1.3759	70
$C_7H_{17}SiF$	n-$C_7H_{15}SiH_2F$	138.1	—	0.828	1.3997	70
$C_7H_{17}SiF$	CH_3(n-$C_3H_7)_2SiF$	130.2	—	—	1.3942^{19}	124
$C_7H_{17}SiF$	CH_3(iso-$C_3H_7)_2SiF$	124.5	—	—	1.3958^{21}	124
$C_7H_{17}SiFO$	$(C_2H_5)_2[CH_3CH(CH_3)O]SiF$	127(750)	—	0.8745	1.3803	76
C_8SiF_{12}	$(CF_2{=}CF)_4Si$	119—120	—	1.6182	1.3621	188
$C_8H_3SiCl_3F_6$	2,5-$(CF_3)_2C_6H_3SiCl_3$	80(25)	—	—	—	166,167
$C_8H_3SiCl_3F_6$	3, 5-$(CF_3)_2C_6H_3SiCl_3$	55—57.2(1.7)	—	1.532^{30}	1.4322	166,167
$C_8H_6SiCl_3F_3$	$CH_2Cl(CF_3C_6H_4)SiCl_3$	86(3.6)	—	1.4663^{25}	1.4839^{25}	171
$C_8H_6SiCl_6F_2$		102—103(2.5)	—	1.5483	1.5110	37
$C_8H_6SiCl_6F_2$		130(8)	—	1.6041	1.5121	37
$C_8H_7SiCl_2F_3$	$CH_3(m\text{-}CF_3C_6H_4)SiCl_2$	115.5(50)	—	1.3436^{25}	1.4639^{25}	166,169,170
$C_8H_7SiCl_5F_2$		122(8)	—	1.5355	1.5066	37
$C_8H_8SiF_{12}O_4$	$(CF_3CH_2O_2)_4Si$	165—166(750)	—	—	—	237
$C_8H_9SiF_3$	$CH_3(m\text{-}CF_3C_6H_4)SiH_3$	43(15)	—	1.1042	1.4460	30
$C_8H_{10}SiClF$	$(CH_3)_2(p\text{-}ClC_6H_4)SiF$	198	—	—	1.4930^{25}	113
$C_8H_{10}SiF_2$	$C_2H_5(C_6H_5)SiF_2$	163—164	—	—	—	96,97
$C_8H_{11}SiF$	$(CH_3)_2(C_6H_5)SiF$	161—162	—	—	1.4712^{25}	113
$C_8H_{12}SiClF_3$	$(CH_3)_2(CH_2{=}CH)(\overline{CH_2CF_2CClFCH})Si$	82(30)	—	1.144^{25}	1.4220^{25}	196
$C_8H_{13}SiF_3$	$CH_3(CH_2{=}CH)_2(CF_3CH_2CH_2)Si$	134	—	—	1.395^{25}	196
$C_8H_{13}SiF_7$	$(CH_3)_3(CF_3CF_2CF_2CH_2CH_2)Si$	36(30)	—	—	1.3390^{25}	217
$C_8H_{14}SiCl_2F_4O$	n-$C_3H_7(CHF_2CF_2OCH_2CH_2CH_2)SiCl_2$	101(11)	—	1.2484	1.4062	201
$C_8H_{14}SiCl_3F_3O$	n-$C_3H_7(CHClFCF_2OCH_2CH_2CH_2)SiCl_2$	115,5(8)	—	1.2763	1.4270	200
$C_8H_{14}SiF_6O_2$	$(CF_3CH_2CH_2)_2Si(OCH_3)_2$	175—176	—	1.256	1.3531	185,213
$C_8H_{15}SiClF_4O$	$CH_3(C_2H_5)(CHF_2CF_2OCH_2CH_2CH_2)SiCl$	199(749)	—	1.1681	1.3956	201
$C_8H_{15}SiCl_2F_3O$	$CH_3(C_2H_5)(CHClFCF_2OCH_2CH_2CH_2)SiCl$	223(746)	—	1.1918	1.4175	200
$C_8H_{16}SiClF_3O$	$(CH_3)_3(CHClFCF_2OCH_2CH_2CH_2)Si$	182(742)	—	1.0866	1.3985	200
$C_8H_{16}SiF_4O$	$(CH_3)_3(CHF_2CF_2OCH_2CH_2CH_2)Si$	156(746)	—	1.0453	1.3732	201
$C_8H_{16}SiF_4O_4$	$(CH_2FCH_2O)_4Si$	258(766)	—	1.2750	1.3891	238
$C_8H_{17}SiF_3$	$CH_3(CH_2)_4CH(CH_3)CH_2SiF_3$	50—54(24)	—	—	—	106
$C_8H_{18}SiF_2$	(n-$C_4H_9)_2SiF_2$	156(733)	—	0.8999	1.4049^{25}	81,98,99,106
$C_8H_{18}SiF_2$		145	—	—	—	125
$C_8H_{18}SiF_2O_2$	(n-$C_4H_9O)_2SiF_2$	58—59(13)	—	—	—	157,158
$C_8H_{19}SiFO$	$(C_2H_5)_3SiOCH_2CH_2F$	173.5—(764)	—	0.9062	1.4129	238
$C_9H_7SiCl_2F_3$	$m\text{-}CF_3C_6H_4(CH_2{=}CH)SiCl_2$	91—92(10)	—	—	1.4755	172
$C_9H_7SiF_9O_6$	n-$C_3H_7Si(OCOCF_3)_3$	157	—	1.434	1.3277	236
$C_9H_8SiCl_2F_4$	$p\text{-}FC_6H_4(CF_3CH_2CH_2)SiCl_2$	101—103(10)	—	1,3641	1.4645	202
$C_9H_9SiCl_2F_3$	$C_6H_5(CF_3CH_2CH_2)SiCl_2$	99—100(10)	—	1.3048	1.4737	202
$C_9H_9SiCl_2F_3$	$CH_3(CH_2Cl)(CF_3C_6H_4)SiCl$	130.8(25)	—	1.3411	1.4796^{25}	171
$C_9H_{10}SiClF_3$	$(CH_3)_2(o\text{-}CF_3C_6H_4)SiCl$	78(12)	—	—	—	66
$C_9H_{10}SiF_6O_6$	n-$C_3H_7Si(OCOCHF_2)_3$	230	—	1.440	1.3771	236
$C_9H_{12}SiClF$	$(CH_3)_2(p\text{-}ClC_6H_4CH_2)SiF$	217	—	—	1.4955^{25}	113
$C_9H_{13}SiF$	$(CH_3)_3(p\text{-}FC_6H_4)Si$	170.1(745)	—	0.9656	1.4751	160,163,164
$C_9H_{15}SiCl_2F_3$	$(C_2H_5)_3(CCl_2{=}C)(CF_3)Si$	119(28)	—	1.193	1.4532	214
$C_9H_{15}SiF$	$(CH_2{=}CHCH_2)_3SiF$	67(20)	—	—	—	134
$C_9H_{15}SiFO_3$	$(CH_2{=}CHCH_2O)_3SiF$	99—99.5(32)	—	—	—	101
$C_9H_{16}SiCl_2F_2O$	$(CH_3)_2(\overline{C_2Cl_2F_2CH_2CH}CH_2)SiOC_2H_5$	220	<—75	—	1.159^{25}	230
$C_9H_{16}SiF_6$	$CH_3(C_2H_5)_2(CF_3CF_2CHFCH_2)Si$	154—155(747)	—	1.115	1.3687	214
$C_9H_{16}SiF_4O$	$(CH_3)_2(\overline{CF_2CF_2CH_2CH}CH_2)SiOC_2H_5$	176	<—75	1.092^{25}	—	230
$C_9H_{18}SiClF_3O$	$(CH_3)_2(C_2H_5)(CHClFCF_2OCH_2CH_2CH_2)Si$	204(740)	—	1.0771	1.4073	200
$C_9H_{18}SiF_4O$	$(CH_3)_2(C_2H_5)(CHF_2CF_2OCH_2CH_2CH_2)Si$	176(739)	—	1.0402	1.3830	201
$C_9H_{19}SiF_3$	$(C_2H_5)_3(CF_3CH_2CH_2)Si$	166.1—167.8(753)	—	0.961	1.3962	214
$C_9H_{21}SiF$	(n-$C_3H_7)_3SiF$	174.5	—	0.8384	1.4117	92,98,99,119,124
$C_9H_{21}SiF$	(iso-$C_3H_7)_3SiF$	170	—	—	1.4185	124,125
$C_{10}H_3SiF_{15}O_6$	$CH_3Si(OCOC_2F_5)_3$	159	—	1.589	1.3033	236
$C_{10}H_8SiCl_3F_3$	$C_6H_5(\overline{CClFCF_2CH_2CH})SiCl_2$	135(21)	—	1.385^{25}	1.5002^{25}	231
$C_{10}H_{10}SiF_{14}$	$(C_2H_5)_2(CF_3CF_2CF_2)_2Si$	79(12)	—	—	1.3380	184
$C_{10}H_{10}SiF_{14}O_2$	$(CF_3CF_2CF_2CH_2CH_2)_2Si(OH)_2$	—	64.5—65	—	—	183
$C_{10}H_{12}SiClF_3$	$(CH_3)_3[4\text{-}Cl-5-(CF_3)C_6H_3]Si$	213.9	—34.1	1.166^{25}	1.4663^{25}	83,175
$C_{10}H_{13}SiF_3$	$(CH_3)_3(o\text{-}CF_3C_6H_4)Si$	185.5	<—78	1.089^{25}	1.4561^{25}	83
$C_{10}H_{13}SiF_3$	$(CH_3)_3(m\text{-}CF_3C_6H_4)Si$	175.1	<—78	1.053^{25}	1.4413^{25}	83
$C_{10}H_{13}SiF_3$	$(CH_3)_3(p\text{-}CF_3C_6H_4)Si$	180.7	—23	1.052^{25}	1.4403^{25}	83
$C_{10}H_{14}SiCl_2F_8O_2$	$(CHF_2CF_2OCH_2CH_2CH_2)_2SiCl_2$	122(3)	—	1.4222	1.3960	204
$C_{10}H_{14}SiCl_4F_6O_2$	$(CHClFCF_2OCH_2CH_2CH_2)_2SiCl_2$	151—152(6)	—	1.4296	1.4240	202
$C_{10}H_{15}SiF$	$(CH_3)_2(p\text{-}CH_3C_6H_4CH_2)SiF$	201	—	—	1.4775^{25}	113
$C_{10}H_{15}SiFO_2$	$C_6H_5(C_2H_5O)_2SiF$	64—75(200)	—	1.038^{28}	—	64
$C_{10}H_{17}SiF_7O_2$	$CH_3(CF_3CF_2CF_2CH_2CH_2)Si(OC_2H_5)_2$	82—83(28)	—	—	1.3502	185,213
$C_{10}H_{18}SiF_6$	$(C_2H_5)_3(CF_3CF_2CHFCH_2)Si$	173.1(753)	—	1.110	1.3800	214

TABLE 4 (contd.)

Empiral formula	Structural formula	B.p., °C	M.p., °C	d_4^{20}	n_D^{20}	Reference
$C_{10}H_{18}SiF_4O_2$	$CH_3(CF_2CF_2CH_2CHCH_2)Si(OC_2H_5)_2$	201	<-70	1.096^{25}	—	230
$C_{10}H_{20}SiClF_3O$	$CH_3(C_2H_5)_2(CHClFCF_2OCH_2CH_2CH_2)Si$	94(7)	—	1,0776	1.4149	200
$C_{10}H_{20}SiF_4O$	$CH_3(C_2H_5)_2(CHF_2CF_2OCH_2CH_2CH_2)Si$	196.5(749)	—	1.0422	1.3930	201
$C_{10}H_{20}SiF_4O$	$(CH_3)_2(C_3H_7)(CHF_2CF_2OCH_2CH_2CH_2)Si$	193(751)	—	1.0267	1,3886	201
$C_{10}H_{22}SiF_2$	$(\text{n-}C_5H_{11})_2SiF_2$	193	—	$0.8972^{26,5}$	—	81,91
$C_{11}H_5SiF_{15}O_6$	$C_2H_5Si(OCOC_2F_5)_3$	169	—	1.545	1.3091	236
$C_{11}H_{11}SiCl_2F_5O$	$p\text{-}FC_6H_4(CHF_2CF_2OCH_2CH_2CH_2)SiCl_2$	137—137.5(8)	—	1.3695	1,4560	204
$C_{11}H_{11}SiF_9O_6$	$\text{n-}C_5H_{11}Si(OCOCF_3)_3$	181	—	1.363	1.3410	236
$C_{11}H_{12}SiCl_2F_4O$	$C_6H_5(CHF_2CF_2OCH_2CH_2CH_2)SiCl_2$	118.5(4)	—	1.3204	1.4650	204
$C_{11}H_{12}SiCl_3F_3O$	$C_6H_5(CHClFCF_2OCH_2CH_2CH_2)SiCl_2$	145(16)	—	1.3417	1.4825	204
$C_{11}H_{14}SiClF_3O$	$(CH_3)_2(4\text{-}Cl\text{ - }5\text{ - }CF_3C_6H_3)SiOC_2H_5$	65—67(1—2)	—	—	—	175
$C_{11}H_{15}SiF_3$	$(CH_3)_3(m\text{-}CF_3C_6H_4CH_2)Si$	195.6	<-78	1.034^{25}	$1,4451^{25}$	83
$C_{11}H_{16}SiF_6$	$CH_3(CH_2{=}CH)_2(CF_3CH_2CH_2CH)(CF_3)CH_2Si$	89(30)	—	—	1.3903^{25}	196
$C_{11}H_{19}SiF_7O_3$	$CF_3CF_2CF_2CH_2CH_2Si(OC_2H_5)_3$	47(3)	—	—	—	183,185
$C_{11}H_{21}SiCl_2F_3O$	$(\text{n-}C_3H_7)_2(CHClFCF_2OCH_2CH_2CH_2)SiCl$	116.8—117.2(3)	—	1.1377	1,4286	204
$C_{11}H_{21}SiF_3O$	$(C_2H_5)_3\{CH_2{=}C[C(CH_2)(CF_3)(OH)]\}Si$	114—115(22)	—	1,0342	1,4291	199
$C_{12}H_5SiF_9O_6$	$C_6H_5Si(OCOCF_3)_3$	198	—	1.481	1,3784	236
$C_{12}H_7SiF_{15}O_6$	$\text{n-}C_3H_7Si(OCOC_2F_5)_3$	178	—	1,510	1,3156	236
$C_{12}H_8SiCl_2F_2$	$(p\text{-}FC_6H_4)_2SiCl_2$	293,4(738)	—	—	—	163,164
$C_{12}H_8SiF_6O_6$	$C_6H_5Si(OCOCHF_2)_3$	248	—	1.494	1,4290	236
$C_{12}H_8SiF_{20}O_4$	$(CF_3CF_2CH_2O)_4Si$	81—82(10)	—	—	—	237
$C_{12}H_{10}SiClF$	$(C_6H_5)_2SiClF$	123—125(5.5)	—	$1,181^{25,5}$	—	64
$C_{12}H_{10}SiF_2$	$(C_6H_5)_2SiF_2$	247—248	—	$1,151^{25,5}$	—	38,64,71,81 98,99,134,135
$C_{12}H_{11}SiF_9O_6$	$C_6H_{11}Si(OCOCF_3)_3$	200	—	1.418	1,3583	236
$C_{12}H_{15}SiClF_4O$	$CH_3(C_6H_5)(CHF_2CF_2OCH_2CH_2CH_2)SiCl$	118.5—119(3.5)	—	1.2286	1.4600	204
$C_{12}H_{17}SiF_3O_2$	$CH_3(m\text{-}CF_3C_6H_4)Si(OC_2H_5)_2$	105—108(13)	—	1,086	—	174
$C_{12}H_{20}SiF_4O_2$	$(CH_2{=}CHCH_2)(CF_2CF_2CH_2CHCH_2)Si(OC_2H_5)_2$	103(10)	<-75	$1,096^{25}$	—	230
$C_{12}H_{23}SiF_3$	$C_{12}H_{23}SiF_3$	98—102(6—7)	—	$0,9403^{23}$	1.3910^{23}	91
$C_{12}H_{25}SiF_3$	$CH_3(CH_2)_{11}SiF_3$	101—110(3—4)	—	$0,9376^{23}$	—	106
$C_{12}H_{27}SiF$	$(\text{n-}C_4H_9)_3SiF$	225.3	—	0.8404	1.4238	81,92,98,99,100,119
$C_{12}H_{27}SiF$	$(\text{iso-}C_4H_9)_3SiF$	205.5(750)	—	—	1.4218	125
$C_{12}H_{27}SiFO_3$	$(\text{n-}C_4H_9O)_3SiF$	133—134(32)	—	0,9383	—	101,107,158
$C_{13}H_{19}SiF_3O_3$	$m\text{-}CF_3C_6H_4Si(OC_2H_5)_3$	190	—	1,12	—	66,174
$C_{14}H_5SiF_{21}O_6$	$C_2H_5Si(OCOC_3F_7)_3$	199	—	1,624	1,3111	236
$C_{14}H_6SiCl_4F_6$	$(4\text{-}Cl\text{ -}5\text{ - }CF_3C_6H_3)_2SiCl_2$	112—115(1)	—	—	—	175
$C_{14}H_8SiCl_2F_6$	$(m\text{-}CF_3C_6H_4)_2SiCl_2$	124.7(3.4)	—	1.4274^{25}	1.4884^{25}	66,166,167
$C_{14}H_{10}SiF_6$	$(m\text{-}CF_3C_6H_4)_2SiH_2$	125—126(12)	—	1,2927	1,4806	30
$C_{14}H_{11}SiF_{15}O_6$	$C_5H_{11}Si(OCOC_2F_5)_3$	197	—	1.441	1.3267	236
$C_{14}H_{12}SiF_2$	$(o\text{-}CH_3C_6H_4)_2SiF_2$	285—289	—	—	—	125
$C_{14}H_{14}SiF_2$	$(CH_3)_2(p\text{-}FC_6H_4)_2Si$	184—185(60)	—	1.1121	1.5331	163,164
$C_{14}H_{14}SiF_2$	$(C_6H_4CH_2)_2SiF_2$	289—291(657)	—	—	—	134,136
$C_{14}H_{18}SiF_{14}O_2$	$(CF_3CF_2CF_2CH_2CH_2)_2Si(OC_2H_5)_2$	117.5—118(25)	—	—	—	183
$C_{14}H_{20}SiF_8O_2$	$(CF_2CF_2CH_2CHCH_2)_2Si(OC_2H_5)_2$	117(3)	<-75	$1,259^{25}$	—	230
$C_{15}H_5SiF_{15}O_6$	$C_6H_5Si(OCOC_2F_5)_3$	215	—	1,546	1.3551	236
$C_{15}H_7SiF_{21}O_6$	$\text{n-}C_3H_7Si(OCOC_3F_7)_3$	208	—	1.584	1.3164	236
$C_{15}H_9SiCl_3F_6$	$CH_3(4\text{-}Cl\text{ - }5\text{ - }CF_3C_6H_3)_2SiCl$	128—129(1)	—	—	—	175
$C_{15}H_{10}SiCl_2F_6$	$(CH_2Cl)(CF_3C_6H_4)_2SiCl$	152(3.5)	—	1.4407^{25}	$1,4987^{25}$	171
$C_{15}H_{11}SiClF_6$	$CH_3(m\text{-}CF_3C_6H_4)_2SiCl$	123(4)	—	1.3535^{25}	1.4841^{25}	166,170
$C_{15}H_{11}SiF_{15}O_6$	$C_6H_{11}Si(OCOC_2F_5)_3$	216	46	—	—	236
$C_{15}H_{12}SiF_{21}Cl$	$(CF_3CF_2CF_2CH_2CH_2)_3SiCl$	133—134(15)	34—35	—	—	183
$C_{15}H_{13}SiF_{21}O$	$(CF_3CF_2CF_2CH_2CH_2)_3SiOH$	151—153	—	—	1.3378	183
$C_{15}H_{33}SiF$	$(\text{n-}C_5H_{11})_3SiF$	267(745)	—	0.8389^{25}	$1,4305^{25}$	81,119
$C_{16}H_6SiCl_2F_{12}$	$[2,5\text{-}(CF_3)_2C_6H_3]_2SiCl_2$	109.5—110(3)	—	—	1.4248^{30}	166,167
$C_{16}H_6SiCl_2F_{12}$	$[3,5\text{-}(CF_3)_2C_6H_3]_2SiCl_2$	116.6(214)	—	1.567^{30}	$1,4424^{30}$	165,166,167
$C_{16}H_8SiF_{12}O_2$	$[3,5\text{-}(CF_3)_2C_6H_3]_2Si(OH)_2$	—	220	—	—	167
$C_{16}H_{12}SiCl_2F_6$	$(CH_3)_2(4\text{-}Cl\text{ - }5\text{ - }CF_3C_6H_3)_2Si$	326.2	45,4	—	—	83,175
$C_{16}H_{13}SiClF_6$	$CH_3(CH_2Cl)(CF_3C_6H_4)_2Si$	130.8—131.8(1.5)	—	1.3434^{25}	$1,4925^{25}$	171
$C_{16}H_{33}SiF_3$	$\text{n-}C_{16}H_{33}SiF_3$	171(45)	—	0,9221	—	98,99
$C_{18}H_5SiF_{21}O_6$	$C_6H_5Si(OCOC_3F_7)_3$	245	—	1,617	1.3495	236
$C_{18}H_{11}SiF_{21}O_6$	$C_6H_{11}Si(OCOC_3H_7)_3$	243	—	1.566	1.3370	236
$C_{18}H_{15}SiF$	$(C_6H_5)_3SiF$	200—210(10)	64	—	—	38,100,120,130,132,135, 146
$C_{18}H_{18}SiF_6O_2$	$(m\text{-}CF_3C_6H_4)_2Si(OC_2H_5)_2$	104—115(1)	20	—	—	66
$C_{18}H_{33}SiF$	$(C_6H_{11})_3SiF$	160—170(5)	45—46	—	—	100,125,133
$C_{20}H_{14}SiF_2$	$(\alpha\text{-}C_{10}H_7)_2SiF_2$	210—213(3)	79—81	—	—	126
$C_{20}H_{16}SiF_{28}$	$(CF_3CF_2CF_2CH_2CH_2)_4Si$	71—72(25)	—	—	—	183
$C_{21}H_{12}SiClF_9$	$(m\text{-}CF_3C_6H_4)_3SiCl$	174.2(0,7)	—	—	1.5018^{25}	166,167
$C_{21}H_{12}SiF_{10}$	$(m\text{-}CF_3C_6H_4)_3SiF$	168—174(1—2)	—	1.4008^{25}	1.4858^{25}	161
$C_{21}H_{13}SiF_9$	$(m\text{-}CF_3C_6H_4)_3SiH$	322—325	—	1.3500	1,4948	178
$C_{21}H_{13}SiF_9$	$(p\text{-}CF_3C_6H_4)_3SiH$	—	82—83	—	—	162
$C_{21}H_{21}SiF$	$(o\text{-}CH_3C_6H_4)_3SiF$	—	86,5	—	—	100
$C_{21}H_{21}SiF$	$(p\text{-}CH_3C_6H_4)_3SiF$	324—327	108—109	—	—	132,146
$C_{21}H_{21}SiF$	$(C_6H_5CH_2)_3SiF$	235.5(7.5)	79	—	—	121,136
$C_{22}H_{15}SiF_9$	$CH_3(p\text{-}CF_3C_6H_4)_3Si$	—	106—107,5	—	—	162
$C_{24}H_9SiClF_{18}$	$[2,5\text{-}(CF_3)_2C_6H_3]_3SiCl$	155—160(3)	—	—	1.4549^{30}	166,167
$C_{24}H_9SiClF_{18}$	$[3,5\text{-}(CF_3)_2C_6H_3]_3SiCl$	186—188(20)	—	1.5523^{30}	$1,4445^{30}$	165,166,167
$C_{24}H_{51}SiF$	$(\text{n-}C_8H_{17})_3SiF$	177—180(0.5—1)	—	—	1.4455^{25}	133
$C_{25}H_{19}SiF_3$	$(C_6H_5)_3(m\text{-}CF_3C_6H_4)Si$	—	101	—	—	173
$C_{26}H_{18}SiF_6$	$(C_6H_5)_2(m\text{-}CF_3C_6H_4)Si$	375—378	97—98	—	—	178
$C_{27}H_{17}SiF_9$	$C_6H_5(m\text{-}CF_3C_6H_4)_2Si$	370—374	81	—	—	178
$C_{28}H_{16}SiF_{12}$	$(m\text{-}CF_3C_6H_4)_4Si$	362	102—103	—	—	161,178
$C_{30}H_{21}SiF$	$(\alpha\text{-}C_{10}H_7)_3SiF$	290—292(3)	224	—	—	127,128
$C_{36}H_{75}SiF$	$(\text{n-}C_{12}H_{25})_3SiF$	275—295(2)	18,6	—	1.4530^{25}	133
$C_{42}H_{87}SiF$	$(\text{n-}C_{14}H_{29})SiF$	310—330(3)	61—62	0.834	—	133
$C_{54}H_{111}SiF$	$(\text{n-}C_{18}H_{37})_3SiF$		64—66	—	—	133

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ADVANCES IN THE SYNTHESIS OF ALKYLPYRIDINES

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CONTENTS

I. INTRODUCTION

By virtue of their valuable properties the pyridine bases are acquiring an increasing importance in chemical industry. Pyridine and its homologues are widely used as solvents, and in the synthesis of rubber, plastics, and drugs. Interest in the synthesis of pyridine bases has been stimulated by the discovery that α-vinylpyridine, 2-methyl-5-vinylpyridine, and other vinylpyridines may act as valuable copolymers in the manufacture of synthetic rubber and plastics[1-11]. For instance, copolymers of butadiene and 2-methyl-5-vinylpyridine, and tripolymers of butadiene, styrene, and 2-methyl-5-vinylpyridine are used as latex for the impregnation of tyre cord because they increase the strength of the resin bond with the cord by 80–100%. Nicotinic and isonicotinic acids are of special significance. The former is a constituent of vitamin PP, which prevents and cures pellagra, and fortifies the nervous system. The latter is the main starting material in the synthesis of a series of antitubercular preparations of the isoniazid type[12].

Wider application of pyridine bases in organic synthesis is limited by the fact that the starting alkylpyridines are difficult to obtain.

The preparation of alkylpyridines has not been discussed in sufficient detail, although there are several reviews on the chemistry of pyridine derivatives[13-19]. We have therefore undertaken to describe systematically all the most important methods for the synthesis of alkyl- and aryl-pyridines which had appeared up to 1959. We divided these methods into two groups: (1) synthesis of pyridine bases from compounds not containing a pyridine ring; (2) synthesis from compounds containing a pyridine ring.

Compounds of the pyridine series can also be obtained by pyrolysis. Pyrolysis of coals and shales yields tar containing small quantities of a complex mixture of alkylpyridines which are difficult to separate. Although methods for the separation of individual compounds from the mixture of bases have been studied for many years[20], the problem is still not completely solved, and the practical use of mixtures of pyrogenic pyridines is still out of the question.

II. SYNTHESIS OF PYRIDINE BASES FROM COMPOUNDS NOT CONTAINING A PYRIDINE RING

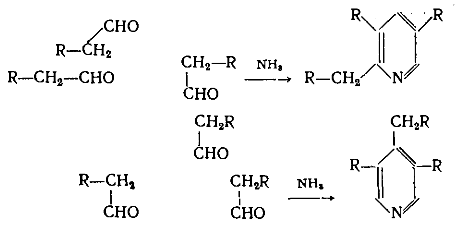
1. Synthesis Based on the Chichibabin Reaction

In 1869 Baeyer[21,22] carried out one of the first syntheses of pyridine, by passing acrolein through an aqueous solution of ammonia. He identified β-picoline in the reaction products by means of chloroplatinate. Dürkopf[23-25] carried out an analogous reaction, at almost the same time, by heating a mixture of aliphatic aldehydes and ammonium acetate in sealed tubes to 200°, and obtained a mixture of pyridine bases. He obtained the best results using paraldehyde, when he isolated 2-methyl-5-ethylpyridine from the mixture of reaction products.

Chichibabin and his collaborators carried out a good deal of work in this field. They synthesised pyridine by two methods: (1) heating aldehydes with aqueous ammonia in sealed tubes; (2) passing a mixture of aldehyde vapours and ammonia over a dehydration catalyst. Using the first method[27-30] they obtained α- and γ-methylpyridines and

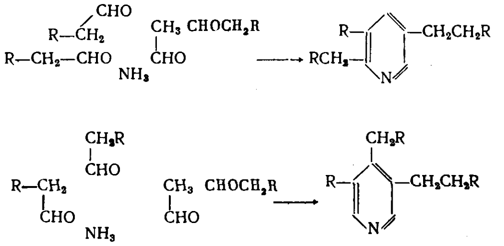
2-methyl-5-ethylpyridine from acetaldehyde and ammonia, and 3,5-dimethyl-2-ethylpyridine as the main product from propionaldehyde and ammonia. The preparation of 2-methyl-5-ethylpyridine from acetaldehyde in 70–80% yield[31-39] stimulated an interest in the further development of the Chichibabin reaction with a view to its use in industry. Of special interest in this respect was the work of Farberov and his associates[9], who found a suitable catalyst, giving high yields of 2-methyl-5-ethylpyridine from paraldehyde and ammonia, and thus succeeded in applying this process on an industrial scale.

From a mass of experimental data Chichibabin managed to establish certain definite principles governing this reaction. He showed that saturated aldehydes of the type of acetaldehyde and its monosubstituted homologues can react in two ways:


(1)

(2)

By using different aldehydes the reaction can be made to proceed according to the following schemes:

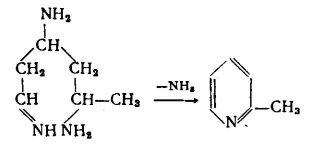

(3)

(4)

Although the mechanism of these reactions was studied by Chichibabin[27] and by other research workers[40-43], it has still not been completely elucidated. Opinions regarding the course of the reaction are rather controversial. Some[42] consider that aldehyde reacts primarily with ammonia, whereby the resulting imine undergoes an aldol condensation followed by an intramolecular cyclisation to pyridine bases. For instance, the formation of α-picoline from acetaldehyde is described by the following scheme:

$$CH_3CHO + NH_3 \longrightarrow CH_3{-}CH{=}NH$$

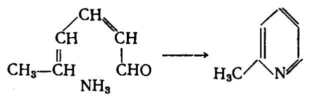
$$CH_3CH{=}NH + CH_3CH{=}NH + CH_3CH{=}NH \longrightarrow CH_3\underset{NH_2}{CH}CH_2\underset{NH_2}{CH}CH_2CH{=}NH$$



Others think that acetaldehyde is first condensed to crotonaldehyde, which undergoes a 1,4-addition followed by ring closure with the participation of nitrogen. They do not think that ammonia plays any part in the first stage of the reaction[40-43]:

$$CH_3CHO + CH_3CHO \longrightarrow CH_3CH{=}CHCHO$$

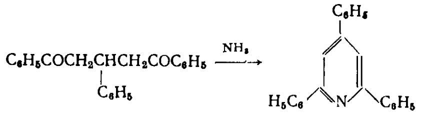
$$CH_3CH{=}CH{-}CHO + CH_3{-}CHO \longrightarrow CH_3CH{=}CH{-}CH{=}CH{-}CHO$$



This reaction was later extended to the preparation of arylpyridines from aromatic aldehydes[41,44] or from a mixture of aldehydes and ketones[46,47]. Weiss[46] showed that by simultaneously using aromatic aldehydes and ketones the reaction can be carried out simply by boiling with ammonium acetate in acetic acid solution. Individual products are obtained in good yields. For instance, acetophenone and benzaldehyde gave 70% of 2,4,6-triphenylpyridine. Weiss considers this reaction to proceed by the following scheme:

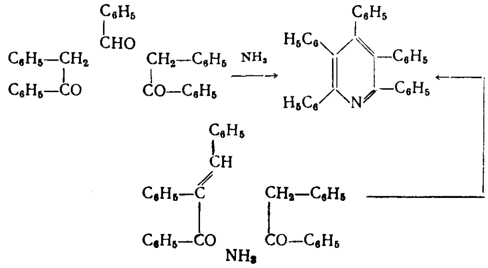
$$CH_3COC_6H_5 + C_6H_5CHO \longrightarrow C_6H_5CH{=}CH{-}CO{-}C_6H_5$$

$$C_6H_5CH{=}CH{-}CO{-}C_6H_5 + C_6H_5COCH_3 \longrightarrow C_6H_5COCH_2{-}\underset{C_6H_5}{CH}{-}CH_2COC_6H_5$$



Weiss has failed as yet to extend this method to alkylpyridines.

Frank and Seven[40] obtained pentaphenylpyridine by boiling benzaldehyde and phenyl benzyl ketone with ammonium acetate, or benzaldeoxybenzoin and phenyl benzyl ketone with ammonium acetate. Equal yields of pentaphenylpyridine in the two cases indicate that an aldol mechanism operates:

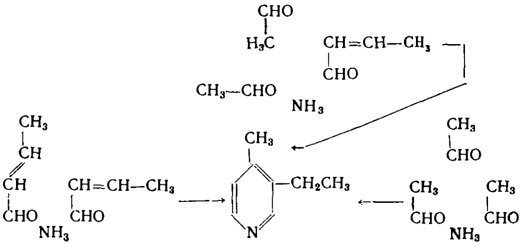


Eliel *et al.*[41] pointed out that the synthesis of arylpyridines from aromatic aldehydes does not proceed according to the Chichibabin reaction scheme. For instance, instead of the expected 2-benzyl-3,5-diphenylpyridine, the main reaction products from phenylacetaldehyde are 3,5-diphenylpyridine and toluene. In their opinion the Chichibabin mechanism for the anomalous condensations in the aliphatic series does not apply to aromatic compounds, and is also doubtful in the case of aliphatic aldehydes. They account for the formation of 3,5-diphenylpyridine by the splitting off of toluene in the course of reaction from the primary reaction product, *viz*. 2-(or 4-)benzyl-3,5-diphenylpyridine.

Chichibabin showed in his later studies[45,48] that the condensation of aldehydes with ammonia can be carried out in the gas phase using various catalysts. Here it is somewhat more difficult to control the course of the reaction than if the synthesis is carried out in an aqueous medium. The reaction usually results in a complex mixture of products in small yields. Only by careful selection of the reaction conditions can the main reaction product be obtained in satisfactory yield. For instance, by passing a mixture of acetaldehyde and ammonia over alumina at 300°–330°, a mixture of pyridine bases consisting of 28% α-picoline, 30% γ-picoline, 33% 2-methyl-5-ethylpyridine, and 6% 4-methyl-3-ethylpyridine is obtained[48] in 60% yield. It should be noted that in aqueous medium 2-methyl-5-ethylpyridine is the main reaction product, while the gas phase reaction yields this material accompanied by an equal quantity of γ-picoline. The formation of 4-methylpyridine and 4-methyl-3-ethylpyridine can be accounted for by the reaction schemes (2) and (4) given above, where R = = H. The condensation of propionaldehyde with ammonia over alumina at 310°–320° gave 40% of a mixture of pyridine bases, from which 2-ethyl-3,5 dimethylpyridine (60%), small quantities of 4-ethyl-3,5-dimethylpyridine, and 18% of 3,5-dimethylpyridine were isolated[39].

To prepare 3,5-dimethylpyridine Chichibabin and Oparina treated propionaldehyde with formaldehyde and ammonia in the presence of an alumina catalyst[50]. The condensation of butyraldehyde with ammonia over silica at 300°–330° gave 3,5-diethylpyridine and 2-propyl-3,5-diethylpyridine[51]. The condensation of two moles of propionaldehyde and 1 mole of acetaldehyde in the presence of alumina at 330°–340° yielded 2,3,5-trimethylpyridine[49]. When aromatic aldehydes are used, aryl-substituted pyridine bases are obtained[45,52].

Judging from experimental results[53], the reaction in the gaseous phase proceeds *via* the intermediate formation of β-unsaturated aldehydes. This reaction scheme is confirmed by the fact that identical reaction products are obtained from acetaldehyde and crotonaldehyde[53,54]:

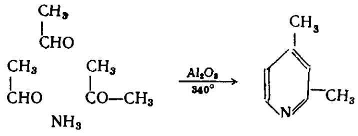


Similarly, the reaction of α,β-unsaturated aliphatic aldehydes with ammonia at 300°–350° in the presence of Al_2O_3, BPO_4, etc. gave various alkylpyridines[55,56]. For example, α-methylacrolein and ammonia, heated at 325°–370° over boron phosphate, gave mainly 3,5-dimethylpyridine, while α-ethylacrolein yielded 3,5-diethylpyridine under the same conditions[57].

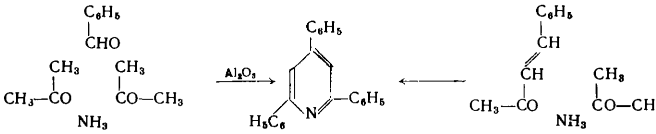
In view of the importance of β-picoline, the catalytic preparation of this compound from acrolein and ammonia, first carried out by Baeyer[21], has been studied in great detail. With the aim of applying this method to industrial preparation, special studies were undertaken, in which β-picoline was obtained in 45% yield[58,59].

The reaction of ammonia with allylamine[60], glycerol[61], or allyl alcohol[62-64] instead of acrolein, also yields β-picoline. The alcohols are evidently dehydrogenated to acrolein, or allylamine is formed and subsequently undergoes ring-closure to form a pyridine ring.

The catalytic reaction of aldehydes with ketones and ammonia affords pyridine by a series of reactions similar to the above. For instance acetaldehyde and acetone, heated at 340° in the presence of alumina, yield 2,4-dimethylpyridine[65].



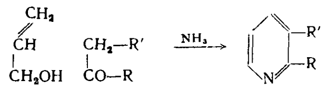
Similarly, the catalytic reaction of 2 moles of acetone and 1 mole of acetaldehyde with ammonia yields symmetrical collidine[66]. Oparina showed that the simultaneous condensation of formaldehyde and acetone (or methyl ethyl ketone) with ammonia yields 2,6-dimethylpyridine (or 2,3,5,6-tetramethylpyridine)[65,67]. A mixture of 2-methyl-4-phenylpyridine and 4-methyl-2-phenylpyridine was obtained[68] by passing acetaldehyde and acetophenone over alumina at 400°. Chichibabin synthesised 2,6-dimethyl-4-phenylpyridine in two ways: (a) from ammonia and benzaldehyde and acetone, and (b) from ammonia, benzylideneacetone, and acetone[45]. This was another confirmation of the reaction mechanism:



Heating a mixture of acetaldehyde, methyl-t-butyl ketone and ammonia with alumina at 310° results in the formation of 2,6-di-t-butyl-4-methylpyridine[69].

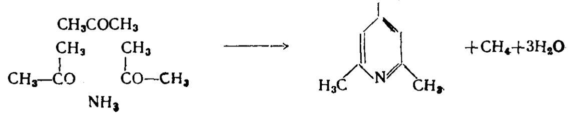
The recent publications of Ishiguro and his co-workers[70,71] showed that pyridines could be obtained by passing over a catalyst a mixture of various ketones with allyl alcohol and ammonia, the allyl alcohol being transformed into acrolein in the course of reaction. They showed that better yields of pyridine bases are obtained if a cadmium phosphate catalyst is used[70].

Similarly, by the catalytic reaction of various alkyl and alkylaryl ketones with allyl alcohol and ammonia, Ishiguro obtained a series of alkyl- and aryl-pyridines in 20–25% yield according to the scheme:



where R′ = alkyl or H; R = alkyl or aryl. 5,6,7,8-Tetrahydroquinoline was synthesised similarly from allyl alcohol, cyclohexanone, and ammonia.

Certain ketones, acetone[72] and acetophenone[73] in particular, react with ammonia to form 2,4,6-trimethylpyridine and 2,4,6-triphenylpyridine respectively. The reaction with acetone was carried out at 110°–140° in the presence of zinc chloride, but the yield of collidine was small and some methane was liberated. This reaction proceeds in the gas phase[74] over a SiO_2/Al_2O_3 catalyst at 400°–500°.

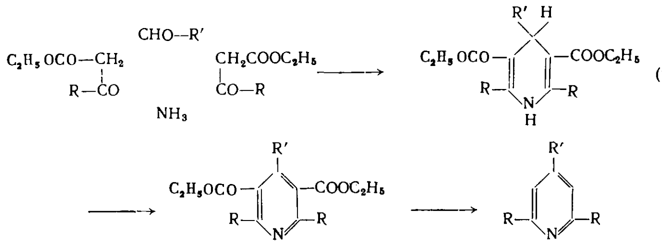


The reaction of acetophenone with ammonia over $Ti(VO_3)_4$ at 370°–380° gave 35% of 2,4,6-triphenylpyridine[73]. Various alkyl- and aryl-pyridines can thus be prepared by the reaction of aldehydes with ammonia, or of aldehydes and ketones with ammonia, in liquid or gas phase over different catalysts.

Since it yields mixtures of pyridines which are difficult to separate, the Chichibabin reaction has found very limited application in the preparation of pyridine bases of specified structure.

2. Synthesis Based on the Hantzsch Reaction

The most widely used synthetic methods for the preparation of individual pyridine derivatives start from 1,5-diketones or dialdehydes, or from compounds which yield 1,5-dicarbonyl derivatives in the course of reaction. The first method of this type was described by Hantzsch[75] in 1882. It consisted in the condensation of one mole of ammonia, two moles of a β-keto-ester and one mole of aldehyde to form a dihydropyridine (I), which was subsequently oxidised by nitric acid to form a 3,5-diethoxycarbonylpyridine (II):


(I)

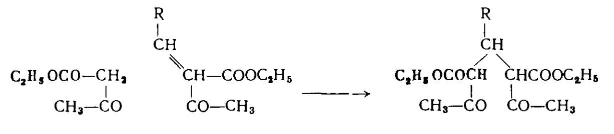
(II) (III)

The conversion of 3,5-diethoxycarbonylpyridines into alkylpyridines (III) is readily accomplished quantitatively by the usual methods. 2,6-Lutidine was obtained by this method in 30–36% yield from formaldehyde and acetoacetic ester[76]. The mechanism of the Hantzsch reaction, like that of the Chichibabin reaction, is still not completely clear. The two most probable reaction schemes are similar, and differ only in the sequence of reaction stages. According to the first, only one molecules of acetoacetic ester first reacts with the aldehyde, forming an alkylidene-(or arylidene-)acetoacetic ester (IV):

$$\mathrm{CH_3COCH_2COOC_2H_5 + RCHO \longrightarrow CH_3CO\overset{\overset{COOC_2H_5}{|}}{C} = CH-R + H_2O}$$

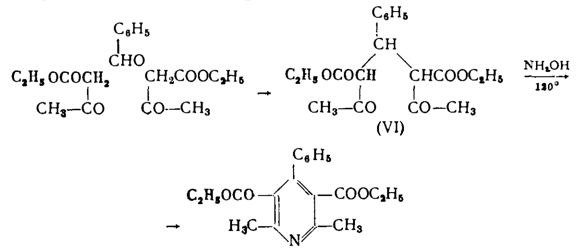
(IV)

Compound (IV) undergoes Michael condensation with another molecule of acetoacetic ester, forming a 1,5-diketone (V):

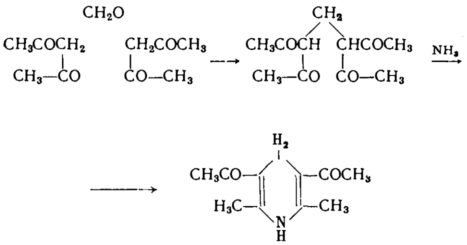

(V)

A number of authors[77-82] have confirmed that ring-closure of 1,5-diketones to form a dihydropyridine derivative (I) is possible. At this stage the 1,5-diketone evidently reacts in the enolic form.

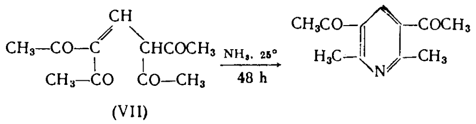
Knoevenagel[83,84] modified the original Hantzsch synthesis. He isolated the intermediate product (VI) of the condensation of acetoacetic ester and aldehyde, and treated it with hydroxylamine in aqueous solution at 120°. Three molecules of water were split off to give the pyridine, thus avoiding the oxidation stage:



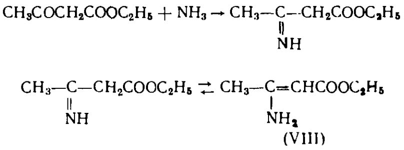
The substitution of acetoacetic ester by acetylacetone[85] makes no difference to the course of the reaction. Acetylacetone, formaldehyde, and ammonia react according to the Hantzsch scheme to form 2,6-dimethyl-3,5-diacetyldihydropyridine:



By amination of the tetraketone (VII) with concentrated ammonia at room temperature, Claisen[77] obtained 2,6-dimethyl-3,5-diacetylpyridine:


(VII)

The alternative is equally probable. Here, one molecule of acetoacetic ester is supposed to react first with ammonia, to form β-aminocrotonic ester (VIII):

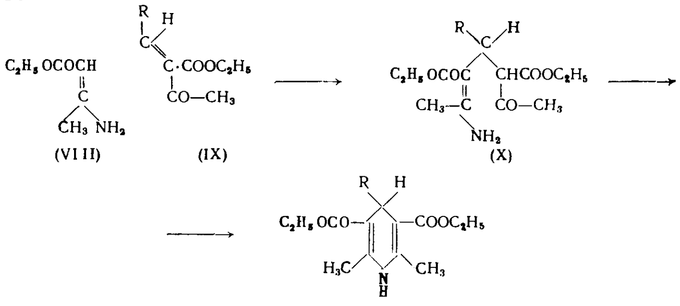


$$\mathrm{CH_3COCH_2COOC_2H_5 + NH_3 \rightarrow CH_3-\underset{\underset{NH}{\|}}{C}-CH_2COOC_2H_5}$$

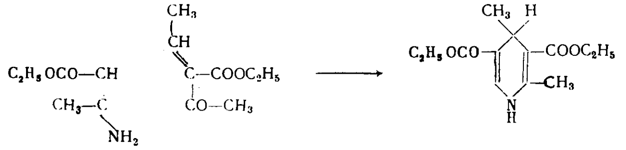
$$\mathrm{CH_3-\underset{\underset{NH}{\|}}{C}-CH_2COOC_2H_5 \rightleftarrows CH_3-\underset{\underset{NH_2}{|}}{C}=CHCOOC_2H_5}$$

(VIII)

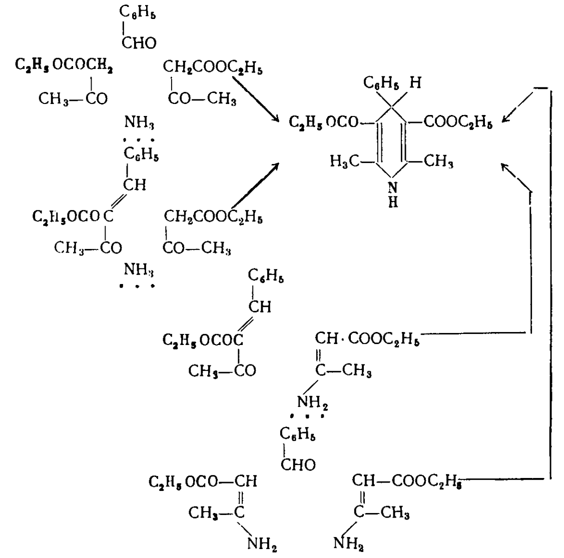
The alkylidene- (or arylidene-)acetoacetic ester (IX) formed in the Hantzsch reaction enters into the Michael condensation with aminocrotonic ester. The resulting ketoamine (X) undergoes ring-closure to give a dihydropyridine:



The formation of compound (X) was confirmed by the work of Collie[86], who succeeded in adding β-aminocrotonic ester to alkylideneacetoacetic ester. Knoevenagel[87] showed that heating β-aminocrotonic ester with ethylideneacetoacetic ester yields a dihydropyridine derivative:

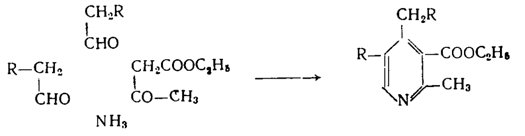


The above data support the second mechanism for the Hantzsch reaction. The reaction may, however, proceed simultaneously by both paths, yielding the same reaction product. This suggestion seems to be the most likely one, since 2,6-dimethyl-4-phenyl-3,5-diethoxycarbonyl-1,4-dihydropyridine may be obtained from the products of preliminary amination, as well as by the subsequent amination of 1,5-diketones[87]:

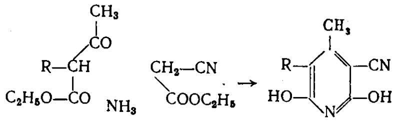


The Hantzsch synthesis is the classical method for the preparation of individual pyridine bases of strictly determined structure and in satisfactory yields. The main feature of the Hantzsch synthesis and all its modifications is the use of compounds containing active hydrogen atoms. By appropriate selection of β-keto-esters (or other 1,3-dicarbonyl compound) and aldehydes, this method can yield a great variety of pyridine derivatives[88].

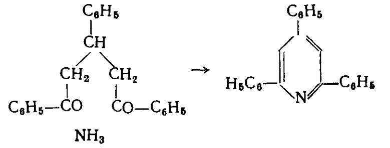
Subsequent modifications of this reaction were confined to improvements in the yields and extension of its scope[78-82,89,90]. For instance, if two moles of aldehyde and one mole of acetoacetic ester are made to react[91] instead of the usual two moles of the ester of a β-keto-acid and one mole of aldehyde, pyridines with substituents in the β-position can be obtained. It should be noted that in this case the dihydropyridine stage is bypassed and the pyridine derivative is obtained directly, the excess of aldehyde acting as an oxidising agent:



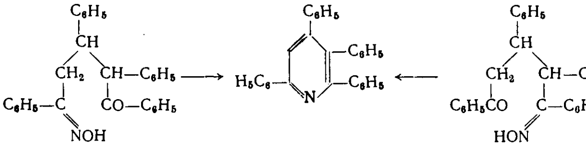
No aldehyde is used in the Guareschi–Thorpe modification of the Hantzsch reaction; its part is played by one of the keto groups in the ester of the keto-acid. This reaction yields hydroxycyano-pyridines, which can easily be converted to alkyl-pyridines[90,92,93].



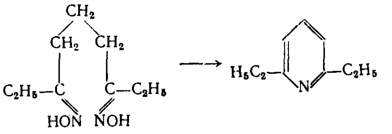
Substituted pyridines are obtained from 1,5-diketones, their oximes and other related compounds. The condensation of benzaldiacetophenone with ammonia or hydroxylamine in alcoholic solution yielded 2,4,6-triphenylpyridine[79,81]:



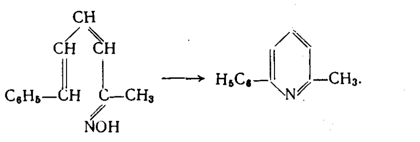
2,3,6-Phenylpyridine was synthesised in a similar manner[80]. By heating the mono-oximes of the 1,5-diketone to 80° with alcoholic hydrogen chloride, Knoevenagel[78] prepared 2,3,4,6-tetraphenylpyridine:



2,6-Diethylpyridine was obtained similarly in 60% yield[82]:

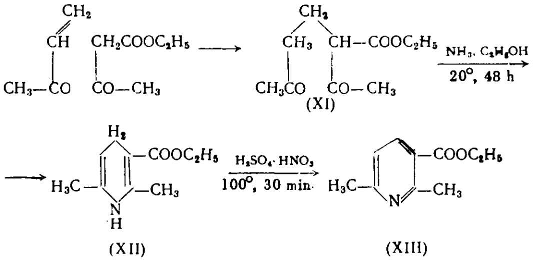


Scholtz prepared 2-methyl-6-phenylpyridine in 25% yield by the destructive distillation of the oxime of 6-phenol-3,5-hexadien-2-one[94]:



A series of other alkyl- and aryl-pyridines was obtained similarly[95].

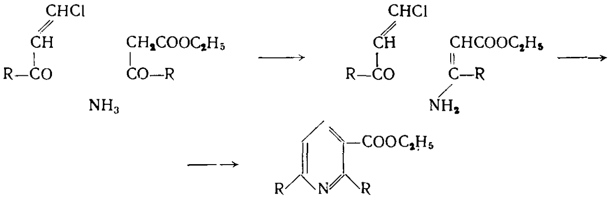
Tanaka and Murata[96] synthesised 2,6-dimethylpyridine from acetoacetic ester and methyl vinyl ketone. This synthesis is a clear confirmation of one of the routes postulated for the Hantzsch reaction:



(XI) (XII) (XIII)

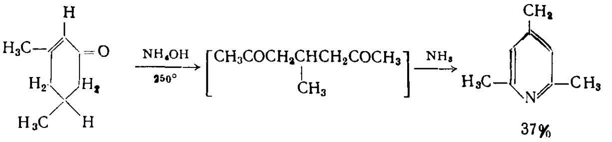
The first stage of this reaction yields 3-ethoxycarbonylheptane-2,6-dione (XI) by Michael condensation in aqueous-alcoholic solution. On standing for 48 h at room temperature with alcoholic ammonia, (XI) yields 2,6-dimethyl-3-ethoxycarbonyl-1,4-dihydropyridine (XII), which is oxidised by a mixture of sulphuric and nitric acid to 2,6-dimethyl-3-ethoxycarbonylpyridine (XIII).

Nesmeyanov and Kochetkov developed a preparative method for dialkylnicotinic acids and dialkylpyridines. By condensation of alkyl-β-chlorovinyl-ketones with esters of β-keto-acids in the presence of ammonia 50–75% yields of the esters of 2,6-dialkylnicotinic acids are obtained[97,98]:

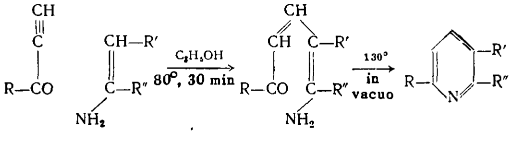


They showed that the reaction proceeds *via* the intermediate formation of the aminocrotonic ester, which subsequently condenses with an alkyl-β-chlorovinyl ketone into a pyridine base. 2,6-Dimethyl-3-ethoxycarbonylpyridine was thus obtained in 75% yield by heating methyl-β-chlorovinyl ketone and aminocrotonic ester at 25°, followed by heating on a water-bath.

An interesting modification of the Hantzsch synthesis[99,100] is afforded by heating alkylcyclohexen-2-ones to 250° in the presence of an aqueous solution of ammonia and ammonium acetate. Thus, 3,5-dimethyl-2-cyclohexen-1-one, 2-methyl-5-phenyl-2-cyclohexen-1-one, and 3-phenyl-2-cyclohexen-1-one yield 2,4,6-trimethylpyridine, 2,6-dimethyl-4-phenylpyridine, and 2-methyl-6-phenylpyridine respectively in yields up to 37%. The authors assumed that during the reaction the cyclohexene ring was cleaved at the double bond forming a 1,5-diketone intermediate. This subsequently underwent normal ring-closure with ammonia, forming a pyridine ring.

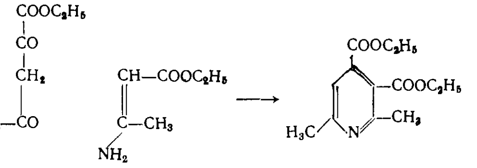


Quite recently Bohlman and Rahtz[101] synthesised pyridine derivatives from acetylenic carbonyl compounds and vinylamines:

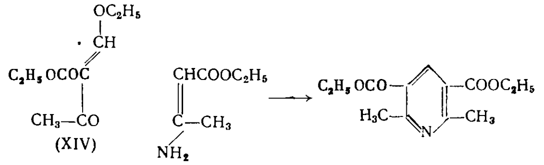


where R = H, R′ = $COOC_2H_5$, R″ = CH_3. Various pyridine bases were obtained in good yield by this general scheme.

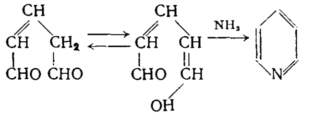
A particular case of the Guareschi–Thorpe synthesis is the condensation of β-aminocrotonic ester with the ester of acetylpyruvic acid. The reaction proceeds readily, giving good yields of 2,6-dimethyl-3,4-diethoxycarbonylpyridine[102]:



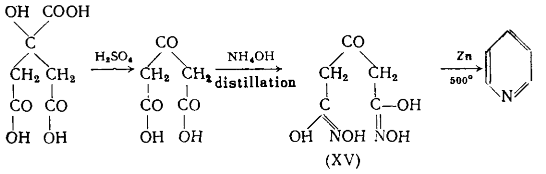
This modified method can also use ethoxymethyleneacetoacetic ester (XIV)[103]:



Finally, pyridine bases can also be obtained from glutaconic aldehyde, glutaconic acid, and their derivatives. Glutaconic aldehyde reacts with ammonia to form pyridine:



Pyridine is similarly formed from acetone dicarboxylic acid, prepared from citric acid[104].



Citric acid is first decarboxylated and oxidised by oleum to form acetone dicarboxylic acid. Upon distillation with aqueous ammonia the latter yields the di-imide (XV)† which is reduced by zinc at 500° to pyridine. The yield, referred to citric acid, is 35%. Heating oximes of glutaric aldehyde with an excess of hydrochloric and sulphuric acid also results in the formation of pyridine bases in 50–70% yields[105,106]. In spite of all their merits the Hantzsch method and its modifications have the disadvantage of starting, as a rule, from complex compounds difficult to obtain.

3. Synthesis from Acetylenic Hydrocarbons

The search for new starting materials for the preparation of pyridine bases has included compounds such as acetylenic hydrocarbons. There are data in the literature on the preparation of pyridines directly from acetylene and ammonia, in the presence of various catalysts at high temperature or in an autoclave under pressure.

In 1915 Chichibabin[107] carried out the first experiments on the synthesis of pyridine bases from acetylene and ammonia by passing their vapours over alumina at 300°–330°. In Chichibabin's own words "the bulk of the reaction product consisted of pyridine bases". He succeeded in isolating α- and γ-picoline, 2-methyl-5-ethylpyridine, and

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† An error occurs in the original at this point (Ed. of Translation).

pyrrole. This communication was followed by a series (mainly patents) devoted to the catalytic preparation of pyridine bases from acetylene[108-123], which described in detail its condensation with ammonia. It was established that, depending on the conditions, pyridine bases or acetonitrile are formed. In all cases the reaction was carried out in a tube packed with granulated catalyst. A mixture of acetylene and ammonia of fixed molar ratio was passed over a layer of catalyst at 350°–500°, and the reaction products were isolated in the usual manner. The composition and the yield of the reaction products is influenced mainly by the catalyst. The oxides of heavy metals, *e.g.* molybdenum[121,123], tungsten[120,121,123], vanadium[123], chromium[119-121], zinc[110,111,119], cadmium[119-122], iron[107,111], and thorium[119], as well as aluminium oxide[107,111,119], were mainly used as catalysts. Catalysts were usually deposited on carriers such as pumice, fuller's earth, various clays, alumina or silica gel. Certain authors used various salts of heavy metals, *e.g.* $CdCrO_4$, $CdMoO_4$, $CdWO_4$, $Cd(VO_4)_2$, deposited on acid clay, or $Cd_3(PO_4)_2$ deposited on fuller's earth[117]. Others used mixed oxide catalysts, for example $ZnO/Cr_2O_5/Al_2O_3$,[118] or V_2O_5/Mo_2O_5/pumice[122]. Cadmium phosphate deposited on fuller's earth was found to be the most selective catalyst. Ishiguro[119] found that as compared with oxides of cadmium, zinc, aluminium, and chromium, the use of this catalyst considerably reduces the formation of acetonitrile in the reaction. For instance, passing a 1 : 1 mixture of acetylene and ammonia at 400° over zinc oxide gave up to 91% acetonitrile and 0.8% pyridine bases[124], whereas when $Cd_3(PO_4)_2$ deposited on fuller's earth was used as catalyst at 300°, only negligible quantities of acetonitrile were formed, the main reaction product being pyridine bases. The authors also observed that at temperatures above 350° the relative content of acetonitrile in the reaction products was increased[119].

In the course of reaction, the catalyst becomes covered by carbon and consequently inactivated. It can be regenerated by passing through it purified air or steam at 400°–500°.

Pyridine bases obtained by the catalytic process consist mainly of α- and γ-picoline and 2-methyl-5-ethylpyridine. For instance, by passing 1000 litres of acetylene–ammonia mixture in 1 : 1 molar ratio over $Cd_3(PO_4)_2$ on acid kaolin at 300°–350°, 750–900 ml of product was obtained, from which were isolated 48.4–52.2% crude α-picoline, 15.2–23.2% crude γ-picoline, and 7.3–10.9% 2-methyl-5-ethylpyridine fraction[125]; when $ZnO(Cr_2O_3)Al_2O_3$ was used as catalyst, in addition to the above compounds, small quantities of 2,4-dimethylpyridine, 2,4,6-trimethylpyridine, 2-methyl-4-ethylpyridine, and other nitrogen bases were also obtained[118].

Thus, the pyridine bases obtained from acetylene and ammonia are the same as those obtained under the same conditions from acetaldehyde and ammonia. It is probable, as Chichibabin[107] first suggested, that acetylene is hydrated first to acetaldehyde, which is subsequently condensed with ammonia to yield α- and γ-picoline and 2-methyl-5-ethylpyridine. The main drawkback of this method is the formation of a mixture of pyridine bases which are difficult to separate. This method can be extended by using in addition to acetylene and ammonia other organic compounds, containing one to three carbon atoms, *e.g.* CH_3OH, CH_2O, CH_3CHO or acetone, when the reaction product includes, beside α- and γ-picoline, other alkylpyridines whose structure depends on the structure of the compound introduced[60,125-127]. Various salts of cadmium, *e.g.* $Cd_3(PO_4)_2$,[60,125,127] $CdCrO_4$,[60,127,128] $CdWO_4$,[60,127] $CdTiO_3$, $Cd(VO_3)_3$,[127] $CdMoO_4$,[128] and of other metals, *e.g.* $PbCrO_4$ and $Zn_3(PO_4)_2$,[128] $ZnCl_2$[126] on various carriers like fuller's earth, alumina, pumice, and acid clay, were tested as catalysts. The catalytic reaction was carried out under the same conditions as the reaction between acetylene and ammonia. By passing an equimolar mixture of acetylene, methanol, and ammonia over zinc phosphate, deposited on acid clay, at 400° about 65% of pyridine bases was obtained, containing about 25.4% of acetonitrile, 31.2% of pyridine, 19.3% of picoline isomers, and 14.5% of a mixture of 3,5-dimethylpyridine and 2-methyl-5-ethylpyridine[125].

Cislak[128] made a thorough study of the catalytic reaction of acetylene, methanol, and ammonia, and established the correlation between the qualitative and quantitative composition of the reaction products and the relative quantity of methanol in the mixture of reactants. The results of his experiments, carried out over ZnF_2/Al_2O_3 at 425°, are collected in the table. The molar ratio of acetylene to ammonia was 1 : 1 in all cases.

The reaction between formaldehyde, acetylene, and ammonia over $ZnCl_2/Al_2O_3$ seems to follow a similar course, yielding α- and γ-picolines in the reaction mixture[125,126]. Methylamine, acetylene, and ammonia react over cadmium phosphate at 400° forming a mixture of pyridine, α-, β-, and γ-picolines, as well as acetonitrile and high-boiling pyridine bases[125]. Addition of acetone sharply changes the composition of the products. The catalytic reaction of a mixture of acetone, acetylene, and ammonia over zinc phosphate at 400° yields 38% of a mixture of pyridine bases, consisting mainly of 2,4,6-trimethylpyridine[60,125,126]. There are grounds for supposing that in this case it is the hydration product of acetylene which enters the reaction. This is confirmed by the fact that α- and γ-picolines are obtained by the condensation of crotonaldehyde with acetylene and ammonia[126].

Of special interest is the liquid-phase catalytic condensation of acetylene with ammonia, which yields 2-methyl-5-ethylpyridine, a valuable industrial product. The reaction is carried out in an autoclave at high pressure and temperature, and salts of cadmium[129-131], mercury and copper[129], cobalt, nickel, and titanium[132] are used as catalysts.

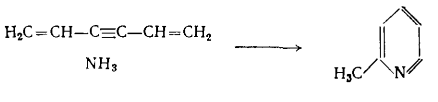
Reppe[132] patented the preparation of 2-methyl-5-ethylpyridine from acetylene and aqueous ammonia at 140° in the presence of $CoCl_2$. A mixture of pyridines containing 75% of the main product is obtained. Nozu[131] showed that in addition to 2-methyl-5-ethylpyridine the liquid-phase condensation over CdO/Al_2O_3 also yields acetonitrile, α-picoline, γ-picoline, 4-methyl-5-ethylpyridine, and a small amount of ethylamine. The reaction can proceed[133] in the presence of acetic acid at 180°–190° at 20 atm.

TABLE.

CH_3OH content in reactant mixtures, moles	Content of pyridines in the mixture of bases			
	pyridine	β-picoline	α-picoline	γ-picoline
2	14.5	22.5	4.5	0.0
1	21.0	18.0	9.5	traces
0.5	14.5	17.5	16.0	17.5
0.25	11.0	17.0	24.5	17.0
0.0	0.0	0.0	32.0	28.0

In 1877 Ramsey[134] obtained traces of pyridine by passing a mixture of acetylene and hydrocyanic acid through a hot tube. Meyer[135] later succeeded in repeating this experiment.

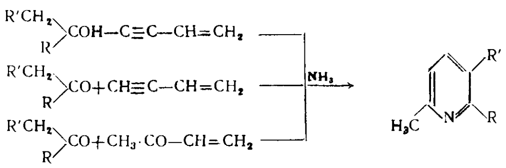
The synthesis of pyridine bases from acetylene derivatives has only been discussed in two papers, one of which has already been mentioned[101]. The other publication was a patent which only disclosed that "by passing a vapour-phase mixture of divinylacetylene and ammonia over a freshly prepared catalyst consisting of lead or cadmium deposited on alumina, α-picoline was obtained containing small admixtures of other products"[136].



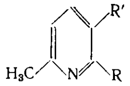
Finally, Cairns[137] demonstrated the possibility of preparing pyridines by the reaction of acetylene with benzonitrile:

The reaction is carried out by treating benzonitrile with metallic potassium in an autoclave followed by passing in acetylene. The reaction temperature is kept at 175°–200°, and the pressure at 8 atm. The yield of 2-phenylpyridine is 1.8%; 29% of 2,4-diphenylpyridine is also obtained.

The authors of this review have recently developed[138-143] a new method for the synthesis of pyridine bases of specified structure consisting of the catalytic condensation of tertiary vinylacetylenic alcohols of general formula $R'CH_2C(R)OH-C\equiv CCH=CH_2$ with ammonia. 2-Methyl-5-R′-6-R-pyridines, where R = alkyl or aryl, R′ = alkyl or hydrogen, were obtained as main reaction products. The yields were not above 32% of the theoretical. The reaction is carried out in the presence of aromatisation or hydration catalysts based on alumina-supported chromic oxide or cadmium salts at 350°–450°. Thus, dimethylvinylethynylcarbinol and methylphenylvinylethynylcarbinol gave with ammonia 2,6-lutidine (about 10%) and 2-methyl-6-phenylpyridine (14.4%) respectively. This method was used for the preparation of various dialkyl- and alkylaryl-pyridines. The reaction mechanism has been studied. It was shown that at 350°–450° tertiary vinylacetylenic alcohols decomposed under the influence of the hydration catalyst into a ketone and vinylacetylene, and that the latter, in the presence of the catalyst and water, was hydrated to form methyl vinyl ketone, which in its turn reacted with the ketone and ammonia yielding pyridine bases:



Knowledge of the reaction mechanism has made possible the synthesis, from ammonia and either vinylacetylene and a ketone or methyl vinylketone and methylketones, of pyridine bases in yields far higher than those obtained from vinylacetylenic alcohols. From various ketones, vinylacetylene, and ammonia over a cadmium phosphate/alumina catalyst, at 400°, pyridine bases of the following general formula were thus obtained in 29–49% yields:

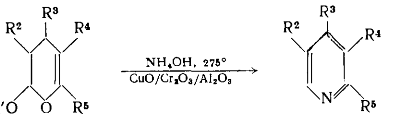


where R = alkyl or aryl, R′ = hydrogen or alkyl. Similarly, cyclohexanone and cyclopentanone gave with vinylacetylene and ammonia 2-methyl-5,6,7,8-tetrahydroquinoline and 2-methyl-6,7-dihydropyridine, in 25% and 15.5% yields respectively.

The same pyridine bases were obtained similarly from methyl vinyl ketone, aliphatic and aromatic ketones, and ammonia.

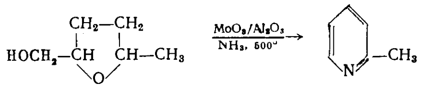
4. Synthesis from Heterocyclic Compounds

Pyridines can be obtained by chemical transformations of various heterocyclic compounds. However, most of these reactions are of theoretical importance only. Passing 2-alkoxy-3,4-dihydro-2H-pyrans with ammonia in the presence of steam at 275° over a copper–chromium catalyst deposited on alumina results in the formation of pyridine bases[144]. For example, pyridine of high purity was obtained from 2-ethoxy-3,4-dihydro-2H-pyran:



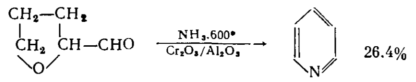
where R′ = alkyl, R²–R⁵ = H or alkyl.

Hydrofurylcarbinols and ammonia over a molybdenum catalyst at 450°–500° gave 45–55% of pyridine bases[145], *e.g.*:

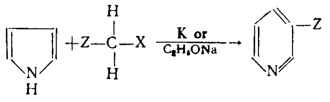


One German patent[146] claims the preparation of pyridines from furfural (or its hydrogenation products) and hydrogen and ammonia at 200° under pressure, in the presence of hydrogenation catalysts such as platinum, nickel, cobalt, or copper compounds. Kline and Turkevich[147], however, did not succeed in obtaining pyridines from furfural and ammonia, either in liquid or the vapour phase, over Cr_2O_3/Al_2O_3.

Pyridine can be synthesised[147,148] from tetrahydrofurfural over Cr_2O_3/Al_2O_3 at 600°.

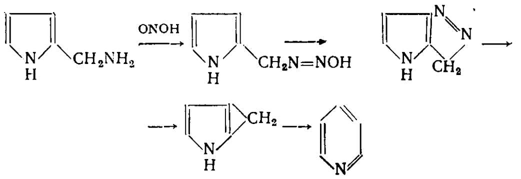


In 1904 Pictet[149] found that by passing 1-methylpyrrole through a heated tube, small quantities of pyridine are formed, in addition to 2-methylpyrrole. It was shown later that *N*- and α-substituted pyrroles are transformed into pyridine bases on heating[150]. Pyridine bases were later obtained by heating alkyl halides with pyrrole in the presence of alkali[151]. Alexander[165] made a thorough study of the ring-enlargement of pyrrole by the action of $CHCl_3$ and $CHBr_3$ on pyrrole-potassium or pyrrole[152-164] in the presence of alkali and found that the yield of β-substituted pyridines depends on the nature of the halide and alkali used in the reaction. He suggested the following general reaction scheme:

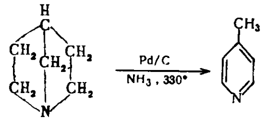


where Z = halogen, hydrogen, or phenyl.

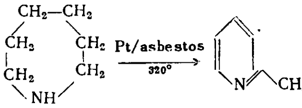
Putokhin[166] studied the oxidation of α-pyrrolylmethylamine by nitrous acid and found that at high dilution, in the cold, ring-enlargement occurred and pyridine was formed. He gave the following reaction scheme for the formation of pyridine from α-pyrrolylmethylamine:



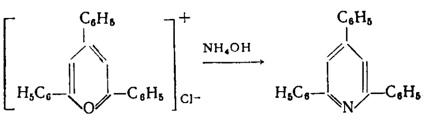
On being heated with palladium on activated charcoal, or with selenium, the bicyclic compounds of type 1-azabicyclo-(2,2,1)-heptane and 1-azabicyclo-(2,2,2)-octane gave γ-methylpyridine and γ-ethylpyridine respectively[167].



The dehydrogenation of hexamethylenimine on platinised asbestos at 320° yielded α-picoline[168].



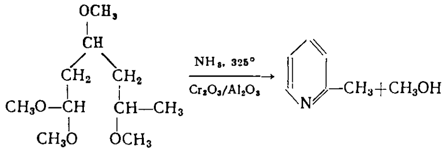
Pyridine can also be obtained in good yields by the ammonolysis of pyrylium salts[169].



5. Miscellaneous Methods for the Formation of the Pyridine Ring

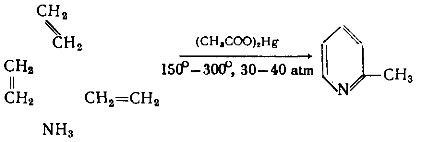
In addition to the above methods for the preparation of pyridine bases there are a number of others. One of them is the diene synthesis using nitriles, by the Diels–Alder method[170,171]. This reaction proceeds in the vapour phase over various oxide catalysts, the most successful being Cr_2O_3/Al_2O_3.[172,173] By passing a butadiene–benzonitrile mixture over alumina at 400°, 50–60% of 2-phenylpyridine was obtained. 2-Ethylpyridine, 2-methyl-6-phenylpyridine, 2-phenyl-4-methylpyridine, and 2-phenyl-4,6-dimethylpyridine were obtained in a similar manner.

Passing a 1,1,3,5-tetra-alkoxypentane, containing identical or different lower alkoxy groups (CH_3O, C_2H_5O, etc.), or an alkoxypentane substituted in position 5 by an alkyl or alkoxyl radical, with ammonia, over a dehydration catalyst (Al_2O_3, Cr_2O_3, silica gel, etc.) at 300°–350° resulted in the formation of 60% of pyridine or α-substituted pyridines[174].



Similar liquid-phase syntheses of pyridine from alkoxypentanes have been patented[175,176]. Treatment of 1,1,3,5,5-pentaethoxypentane with ammonia in a solution of ammonium chloride at 80°–90° gave 54% of pyridine.

α-Picoline (60%) was obtained by the reaction of ethylene and 25% aqueous ammonia in the presence of mercuric acetate at 150°–300° and at 30–40 atm.[177]



A number of patents have recently appeared dealing with the synthesis of 2-methyl-5-ethylpyridine from alkyl vinyl ethers and ammonia[178-181]. This reaction is carried out in the liquid phase, at elevated temperature and pressure, and in the presence of various catalysts [CuS, $Cu_3(PO_4)_2$, Cu_2Cl_2, NiI_2, NH_4F, etc.].

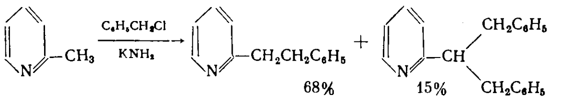
Some methods for the preparation of individual pyridine bases may also be mentioned. Thus, at 130°, vinyl acetate, methanol, and ammonia gave 2-methyl-5-ethylpyridine[182]. The treatment of isobutylene with formaldehyde and ammonium chloride at 107°, followed by dehydrogenation of the reaction products, gave γ-picoline[183]. Passing butadiene and ammonia vapours over a nickel or cobalt catalyst resulted in the formation of pyridines and nitriles[184]. The vapour-phase catalytic reaction of methanol with ammonia over CdO/Al_2O_3 also gave pyridine bases[185,186]. The vapour-phase reaction of butanediol with ammonia over alumina catalyst gave lutidines in addition to indole and tetramethylpyrazine[187]. The reaction of methyl vinyl ketone with ammonia at 120°–140° resulted in small amounts of 2,3,4-trimethylpyridine[188].

III. SYNTHESIS FROM COMPOUNDS CONTAINING A PYRIDINE RING

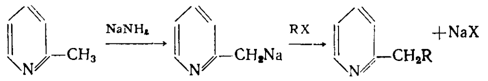
Pyridines can also be obtained by the chemical transformation of compounds already containing a pyridine ring. These reactions are generally similar to reactions in the benzene series, although some are specific for the pyridine ring.

1. Alkylation Methods

Although the Friedel–Crafts synthesis is the chief method for alkylations in the aromatic series, it is entirely inapplicable to pyridine compounds. The most important and most widely used methods for alkylation in the pyridine series involve the use of organometallic compounds. The first synthesis of alkylpyridines using sodamide was carried out in 1936 by Chichibabin[189]. To alkylate α- and γ-picolines he used mostly the higher alkyl halides. In alkylations of α- and γ-methylpyridines, *viz.* compounds containing an active methyl group, the action of alkyl halides results in the extension of the methyl group by the number of carbon atoms contained in the alkyl halide. Sodium, potassium, and lithium amides can be used as condensing agents in this reaction[203]. For instance, the treatment of α-picoline by potassamide and an alkyl (or aryl) halide gives rise to the substitution of a hydrogen in the methyl group of picoline by an alkyl or aryl radical, as in the case of benzyl chloride, when 1-phenyl-2-(α-pyridyl)ethane is formed. Since the resulting compound contains further active hydrogen atoms, the reaction can continue, yielding, in the presence of an excess of potassamide, 1,3-diphenyl-2-(α-pyridyl)propane:



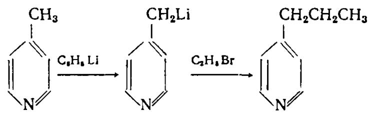
The reaction of α-picoline with sodamide consists in the substitution of a methyl hydrogen atom by sodium, *viz.* in the formation of picolylsodium. Picolylsodium reacts with an alkyl halide, yielding the alkylpyridine:



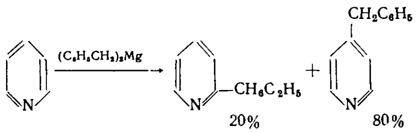
Using this method, many different α- and γ- alkyl- and aryl-pyridines were prepared in good yields from the lower pyridines (picolines, lutidines, etc.), which are relatively easy to obtain, and alkylaryl halides[195-197]. Alkylcyclohexyl halides gave alkylcyclohexylpyridines[198]. Notwithstanding their low reactivity, aryl halides also react with picolines. Thus, as shown by Bergstrom, in the presence of potassamide chlorobenzene reacted with α-picoline to form 24% of benzylpyridine[191].

For a long time it was thought that this method did not apply to β-substituted alkylpyridines, since the methyl group in β-picoline does not contain active hydrogen atoms. Only recently was it shown[192,199-202] that β-alkylpyridines, like the α- and γ-substituted derivatives, readily undergo alkylation with potassium or sodium amides, with yields reaching 70%. For the alkylation of pyridines Ziegler and Zeiser[203,204] used organolithium compounds. They prepared 2-butylpyridine by treating pyridine with butyllithium in benzene solution at 90°–100° and then adding water to the reaction mass.

This reaction was at first used only for the synthesis of α-substituted pyridine bases[205-209], but the method was later extended to γ-alkylpyridines. Thus, the reaction of γ-picoline with phenyllithium, followed by treatment with ethyl bromide, gave γ-propylpyridine as the main product[210]:

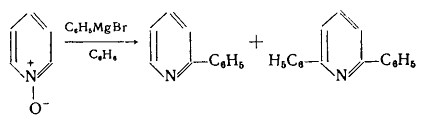


Walters[207] obtained 40% of 2-phenylpyridine by heating phenyllithium with pyridine in a sealed tube. The application of Grignard reagents has extended the possibilities for the preparation of pyridine compounds, and simplified the experimental procedure. In 1932 Bergman and Rosenthal[211] found that benzylmagnesium bromide reacts with pyridine in ether solution forming 2-benzylpyridine. It was later shown[212-215] that the alkylation of pyridine with organomagnesium compounds mainly yielded a mixture of α- and γ-substituted alkylpyridines (40–50%). Benzylpyridines can readily be prepared using dibenzylmagnesium in dioxane[213].



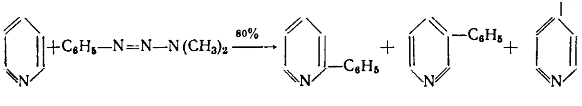
The mixture contains 80% of the γ-isomer. 2-Ethylpyridine was also obtained by heating ethylmagnesium bromide with pyridine in an autoclave[215].

Ochiai and Arima[216] showed that 2-phenylpyridine and a small amount of 2,6-diphenylpyridine are obtained by treating phenylmagnesium bromide with pyridine 1-oxide:

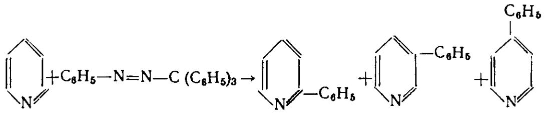


One of the older methods for the alkylation of the pyridine ring is that devised by Ladenburg[217,218]. He obtained mixtures of α- and γ-alkylpyridines by heating the simple pyridine alkyl halides in a sealed tube to 300°. Chichibabin[219] improved this reaction and found that cuprous chloride or bronze catalyse the Ladenburg rearrangement and increase the yield of benzylpyridines. As a result, this method has become widely used in the laboratory for the preparation of substituted pyridines.

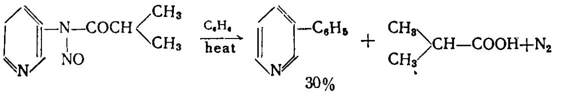
A number of methods for the preparation of alkyl- and aryl-pyridines are based on free-radical reactions. Thus, arylpyridines can be obtained by arylation with aryldiazonium salts. As early as 1893 a mixture of phenylpyridine isomers, containing 18% of α-phenylpyridine, was obtained by the reaction of benzenediazonium chloride with pyridine[220]. Chichibabin[221] later obtained "a very small" yield of a phenylpyridine mixture by adding to acetic acid a mixture of aniline, sodium nitrite, and pyridine. Heilbron[222-224] recently extended this reaction to the synthesis of various arylpyridines. The reaction is usually carried out by running an aryl diazonium chloride into pyridine, followed by heating and distilling off the unchanged pyridine. The yield of the mixture of three arylpyridine isomers sometimes reaches 80%, the α-isomer predominating in the mixture. The preparation of an arylpyridine from 1-aryl-3,3-dimethyltriazenes[225] or benzeneazotriphenylmethane proceeds likewise[226]:



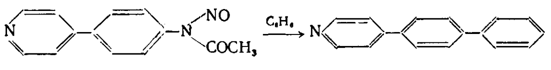
In contrast to the previous reactions, the α-isomer is here a minor product.



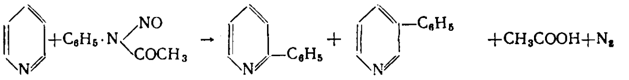
The Gomberg reaction can also be used for the preparation of pyridine bases. An example consists of heating *N*-(3-pyridyl)-*N*-nitrosoisobutyramide with benzene to form β-phenylpyridine[227].



4-γ-Pyridylbiphenyl was prepared similarly[224]:



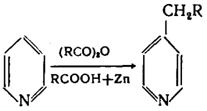
The reaction of nitrosoacetanilide with pyridine yielded a mixture of phenylpyridine isomers[228].



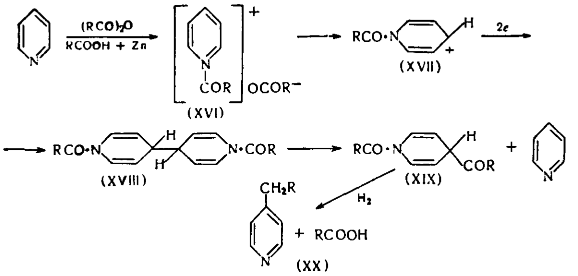
By electrolysis of various aliphatic acids in pyridine solution α- and γ-alkylpyridines, containing small amounts of 2,4-dialkylpyridines, were obtained at the platinum cathode[229]. 2-Methyl-, 2-ethyl-, and 2-propyl-pyridine were obtained by this method from pyridine and acetic, propionic and butyric acids, respectively, together with small quantities of the corresponding γ-isomers and α,γ-derivatives. Benzoyl peroxides and pyridine gave a mixture of α- and γ-phenylpyridines[229,230].

A mixture of α- and γ-pyridines is obtained by the reaction of diacylperoxides with pyridines[231], *e.g.* α- and γ-phenylpyridines were obtained by heating dibenzoyl peroxide with pyridine[232]. Heating a mixture of pyridine with the lead salts of organic acids to 80°–120° gave α- and γ-alkylpyridines[233]. For instance, pyridine and lead acetate in acetic acid solution gave a mixture of α- and γ-picolines. Heated to 110° with Pb_3O_4 in acetic acid, 3-butylpyridine gave in 45% yield a mixture of 2-, 4-, and 6-methyl-3-butylpyridines and 2,6-dimethyl-3-butylpyridine, with 2-methyl-3-butylpyridine predominating[234].

The Wibaut–Arens reaction, which consists in heating pyridine with acid anhydrides in the presence of zinc powder, can also be used for the preparation of the γ-derivatives of pyridine



The authors made a thorough study of the mechanism of the formation of γ-alkylpyridines[235]. They established that in acid media pyridine forms a salt (XVI), which, reacting in the 1-acyl-1,4-dihydropyridine form (XVII), yields *N*,*N*-diacyltetrahydro-4,4-dipyridyl (XVIII)

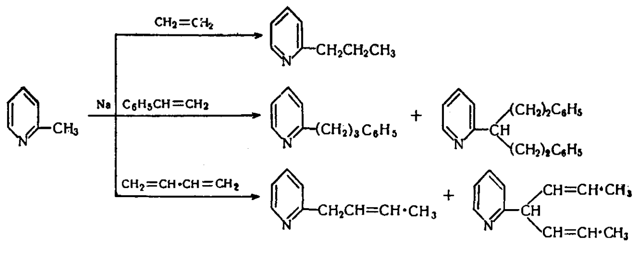


On being heated (XVIII) yields 1,4-diacyl-1,4-dihydropyridine (XIX), which is subsequently converted to 4-alkylpyridine (XX).

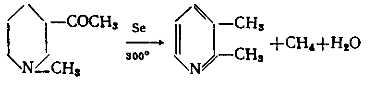
3-Methyl-4-ethylpyridine was obtained in 45% yield by treating a mixture of acetic anhydride and 3-picoline with zinc powder at 35°–40°, followed by boiling. Various 4-alkylpyridines were prepared similarly[236,238-240]. In the synthesis of 4-ethylpyridine iron powder could be used instead of zinc[241].

By passing a mixture of 2-methylpyridine and formaldehyde over alumina at 400°–550° high yields of 2-ethylpyridine and a little 2-vinylpyridine are formed[237].

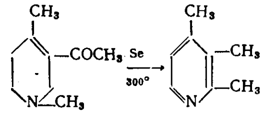
2-Methylpyridine gave higher alkylpyridines[242-244] on being alkylated with olefines in the presence of sodium at 120°–130° and elevated pressure.



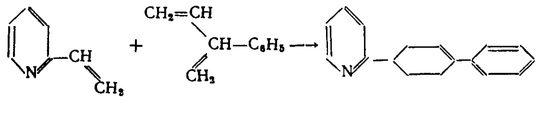
An interesting reaction is observed on heating 3-acetyl-1-methylpiperidines with selenium to 300° in a sealed tube, when a high yield of 2,3-dimethylpyridine results[245].



Similarly, 1,4-dimethyl-3-acetyl-1,2,5,6-tetrahydropyridine gave 88.5% of 2,3,4-trimethylpyridine[246]:



A complex mixture of isomeric picolines and lutidines is obtained by passing pyridine and methanol vapours over activated alumina at 400°–500°.[247] Cyclohexylpyridines were obtained by the Diels–Alder reaction of vinylpyridines with diene hydrocarbons. For example, xylene solutions of α- and γ-vinylpyridines and butadiene, heated in sealed tubes to 170°, gave 60% of α-cyclohexenylpyridine and 44% of γ-cyclohexenylpyridine respectively[249,250]. 2-(4-Phenylcyclohex-3-enyl)pyridine was also obtained from α-vinylpyridine and 2-phenyl-1,3-butadiene in the presence of phenyl-β-naphthylamine[251].



2. Miscellaneous Methods for the Preparation of Pyridine Bases

Methods such as the hydrogenation of unsaturated oxygen- and halogen-containing compounds, the decarboxylation of acids, the dehydrogenation of hydropyridines, and finally, the dealkylation of alkyl derivatives play a significant part in the synthesis of various alkylpyridines.

The hydrogenation of alkenylpyridines is usually carried out over Raney nickel catalyst, in alcoholic solution, at room temperature, and small hydrogen pressure. Yields of alkylpyridines are nearly theoretical. Unsaturated pyridine bases can sometimes be reduced with iodine and red phosphorus. For instance, 2-styrylpyridine was reduced to 1-phenyl-2-(α-pyridyl)ethane[252]. The reduction of alkyl pyridyl ketones is best carried out by the Wolff–Kishner method, giving 80% yields[248,253-257]. The reaction is carried out in the usual manner by heating a mixture of alkyl pyridyl ketone and hydrazine in alcoholic-alkaline media.

In his comparative study of various methods for the reduction of 2-acetylpyridine Furst[258] obtained the best yields of ethylpyridine using the Clemmensen method.

Pyridine bases containing a hydroxyl group in the side-chain can readily be reduced by boiling in aqueous solution with hydroiodic acid and red phosphorus[259,260]. 4-Isopropylpyridine was obtained in this way from dimethyl-(γ-pyridyl)carbinol[261]. Another general method for the synthesis of pyridine is the catalytic reduction of 2- and 4-chloroalkylpyridines, using as a catalyst either palladium on activate charcoal[262-266], barium sulphate, or calcium carbonate[267], or Raney nickel[268,269]. The yields of the reaction products are nearly theoretical.

The preparation of pyridinecarboxylic acids followed by decarboxylation is another important method for obtaining pyridine bases. Pyridinecarboxylic acids can be obtained not only by the oxidation of alkylpyridines, but also from arylpyridines and benzylpyridines and in various other ways. Although many pyridine alkaloids are readily oxidised to pyridinecarboxylic acids, the oxidation of nicotine to yield nicotinic acid is alone of any preparative importance.

Decarboxylation of pyridinecarboxylic acids is widely used for the synthesis of pyridine bases because these acids are easy to obtain and the reaction itself is very simple. For instance, carboxyl groups in positions α and γ are decarboxylated on heating, the α-carboxyl group being eliminated at 180°, and γ-carboxyl groups at 240°. Nicotinic acid is decarboxylated by heating with soda-lime. The ease of decarboxylation of picolinic and isonicotinic acid is explained by the shift of the electron cloud and the lower electron density at positions 2 and 4 of the pyridine ring. For the same reason 2-pyridylacetic acid is easily decarboxylated (at 90°), while 3-pyridylacetic acid is stable at 180°.[270]

Dehydrogenation of various hydropyridines is often used in the synthesis of pyridines. Dehydrogenation of piperidines and other hydropyridines is carried out over palladium[41,271-273] or platinum[274], on asbestos, activated charcoal, or alumina. Selenium can also be used[275]. The dehydrogenation is usually carried out by heating the hydropyridine with the catalyst to 250°–300°, and the yields can be as high as 90%. The dealkylation of alkylpyridines is also a method of great potential importance: it consists in passing an alkylpyridine at 300°–660° over a catalyst of the nickel/alumina type[276], or Zelinskii's nickel catalyst[277]. For instance, passing the vapours of α-picoline and water over Ni/Al$_2$O$_3$ at 415° yields 50% of pyridine. High-temperature dealkylation of picolines and 2,6-lutidine at 595°–666° and at high hydrogen pressure has also been carried out[278]. The pyrolysis of α-picoline at 800° in a stream of hydrogen containing some hydrogen sulphide yields 21% of pyridine[279]. The catalytic oxidation of alkylpyridines by air over a vanadium oxide/molybdenum oxide catalyst deposited on pumice, at 580°, results in the formation of 15.3% of pyridine[280].

In addition to the methods discussed above, there are a large number of particular multistage syntheses, which are only applicable to individual pyridine bases[262-264,267,281-287].

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VULCANISATION OF RUBBERS IN THE PRESENCE OF ORGANIC ACCELERATORS

B. A. Dogadkin and V. A. Shershnev

CONTENTS

I. INTRODUCTION

Craig's extensive review[1] on the vulcanisation of rubber with sulphur, published in 1957, took no account of Soviet, German, and Japanese work published in the last decade. The present review aims to make up in some part this deficiency in Craig's review in respect of the chemistry of vulcanisation of rubber in the presence of accelerators.

In recent years workers on vulcanisation have mainly concentrated their attention on the elementary chemical reactions of the process, the mechanism of action of the accelerators, and on establishing the nature of the vulcanisation structures and their influence on the physico-mechanical properties of the vulcanisate. For these purposes, in addition to purely chemical methods, physical methods of analysis have come to the fore (optical and electron spectroscopy, isotope exchange, and kinetic studies with radioactive sulphur). Substantial results have been obtained in the study of the reactions of sulphur with model low-molecular-weight compounds. Two tendencies are observed in the treatment of the general character of the chemical reactions of sulphur with rubber: in some investigations of the structural changes of rubber on vulcanisation a substantial role has been ascribed to radical processes, whilst in others the elementary reactions are considered as taking place by a polar (ionic) mechanism. The different views on the mechanism of vulcanisation apparently arise not so much from different interpretations of the experimental facts, but rather because a unified approach cannot be applied to the complex phenomenon of vulcanisation. The reaction mechanism depends on the thermodynamic conditions of the reaction, the type of rubber, and, particularly, on the type of accelerators and activators used. These were the conclusions to which Shelton and McDonel came[2]. For this reason the present review, in addition to considering some general features of vulcanisation, contains material relating to various types of vulcanisation systems.

II. VULCANISATION WITH DI- AND POLY-SULPHIDES

1. Vulcanisation with Di-2-benzothiazyl Disulphide (DBTD) and *N,N*-Dithiomorpholine (DTM)

It has been shown[3,4] that DBTD vulcanises sodium butadiene and butadiene–styrene rubber on heating to 143° in the absence of sulphur. The DBTD is partially reduced to the mercaptan and partially combines with the rubber: the extracted vulcanisate contains sulphur and nitrogen (Fig. 1). Of the 60% reacted DBTD ~ 30% is reduced to mercaptobenzothiazole (MBT) and ~ 20% is attached to the rubber as the benzothiazyl sulphide radical. The presence of the latter in the rubber is confirmed by the ability of the vulcanisate to undergo isotopic exchange with DBTD containing ^{35}S in the disulphide group. The MBT is apparently formed by the splitting out of hydrogen from the α-methylene groups and from the tertiary carbon atom of the DBTD radicals formed by its thermal dissociation. The possibility of this decomposition into free radicals at vulcanisation temperatures is confirmed by the initiation of isoprene polymerisation by DBTD.

Determination of the molecular weight by light scattering and calculation of the number of cross-linkages in the vulcanisate indicate that each act of addition of a benzothiazyl sulphide radical to the rubber is accompanied by

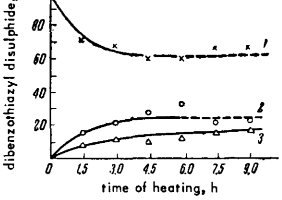
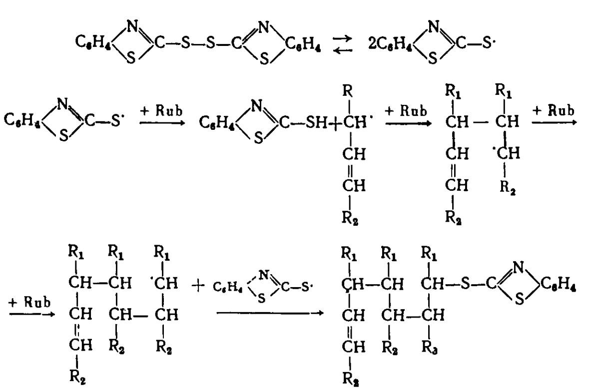


Fig. 1. Change of 1) DBTD, 2) MBT, and 3) sulphur content on heating solutions of butadiene rubber (in percentages of the initial DBTD content).

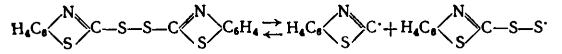
~2.7 elementary additions of rubber molecules; this corresponds to the following scheme for the reaction of DBTD with the rubber:



where Rub = rubber.

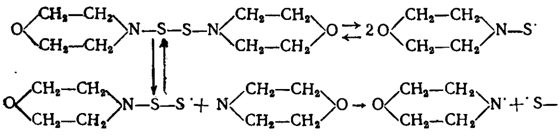
This scheme does not exhaust all possible reactions. It does not cover direct reaction between the benzothiazyl sulphide radicals and the double bonds of the rubber. Cross-linkages can also be formed by reaction between two polymeric radicals formed by the elimination of hydrogen from the α-methylene groups. The formation of C–C bonds between rubber chains by the above scheme is confirmed by the thermal stability of vulcanisates obtained with DBTD without sulphur, approximating to that of vulcanisates obtained by the action of γ-rays[5].

The symmetrical decomposition of DBTD shown in the above scheme is not the only possible one. In a number of experiments using DBTD containing ^{35}S, it was shown that the sulphur activity was not identical in the vulcanisate and in the acetone extract. This observations requires the recognition of the asymmetrical decomposition



There are grounds for supposing that the benzothiazyl disulphide radical is more active in the cross-linking of rubber than the monosulphide radical[6,7].

The kinetics of vulcanisation of rubber with *N,N′*-dithiomorpholine and *N,N′*-dithiopiperidine[8] also indicate that these accelerators undergo asymmetric decomposition, since the amount of sulphur combined with the rubber is considerably greater than the amount of combined nitrogen (Fig. 2). In this case, and unlike vulcanisation with DBTD, elementary sulphur is formed on heating the mixture of rubber and accelerator. The quantity of "free" sulphur, determined by Schulte's method after extraction with acetone at various stages in the vulcanisation, passes through a maximum. These observations suggest the following scheme for the decomposition of *N,N′*-dithiomorpholine:



The kinetic curve *3* (Fig. 2) shows a maximum because in the initial stage of vulcanisation the rate of decomposition of *N,N′*-dithiomorpholine exceeds the rate of addition of sulphur to the rubber.

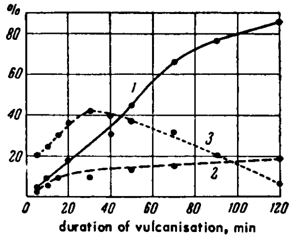
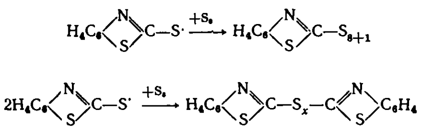


Fig. 2. Kinetics of combination of sulphur and nitrogen during vulcanisation of mixtures containing *N,N′*-dithiomorpholine:
1) combined sulphur; 2) combined nitrogen; 3) "true" free sulphur.

2. Vulcanisation with Sulphur in the Presence of Di-2-benzothiazyl Disulphide

This follows an equation of the first order (with respect to sulphur), the rate constant being directly proportional to the accelerator concentration[3]. In this case, as in heating a rubber–disulphide mixture, the elements of the accelerator are combined with the rubber and the disulphide is reduced to the mercaptan. The only difference is that the mercaptan formed then reacts with the components of the vulcanisation mixture and is almost completely used up by the end of the process. Thus, in addition to the reactions described above for the interaction of rubber with DBTD, the vulcanisation of rubber with sulphur in the presence of DBTD must be assumed to involve the opening of the eight-membered ring of elementary sulphur by the action of accelerator and rubber radicals. In particular, we must assume the formation of the intermediates



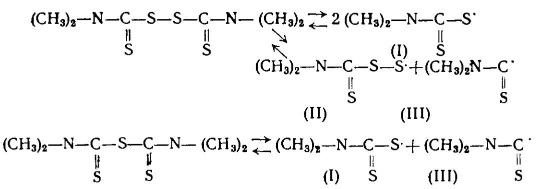
These intermediates are unstable and decompose with the formation of sulphur diradicals containing a variable number of sulphur atoms. These then react with rubber molecules to form cross-linkages. Bresler[9,10] has demonstrated the vulcanisation activity of sulphur diradicals in experiments on the cross-linking of rubber in a vacuum under the action of a molecular beam of elementary sulphur. Since the rate-controlling step in the vulcanisation is the decomposition of the DBTD into radicals, it becomes clear why the rate of addition of sulphur is linearly dependent on the accelerator concentration.

3. Vulcanisation with Thiuram Disulphides

In recent years the mechanism of the vulcanising action of thiuram disulphides has been discussed in great detail in the literature, mainly in a series of studies by Scheele and coworkers[11]. It has been shown that when mixtures containing a tetra-alkylthiuram disulphide and zinc oxide are vulcanised in a press, by which technically valuable thiuram vulcanisates are normally obtained, the thiuram does not undergo extensive thermal decomposition. The only conversion product which is extracted from the vulcanisates is zinc dialkyldithiocarbamate (Zn DTC); the kinetics of its formation follows a first order course, and in the limit 66.6 mole % of the thiuram added to the mixture is converted[12] to Zn DTC.

The radical mechanism given by these workers for the reaction between the thiuram and the rubber with the formation of cross C–C links in the vulcanisate is in general analogous to that suggested earlier by Dogadkin and coworkers[3] for DBTD.

Bielstein and Scheele[13] later showed that the reaction of tetramethylthiuram monosulphide (TMTM) with rubber in the presence of zinc oxide also gives Zn DTC, but the rubber molecules are not cross-linked. It was therefore concluded that the decomposition of tetramethylthiuram disulphide (TMTD) can take place either at the S–S bond or at the C–S bond, while TMTM decomposes only at the C–S bond:

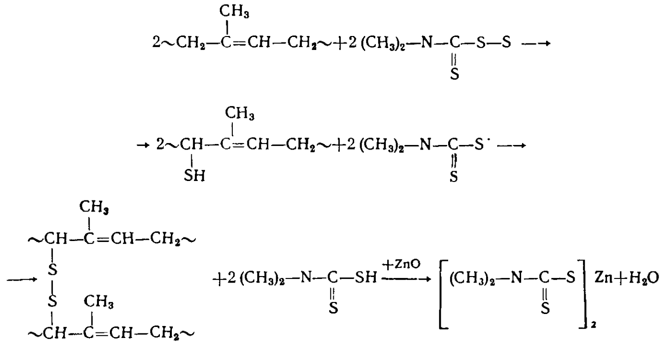


$$(CH_3)_2-N-\underset{\overset{\|}{S}}{C}-S-S-\underset{\overset{\|}{S}}{C}-N-(CH_3)_2 \rightleftarrows 2\,(CH_3)_2-N-\underset{\overset{\|}{S}}{C}-S^{\cdot}\ \text{(I)}$$

$$\rightleftarrows \underset{\text{(II)}}{(CH_3)_2-N-\underset{\overset{\|}{S}}{C}-S-S^{\cdot}}+\underset{\text{(III)}}{(CH_3)_2N-\underset{\overset{\|}{S}}{C}^{\cdot}}$$

$$(CH_3)_2-N-\underset{\overset{\|}{S}}{C}-S-\underset{\overset{\|}{S}}{C}-N-(CH_3)_2 \rightleftarrows \underset{\text{(I)}}{(CH_3)_2-N-\underset{\overset{\|}{S}}{C}-S^{\cdot}}+\underset{\text{(III)}}{(CH_3)_2-N-\underset{\overset{\|}{S}}{C}^{\cdot}}$$

Cross-linkages are formed only by the reaction of the rubber molecules with the TMTD radical (II):



$$2\sim CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2\sim+2\,(CH_3)_2-N-\underset{\overset{\|}{S}}{C}-S-S\longrightarrow$$

$$\rightarrow 2\sim\underset{\underset{SH}{|}}{CH}-\overset{\overset{CH_3}{|}}{C}=CH-CH_2\sim+2\,(CH_3)_2-N-\underset{\overset{\|}{S}}{C}-S^{\cdot}\longrightarrow$$

$$\longrightarrow \begin{array}{l}\sim CH-\overset{\overset{CH_3}{|}}{C}=CH-CH_2\sim\\ \quad |\\ \quad S\\ \quad |\\ \quad S\\ \quad |\\ \sim CH-\overset{\overset{CH_3}{|}}{C}=CH-CH_2\sim\end{array}+2\,(CH_3)_2-N-\underset{\overset{\|}{S}}{C}-SH\xrightarrow{+ZnO}\left[(CH_3)_2-N-\underset{\overset{\|}{S}}{C}-S\right]_2Zn+H_2O$$

In accordance with this mechanism, the vulcanisate should contain combined sulphur and nitrogen from the TMTD, and this was later demonstrated by Dogadkin and Shershnev[14]. An interesting feature of the reaction of TMTD with rubber is the presence of a maximum on the kinetic curves of sulphur combination in the initial period[14-16]. After a slight decrease, the amount of TMTD sulphur combined with the rubber remains constant, but in mixtures containing zinc oxide the formation of cross-linkages continues (Fig.3), *i.e.* the thiuram vulcanisate contains C–C bonds in addition to C–S bonds[17-19].

When TMTD reacts with rubber, it apparently decomposes into symmetrical and asymmetrical radicals in a definite ratio, and this is the reason for the limiting amounts of combined sulphur and Zn DTC formed[11,14,16,20].

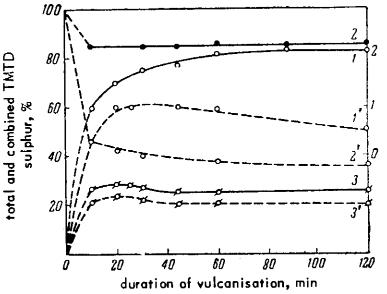
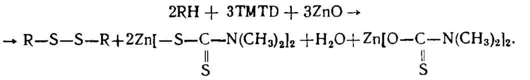


Fig. 3. Kinetics of the vulcanisation of polyisoprene rubber with TMTD:
1) and 1′) change of the number of cross--linkages in mixtures with and without zinc oxide; 2) and 2′) change of total TMTD sulphur content in mixtures with and without zinc oxide; 3) and 3′) change of combined TMTD sulphur in mixtures with and without zinc oxide.

Free-radical vulcanisation mechanisms and polymerisation mechanisms in the presence of TMTD and TMTM have been investigated in a number of studies[21-26]. Recently Bevilacqua[27] proposed a mechanism for vulcanisation with thiuram based on the symmetrical decomposition of TMTD into radicals under the vulcanisation conditions, with the formation of only disulphide cross-linkages:



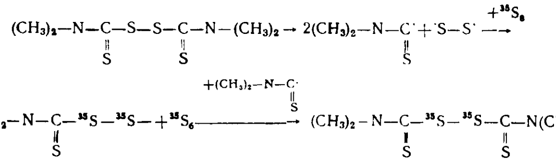
$$2RH+3TMTD+3ZnO\rightarrow$$
$$\rightarrow R-S-S-R+2Zn[-S-\underset{\overset{\|}{S}}{C}-N(CH_3)_2]_2+H_2O+Zn[O-\underset{\overset{\|}{S}}{C}-N(CH_3)_2]_2.$$

A discussion of the role of zinc oxide in this process will be given later, since this is closely related to the mechanism of action of activators and the explanation of the reversion effect in vulcanisation.

4. Vulcanisation with Sulphur in the Presence of Thiurams and Dithiocarbamates

Bresler and coworkers[9] consider that the rate-determining step in the vulcanisation of rubber with sulphur in the presence of a thiuram is the reaction of the elementary sulphur (S_8) with the accelerator. This follows from their demonstration that the velocity constant for the combination of sulphur with the rubber is identical with the isotope exchange constant for the exchange of sulphur with the thiuram. They consider that the two sulphur atoms in the disulphide bridge of the TMTD take part in the exchange with the elementary sulphur, which is not in agreement with Craig's results[28].

The mechanism suggested is



$$(CH_3)_2-N-\underset{\overset{\|}{S}}{C}-S-S-\underset{\overset{\|}{S}}{C}-N-(CH_3)_2\rightarrow 2(CH_3)_2-N-\underset{\overset{\|}{S}}{C}^{\cdot}+{}^{\cdot}S-S^{\cdot}\xrightarrow{+{}^{35}S_8}$$

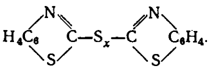
$$\rightarrow (CH_3)_2-N-\underset{\overset{\|}{S}}{C}-{}^{35}S-{}^{35}S-+{}^{35}S_6\xrightarrow{+(CH_3)_2-N-\underset{\overset{\|}{S}}{C}^{\cdot}}(CH_3)_2-N-\underset{\overset{\|}{S}}{C}-{}^{35}S-{}^{35}S-\underset{\overset{\|}{S}}{C}-N(CH_3)_2.$$

The rubber molecules are cross-linked by the •S–S• diradical, and an activated S_8 molecule can attach itself at the points of cross-linking to form polysulphide bonds.

Scheele and Franck[29] consider that Zn DTC is also formed in vulcanisation with sulphur in the presence of TMTD and zinc oxide. Scheele and Birghan[30] showed that the vulcanisation of rubber with sulphur in the presence of zinc diethyldithiocarbamate is a zero-order reaction. Deviations are observed with a molar ratio S_8/Zn DTC > 1. The percentage of Zn DTC consumed also increases, but the quantitative relations are very complex. If zinc oxide is also present in the mixture, there is very little conversion of the Zn DTC. It was suggested that in these cases an intermediate is formed which contains a sulphur chain: this decomposes, liberating active sulphur, which then cross-links the rubber molecules.

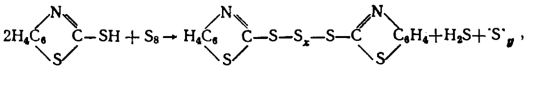
III. VULCANISATION IN THE PRESENCE OF MERCAPTOBENZOTHIAZOLE (MBT)

Sulphur reacts with MBT at vulcanisation temperatures to form hydrogen sulphide and a polysulphide of structure:



Dogadkin and Tutorskii[31] have studied the kinetics of this process. On heating a mixture of sulphur and MBT in liquid paraffin, H_2S is given off at a constant rate v (Fig. 4) which depends on the total concentration C of sulphur and MBT, but the ratio v/C increases with increasing MBT concentration and decreases with increasing sulphur concentration. The latter effect may be due to the absorption of SH radicals by the sulphur under the reaction conditions, forming compounds of type $HS-S_x-SH$. With increasing sulphur concentration the quantity of absorbed SH groups increases.

No hydrogen sulphide is detected when sulphur and MBT are heated in sealed ampoules at 140°, so that the equilibrium represented by the equation



is characterised by a negligible H_2S concentration, and a marked evolution of hydrogen sulphide is only achieved if the latter is continuously removed from the reaction zone.

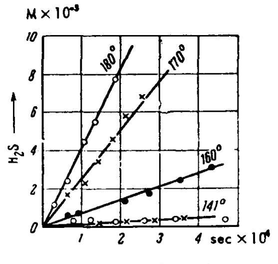
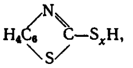


Fig. 4. Kinetics of evolution of hydrogen sulphide on heating sulphur and MBT at various temperatures in liquid paraffin.

The energy of activation for the formation of H_2S by the reaction of sulphur with MBT is ~ 33 500 cal mole^{-1}, while the energy of activation for vulcanisation in the presence of MBT is ~ 21 000 cal mole^{-1}. These facts are in clear opposition to Fisher's theory[32], according to which the main reaction in vulcanisation is the formation of hydrogen sulphide, which then combines with the rubber to form thiol groups which are oxidised to disulphide and polysulphide bridges between the rubber chain molecules.

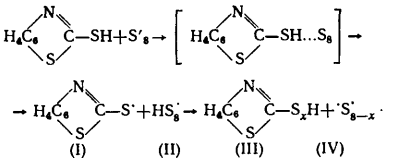
During vulcanisation there is simultaneous combination of sulphur and MBT with the rubber[33] (Fig. 5): the combination of the accelerator with the rubber virtually ceases when the free sulphur is used up; if fresh sulphur (from solution) is added to the vulcanisate, the combination of MBT with the rubber again takes place (Fig. 5, curve *3*).

The kinetics of the combination of the sulphur with the rubber follows an equation of the first order[33-35], the kinetic constants being linearly dependent on the accelerator concentration[33,34,36,37]. Fig. 5 shows that 1 mole of combined accelerator activates approximately 4 moles of sulphur. An intermediate polysulphide of structure



has been separated from the vulcanisate. This compound has an absorption maximum at 330 mμ, characteristic of linear polysulphides. Its sulphur content depends on the time of vulcanisation, passing through a maximum; this has been shown analytically and by isotope exchange with radioactive sulphur. The maximum sulphur content of the intermediate corresponds to a value of x greater than 3.

The above experimental data suggest the following mechanism for the main reaction[33]:



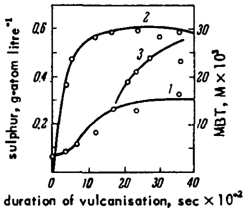


Fig. 5. Kinetics of the combination of (1) sulphur and (2) MBT during vulcanisation of butadiene rubber at 143°; (3) combination of MBT after the introduction of sulphur into the vulcanisate by swelling.

The benzothiazyl sulphide (I) and perthiol (II) radicals are stabilised by conjugation. They react to form the benzothiazyl hydropolysulphide (III) and the diradical (IV) with variable sulphur contents.

The perthiol radical $HS_x^{\cdot}$ may contain a variable number of sulphur atoms. A number of studies[1] have attributed the main role in vulcanisation to the HS· radical. If this were correct, the S–S bonds in the vulcanisate would not contain more than two sulphur atoms, but the experimental results show that the vulcanisates obtained with MBT and diphenylguanidine contain bonds with a substantially greater number of sulphur atoms. In particular, this has been shown by isotope exchange between the vulcanisates and elementary radioactive sulphur. The total quantity of sulphur which can exchange varies with the period of vulcanisation and passes through a maximum (Fig. 6). At the same time the exchange capacity per unit of combined sulphur decreases steadily. This means that polysulphide bonds are formed in the first stages of the vulcanisation, and then rearrange to form bonds with a lower sulphur content. In vulcanisation in the presence of MBT, therefore, the radicals (II) and (IV) play the major part.

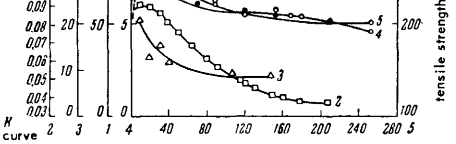


Fig. 6. Change of the physicochemical properties of natural rubber on vulcanisation:

1) combined sulphur $[(S_{comb}/S_{total}) \times 100, \%]$;

2) exchangeable sulphur (moles per litre of rubber);

3) exchange capacity $[(I_0 - I_1)/(I_0 - I_1 S_{free}) + (S_{comb}/S_{total}) \times 100\ (\%)]$ [The correctness of this formula is uncertain because of the poor print in the Russian original (Ed. of Translation).];

4) number of cross-linkages $N_c \times 10^{19}$, mole^{-1};

5) strength.

Tsurugi and Fukuda[38] have studied the reaction of MBT and its zinc salt with diphenylmethane, which they consider to be a rubber model. According to them, it is the resulting MBT Zn salt which possesses accelerating activity in MBT–sulphur–zinc salt systems; this reacts with sulphur to form zinc sulphide, sulphide diradicals, and MBT radicals. The mechanism for the reaction of these radicals with diphenylmethane is analogous to that considered above and suggested by Dogadkin and coworkers[3].

IV. VULCANISATION IN THE PRESENCE OF SULPHENAMIDES

Recently extensive use has been made of sulphenamide accelerators containing the group –C–S–N=, especially *N*,*N*-diethyl-2-benzothiazylsulphenamide (Vulcacite AZ, DEBSA), *N*-cyclohexyl-2-benzothiazylsulphenamide (Vulcacite CZ, CBSA), and others. The main property of these accelerators is the presence of a definite induction period of low velocity on the kinetic curves representing the combination of sulphur and the change of the modulus[39]. This property bestows technical advantages on the sulphenamide accelerators with respect to premature vulcanisation (scorching) and better formability, and consequently they give greater stability of bond in laminated goods, particularly of synthetic rubbers[40]. The kinetics of vulcanisation and mechanism of action of sulphenamide accelerators have been studied by Dogadkin and coworkers[39,41,42].

In the vulcanisation of sodium butadiene rubber the rate of combination of sulphur in the initial period is approximately the same as in vulcanisation without an accelerator (Fig. 7). The energy of activation is ~30 kcal mole^{-1}; this is the energy of activation of vulcanisation without an accelerator and corresponds to the energy of opening of the eight-membered sulphur ring[43]. The energy of activation in the main period of sulphur combination is 14 kcal mole^{-1}, demonstrating the active part played by the accelerator, or rather its decomposition products, in the combination of the sulphur with the rubber in this period. The rate of combination of sulphur in the main period depends on the initial concentrations of sulphur and accelerator, the dependence being linear for the latter.

The formation of a three-dimensional structure in mixtures containing DEBSA is also characterised by a prolonged induction period. A single three-dimensional network with a concentration of cross-linkages of the order of 0.1–0.4 × 10^{-4} mole g^{-1} of rubber is formed after 15–30 min, when the quantity of combined sulphur is ~40% of that added.

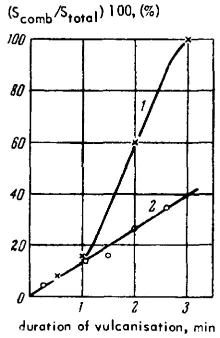
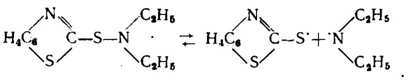


Fig. 7. Kinetics of the combination of sulphur in mixtures:
1) with DEBSA; 2) without an accelerator.

The presence in the vulcanisation system of oxygen and oxygen-containing compounds has a substantial effect on the kinetic curves. The longest induction period is observed in vulcanisation with the exclusion of oxygen (Fig. 8). In pure oxygen there is no induction period and the kinetic curve for the combination of sulphur is transformed from an S-shaped to a convex curve. The acceleration of the combination of sulphur with the rubber caused by molecular oxygen finds explanation in the oxidation of the rubber to form polymeric radicals which can react with the sulphur. Moreover, the peroxide radicals formed in the oxidation of rubber can apparently form an oxidation–reduction system with the sulphenamides[44,45], so that the formation of accelerator radicals is enhanced; indeed, cumene hydroperoxide increases the rate of combination of sulphur in the presence of DEBSA.

Heating rubber with sulphenamide accelerators (in the absence of sulphur) causes vulcanisation, with combination of the accelerator elements with the rubber and the formation, in the case of DEBSA, of 2-mercaptobenzothiazole and diethylamine (Fig. 9). The amount of cross-linking produced in the rubber in this process is proportional to the amount of DEBSA consumed. From these facts, the mechanism of decomposition of DEBSA can be represented by the equation



The accelerator radicals (A$^\cdot$) formed in the decomposition produce cross-linking in the rubber by two reactions:

(a) addition to a doubly bonded carbon atom:

$$\sim CH_2-CH=CH-CH_2\sim + A^\cdot \rightarrow \sim CH_2-CHA-\dot{C}H-CH_2\sim,$$

(b) removal of a hydrogen atom from an α-methylene group (or tertiary atom of structure 1–2):

$$\sim CH_2-CH=CH-CH_2\sim + A^{\cdot\cdot} \rightarrow \sim \dot{C}H-CH=CH-CH_2\sim + AH,$$

where AH is mercaptobenzothiazole or diethylamine. The resulting polymeric radicals react together or with the double bonds of other rubber molecules, forming the cross –C–C– links of the three-dimensional vulcanisate structure.

The conversion of DEBSA in the presence of sulphur and activators is the same as in a binary rubber–accelerator mixture.

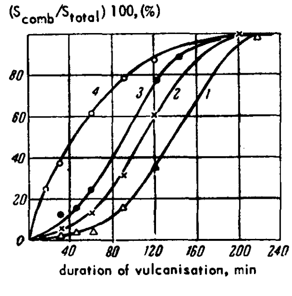


Fig. 8. Influence of oxygen on the combination of sulphur in mixtures with DEBSA: 1) 0.02; 2) 4.7; 3) 21; 4) 100 vol.% O_2.

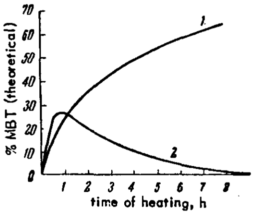
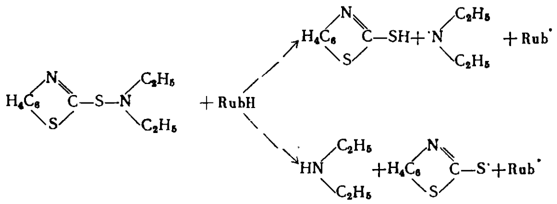


Fig. 9. 1) Combination of the mercaptobenzothiazyl radical (according to the combined-sulphur content) with rubber; 2) change of free MBT content in the system rubber + 6 wt.% DEBSA.

On the basis of the experimental results obtained, the following mechanism of action of DEBSA as a vulcanisation accelerator may be put forward. At the vulcanisation temperature, as indicated above, the accelerator dissociates into benzothiazyl and diethylamine radicals, which react with the rubber by withdrawing hydrogen from the molecular chains, forming mercaptobenzothiazole and diethylamine. The MBT reacts with sulphur by the mechanism given in section III. The curve depicting the concentration of MBT in the mixture has a maximum, which corresponds to the maximum rate of combination of sulphur with rubber. The decreased free MBT concentration beyond the maximum is due to its combination with the rubber, which continues as long as the mixture contains free sulphur[33]. Diethylamine must also be considered as having an analogous action as an accelerator, but it takes part in the vulcanisation to a lesser degree than the mercaptan, so that its content in the vulcanisation mixture gradually increases.

This theory can explain the S-shaped form of the kinetic vulcanisation curve which is typical of sulphenamide accelerators. As indicated above, the rate and energy of activation of sulphur combination in the initial period correspond with those for vulcanisation in the absence of an accelerator. It can therefore be deduced that the molecular form of *N*,*N*-diethyl-2-benzothiazylsulphenamide does not activate sulphur. The activation is due to the benzothiazyl and diethylamine radicals formed by the dissociation of the sulphenamide, and, in particular, to the mercaptobenzothiazole and diethylamine produced by the reaction of DEBSA with the rubber. In accordance with this mechanism,



each reaction of a DEBSA molecule with the rubber produces a molecule of active accelerator (mercaptan or amine) and two free radicals which can react with the sulphur. In other words, a DEBSA molecule is replaced by *three* active groups which can react with sulphur. This type of reaction is also responsible for the auto-acceleration of the process — the transition from the induction period to the main reaction period.

The increase in the rate of combination of sulphur in the main reaction period is also due to the following circumstance. As already stated, during the vulcanisation a considerable proportion of the DEBSA molecule is replaced by twice their number of new accelerators, the mercaptobenzothiazole and diethylamine molecules. The action of these two accelerators is not additive: in admixture they accelerate the combination of sulphur with the rubber to a greater extent than either taken separately in the same molar concentration. The reason for the increased activity of mixtures of two accelerators is discussed in section VI below.

The particular kinetics of the combination of sulphur with rubber in mixtures with sulphenamide accelerators are reflected in the dynamics of formation of the cross-linkages and of the change of plastoelastic properties of the mixture. Unlike other vulcanisation accelerators (MBT, thiuram, etc.), DEBSA leaves the vulcanisation mixture in the viscous-flow condition for a prolonged period, the plasticity of the mixture increasing in the initial stage despite combination of sulphur. This indicates that DEBSA promotes the thermal and thermal-oxidative decomposition of the molecular chains of rubber. There are grounds for supposing that this decomposition proceeds by the free-radical mechanism established by Pike and Watson[46].

V. VULCANISATION IN THE PRESENCE OF ORGANIC BASES

Organic bases are among the few vulcanisation accelerators which do not contain sulphur. The mechanism of their action has been studied in least detail.

Krebs[47] considers that amines react with sulphur and convert it into an active form soluble in rubber, the reaction being an ionic chain reaction:

$$R_3N^+ \rightarrow \overset{\frown}{S}{}_n^- \rightarrow R_3N^+ + S^{\cdots}\!-\!S^- + S_8 \xrightarrow{+\bar{S}_n^-} R_3N^+\!-\!S\ldots S^- \rightarrow R_3N^+\!-\!S^-\ldots\overset{\frown}{S} + S_8 \text{ etc.}$$

Scheele and coworkers[48] have made a kinetic study of vulcanisation in the presence of organic bases. They found that, in the presence of diphenylguanidine (DPG), the reaction between rubber and sulphur, as in the absence of accelerators, has a fractional order (0.75–0.8) with respect to the decrease in the quantity of free sulphur over the temperature range 100°–140°. The energy of activation is 29.8 kcal mole^{-1}. Initially there is a sharp decrease in the DPG concentration, reaching 55% of the original; it then becomes steady, but the free sulphur concentration still decreases. The velocity constant for the last reaction increases linearly with increase of the DPG concentration in the initial mixture up to ~2.5%, after which the constant remains practically unchanged. The initial sulphur and DPG concentrations have no influence on the order of the reaction. Based on the aforementioned work of Krebs, Scheele and coworkers assume an ionic mechanism for the vulcanisation activity of amines:

$$RNH_2 + S_8^- \rightleftarrows S_8^- + H^+$$

$$H^+ + RNH_2 \rightleftarrows RNH_3^+$$

At elevated temperature the negative ion RNH$-S_x^-$ is formed, which then gives up sulphur by the reaction

$$RNH\!-\!S_x^- + \text{Rub} \rightarrow RNH\!-\!S_y^- + \text{Rub}\!-\!S_y.$$

The base is thus a catalyst, and gives an intermediate with the sulphur. The study of various amines as accelerators showed that the velocity constant for the reaction between sulphur and rubber increases with increase of the dissociation constant of the amine, while tertiary amines do not accelerate vulcanisation. Of the amines studied (diethyl- and dimethyl-aniline, monoethyl- and monomethyl-aniline, *α*-naphthylamine, *o*-, *m*-, and *p*-toluidine, aniline, benzylamine) the only exception to this rule was DPG.

Aniline increases the evolution of hydrogen sulphide in the reaction of sulphur with diphenylmethane[49].

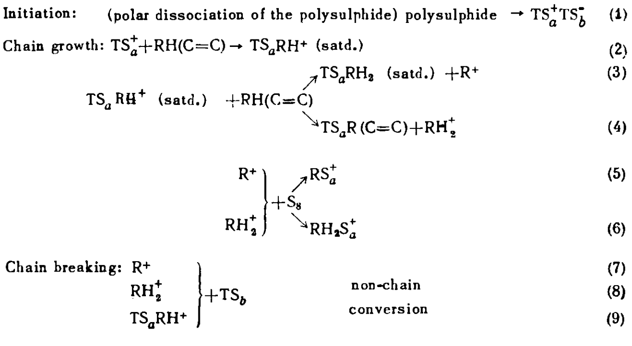
Moore and others[50] studied the reaction of sulphur with low-molecular olefines in the presence of diethylamine, and showed that the latter reacts with sulphur to form hydrogen sulphide and compounds in which sulphur has replaced hydrogen:

$$CH_3\!-\!CH_2\!-\!NHC_2H_5 + 2S \rightarrow H_2S + CH_3CS\!-\!NH\!-\!C_2H_5 \xrightarrow{+(C_2H_5)_2NH}$$
$$\rightarrow C_2H_5NH_2 + CH_3CSN(C_2H_5)_2\,.$$

The quaternary ammonium salt $(C_2H_5)_2NH_2^+SH^-$, which reacts with double bonds, can then be formed. The reaction, according to Moore's results, proceeds by a polar mechanism, considered in more detail below.

The amine accelerator is decomposed during vulcanisation[48,51,52].

In vulcanisation in the presence of DPG, the main feature is apparently the reaction between the decomposition products of the accelerator and the sulphur, giving polysulphides. The part played by such polysulphides and their further heterolytic dissociation has been described by Bateman and coworkers[53-55], who suggested an ionic mechanism for the reactions. They showed that the reaction products of olefines with sulphur at 110°–140° are linear polysulphides and cyclic sulphides. From the kinetics of the process, Bateman suggested the following mechanism:



$$\text{Initiation: (polar dissociation of the polysulphide) polysulphide} \rightarrow TS_a^+TS_b^- \qquad (1)$$

$$\text{Chain growth: } TS_a^+ + RH(C{=}C) \rightarrow TS_aRH^+ \text{ (satd.)} \qquad (2)$$

$$TS_aRH^+ \text{ (satd.)} + RH(C{=}C) \begin{cases} \nearrow TS_aRH_2 \text{ (satd.)} + R^+ & (3) \\ \searrow TS_aR(C{=}C) + RH_2^+ & (4) \end{cases}$$

$$\left.\begin{matrix} R^+ \\ RH_2^+ \end{matrix}\right\} + S_8 \begin{cases} \nearrow RS_a^+ & (5) \\ \searrow RH_2S_a^+ & (6) \end{cases}$$

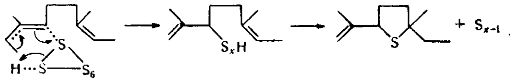
$$\text{Chain breaking: } \left.\begin{matrix} R^+ \\ RH_2^+ \\ TS_aRH^+ \end{matrix}\right\} + TS_b \quad \text{non-chain conversion} \qquad (7),\ (8),\ (9)$$

Here RH(C = C) is a mono-olefine; the term "(satd.)" signifies the absence of a C = C bond; H is the hydrogen of an *α*-methylene group; T = R or RH$_2$; *a* and *b* ⩾ 1.

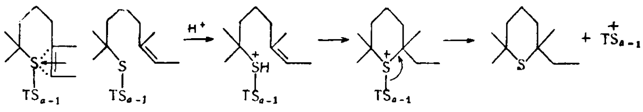
The mechanism of formation of the initial polysulphide is not clear. The fundamental step in the mechanism given above is the heterolytic dissociation of the S–S bond, which the authors consider the most probable process under vulcanisation conditions. The electron donor activity of the olefine double bond (reaction of unsaturated compounds with metal ions) will, in the authors' opinion, facilitate polarisation of the S–S bond in the S$_8$ and polysulphide molecules.

The large number of products obtained in the reaction of sulphur with olefines is due to the various possible directions in which the cation formed can react: combination with an associated anion or sulphur molecule, and exchange with a proton or hydride ion of the olefine molecule.

Bateman and coworkers[53] give detailed schemes for the reaction of sulphur with various low-molecular unsaturated compounds: octene-1, di- and tri-alkylethylenes, and 2,6-dimethylocta-2,6-diene, which explain the formation of complex polysulphides including those of cyclic structure. Cyclic monosulphides are formed as secondary products in the reaction of sulphur with 1,5-dienes. They are produced from the initially formed polysulphides, which react by proton transfer to give thiocarbonium ions, leading to intramolecular heterolysis of the added polysulphide bonds. Cyclic sulphides cannot therefore be formed independently of polysulphides. The reaction is:



Protonation of the double bond adjacent to the added sulphur by means of R^+ or TS_a^+RH produces a cyclic sulphide rather than a cross-linkage. The carbonium ion is converted to a polysulphide ion without combining with the sulphur, and this explains why sulphur reacts with 1,5-dienes more slowly than with mono-olefines. Ross[54] established this experimentally. With polyolefines there is irregular protonation, producing cyclic sulphides by the reaction



The TS_b^- anion formed in the dissociation of the polysulphide is thought to take part mainly in chain breaking by reacting with a carbonium or polysulphide ion, producing polysulphides.

The reaction mechanism suggested for the natural rubber model (2,6-dimethyloctadiene-2,6) can, it is thought, be applied also to reactions in rubber[56].

VI. ACTION OF SYSTEMS OF TWO VULCANISATION ACCELERATORS

Systems of two accelerators are widely used in technology, since they provide more effective vulcanisation than either material used alone. In early studies[57,58] the increased activity of two accelerators was explained by the formation of eutectic mixtures or salt-like compounds having a greater solubility in the rubber and a greater chemical activity. This explanation proved unsatisfactory, and the question received further study by Dogadkin and coworkers[59,60].

The experimental data on the kinetics of vulcanisation in the presence of various combinations of the most widely used accelerators enable the double systems to be divided into three groups: (1) systems with mutual activation of the accelerators; (2) systems with activation of one accelerator (the vulcanisation activity of such systems is no greater than that of the more active accelerator when used alone at the same molar concentration); (3) systems in which the activity of the accelerators is additive.

The first group includes systems of disulphides and mercaptans with organic bases, and disulphides and sulphenamides; the second includes combinations of sulphenamides with organic bases; and the third, combinations of sulphenamides and disulphides with monosulphides, and also combinations of accelerators of a single chemical type.

It is remarkable that vulcanisation in the presence of systems of the first and second groups shows an initial period of slow vulcanisation, in which the rate of vulcanisation is less than the rate expected on the basis of additivity of action of the accelerators (Fig. 10). In other words, in the initial stage for a certain composition, the accelerators exhibit mutual inhibition, and only in subsequent stages is there a sharp increase in the activity of the system. It may thus be concluded that in the initial stage of heating the vulcanisation mixture the accelerators react with one another, forming a less active complex, which then dissociates into free radicals which initiate the reaction of the rubber with the sulphur and polymerisation of the molecular chains of the rubber. The active complex forms at a molar ratio of the accelerators.

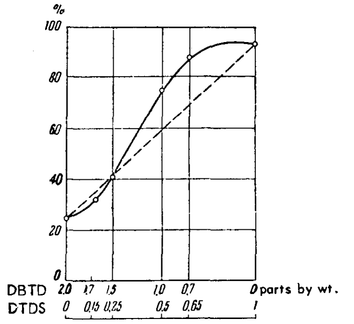


Fig. 10. Change of the amount of sulphur consumed after 5 min vulcanisation in the system DBTD + dimethylthiocarbamyl dimethylsulphenamide (DTDS).

The accelerators of the active systems of the first and second groups interact on heating in xylene and a xylene solution of rubber. There is marked formation of MBT when a mixture of DBTD and DPG is heated in xylene; the diphenylguanidine is here the hydrogen donor for the reduction of the disulphide. On heating DBTD with sulphenamide accelerators, *e.g.* with *N*-cyclohexyl-2-benzothiazylsulphenamide, the mercaptan is only formed when the solution contains rubber, since the benzothiazyl radicals produced by the dissociation of the intermediate complex cannot extract hydrogen from the solvent molecules, and the hydrogen donors are the α-methylene groups of the rubber.

The quantity of MBT produced by the action of an active mixture of two accelerators is many times the quantity of mercaptan formed by the action of either accelerator alone

(Fig. 11; the dotted lines show the formation of mercaptan assuming additivity of action of the accelerators). This is a convincing proof of the interaction of the accelerators and the formation of an intermediate complex which decomposes into free radicals:

$$RSSR+R'R''NH \rightarrow \left[\begin{matrix}RSSR\\R'R''NH\end{matrix}\right] \rightleftarrows RSH+RS^{\cdot}+R'R''N^{\cdot},$$

i.e. the decomposition of the disulphide, like that of a peroxide[61], is activated by an amine.

The further development of the process when using certain accelerators may include the steps:

$$RS^{\cdot}+R'R''NH \rightarrow RSH+R'R''N^{\cdot}$$
$$R'R''N^{\cdot}+RSSR \rightarrow RSNR''R'+RS^{\cdot}.$$

These steps explain the formation of two new extremely active accelerators: MBT (RSH) and the sulphenamide (RSNR″R′), and can also be considered as the reason for the increased vulcanisation activity of the initial binary system of accelerators.

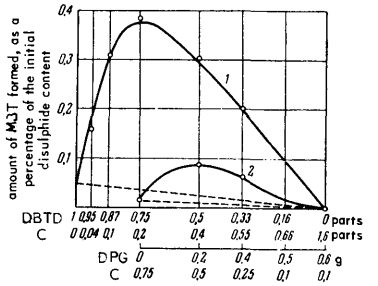
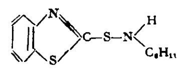
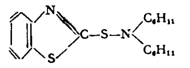
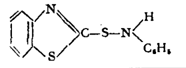
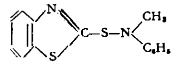
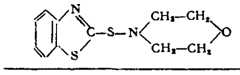
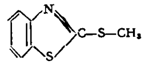
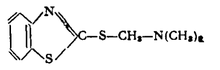
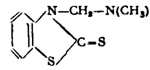
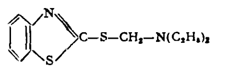
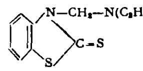
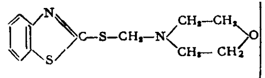
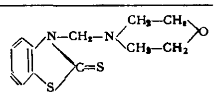
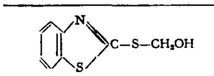
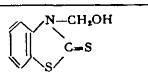
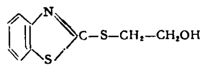
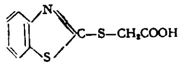


Fig. 11. Formation of MBT by the reaction of *N*-cyclohexyl-2-benzothiazylsulphenamide (C) with (1) DBTD and (2) DPG on heating in a rubber solution for 90 min at 150°.

TABLE 1. Dipole moments of MBT derivatives.

Assumed formula	Molar polarisation	Molar refraction	Dipole moment $\mu\times10^{-18}$, *D*	Formula established from measurement of dipole moment
	246.0	75.6	2,87	as shown
	288.5	101.4	3.01	as shown
	190.8	74.1	2.38	as shown
	202.9	89.1	2.45	as shown
	130.3	68.3	1.73	as shown
	87,5	51.1	1.30	as shown
	463.9	64.3	4.39	
	470.8	73.5	4.38	
	533.4	73.0	4.72	
	486.4	52.6	4.58	
	169	57.3	2,33	as shown
	461,9	54.8	4.44	as shown

VII. STRUCTURE AND ACTIVITY OF VULCANISATION ACCELERATORS

The connection between chemical structure and vulcanisation activity of the accelerators has been often reviewed[62]. Attempts have been made to establish a relationship between accelerator activity and its physical properties, particularly its dipole moment. In recent years the attention of workers has been attracted towards a possible evaluation of the activity of sulphur-containing accelerators by their ability to exchange sulphur with radioactive sulphur. Blokh and coworkers[63-65] used 2-mercaptobenzothiazole derivatives to show that the rate of isotope exchange at vulcanisation temperatures runs parallel to the rate of vulcanisation in the presence of the accelerators. The thiol sulphur of MBT exchanges with elementary sulphur, and substitution of a methyl group causes loss of vulcanisation activity and precludes isotope exchange. However, more recent studies have shown that this relationship is not always observed; thus the zinc salts of mercaptobenzothiazole and dithiocarbamic acid, which are active accelerators, exchange with ^{35}S only with difficulty. In most cases isotope exchange proceeds at a lower rate than the combination of sulphur with the rubber in the presence of equal amounts of accelerators[66]. This is understandable if it is recalled that in vulcanisation reactions, as the experimental data given above show, the reaction of the accelerator with the rubber plays a substantial part.

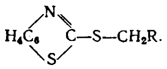
The exchange reaction of disulphides and sulphenamides with compounds containing similar groups with labelled atoms is of undoubted interest for evaluating the activity of these accelerators. Gur'yanova[67] has shown that exchange between disulphides and mercaptans takes place by a radical mechanism:

$$RSSR+R'SH \rightarrow RSSR'+RSH.$$

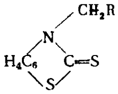
The degree of exchange is determined by the energy of the S-S bond, which, in its turn, depends on the nature of the radicals R and R′. This method has been used to evaluate the vulcanisation activity of sulphenamide accelerators of various structure[68], using exchange with DBTD labelled in the disulphide bridge. The experimental results demonstrated a good correlation between the degree of exchange and the activity of the accelerator.

Of the sulphenamide derivatives of mercaptobenzothiazole, the unsubstituted benzothiazylsulphenamide shows the smallest activity. Substitution of the amino hydrogen by alkyl radicals increases the activity of the accelerator. The introduction of two phenyl groups causes almost complete loss of vulcanisation activity. Substitution of one hydrogen by a phenyl group produces an accelerator of similar activity to DEBSA. Of the compounds studied the most active was *N*-cyclohexyl-2-benzothiazylsulphenamide.

It was shown in section IV that a characteristic feature of sulphenamide accelerators is the existence of an induction period, both as regards taking up of sulphur and change of plasticity. This induction period is not observed with 2-methylthiobenzothiazole derivatives, which can be divided into two groups according to their dipole moment (Table 1). Some have a dipole moment of 2.38–2.87 *D*, indicating that the methyl group is attached to the thiol sulphur:



These have a low vulcanisation activity. Others have a dipole moment of 4.3–4.7 *D*, indicating that the methyl group is attached to the nitrogen:



These compounds possess high vulcanisation activity, apparently because the energy of the $-N-CH_2R$ bond is less than the energy of the $-S-CH_2R$ bond.

VIII. INFLUENCE OF THE STRUCTURE OF RUBBER ON ITS VULCANISATION CAPACITY

The ability of rubber to undergo vulcanisation with sulphur is determined first by the presence of double bonds in its molecular chains. The kinetics of the reaction with sulphur depends on the number of double bonds and the nature of the substituents present. Dogadkin and coworkers[69] used butadiene polymers to show that the position of the double bonds also plays a part. In the vulcanisation of solutions of rubbers containing various ratios of 1,4- and 1,2-structures, it was found that sulphur combines with the double bonds of the main chains at a faster rate than with the double bonds of the vinyl side chains (Fig. 12): the energy of activation for the combination of sulphur with the main chains in the presence of accelerator A-100 is 14 kcal mole^{-1}, but 19 kcal mole^{-1} in the case of combination with the vinyl side chains. The different activity of the double bonds of the 1,4- and 1,2-structures towards sulphur has been demonstrated by observing the change in the absorption bands at a frequency of 965 cm^{-1} (for 1,4-structures) and 909 cm^{-1} (for 1,2-structures) on vulcanisation.

If the vulcanisation is carried out in a press, the difference in the rates of combination of sulphur with rubbers of different structure disappears, apparently because of the increased concentration of double bonds and hence of the increased absolute rates of reaction as compared with vulcanisation in solution.

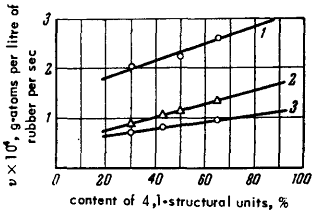


Fig. 12. Rate of combination of sulphur as a function of the structure of the rubber: 1) 155°; 2) 142°; 3) 135°.

According to the spectroscopic data, there is no decrease in the number of double bonds in the initial period of vulcanisation. This means that, in this stage of the vulcanisation, reactions in which the α-methylene groups of the 4,1-structure take part are predominant. Various mechanisms are possible for these reactions; the removal of hydrogen by the accelerator radicals is apparently the main process (see sections II and III). In the main vulcanisation period the decrease in unsaturation is linearly dependent on the amount of combined sulphur, but (unlike cases described in the literature for natural rubber) the decrease in unsaturation is 4–6 times that calculated on the assumption that one atom of sulphur combines with each double bond. This increase may be due to polymerisation of the molecular chains at the double bonds, or to the formation of intramolecular rings.

The degree of cross-linking $\Delta E_\infty/\Delta S$ is a linear function of the number of double bonds of 1,4-structure.

In the vulcanisation of butadiene rubbers with thiuram in the absence of sulphur, the degree of cross-linking increases with increase of their content of 1,4-structures, but the amount of combined TMTD sulphur decreases. The greater reaction of TMTD with rubbers with a higher content of 1,2-structures is apparently due to the combination of TMTD radicals with the vinyl side chains, which does not produce cross-linkages; these arise, as shown above, by reaction of the TMTD with the double bonds or α-methylene groups of 1,4-structure[14].

IX. ROLE OF VULCANISATION ACTIVATORS

Vulcanisates of better quality are obtained in the presence of activators. Some workers[70,71] suggest that the metal oxides used as activators form salt-like compounds with the accelerators which are more soluble in the rubber and therefore more active. They react with sulphur to produce unstable compounds which liberate sulphur in the active form[38]. Dogadkin and coworkers[72,73] have shown that the choice of activator depends on the type of rubber, the accelerator, and the filler.

The most widely used activator is zinc oxide. In its presence sulphur reacts with rubber by a first-order reaction, and in its absence by a reaction of fractional order[48]. The rate of combination of sulphur in mixtures without an accelerator and with MBT in the presence of zinc oxide and stearic acid is either the same as or slightly less than the rate in mixtures without activators (Fig. 13). The activators considerably increase the number of cross-linkages in the vulcanisate[74,75].

In vulcanisation in the presence of zinc oxide, part of the sulphur is combined as zinc sulphide, which is formed to a greater extent in mixtures without an accelerator than in mixtures with accelerators (MBT, DPG). It has been shown experimentally that zinc sulphide can form by various reactions occurring in sulphur vulcanisation: the reaction of zinc oxide or stearate with hydrogen sulphide, the reaction of the zinc salt of the accelerator (MBT) with sulphur or hydrogen sulphide; and the reaction of polysulphides with zinc oxide, stearate, or mercaptide. The last reaction suggests the possible formation of zinc sulphide by the reaction of zinc oxide with the polysulphide bonds of the vulcanisate; this was confirmed by the increase in the zinc sulphide content when the vulcanisate was heated after acetone extraction. The same is observed on prolonged heating of a vulcanisate in which the sulphur is completely combined with the rubber. This reaction explains the sharp increase in the ratio ZnS/S_{comb} which is observed in the final stage of vulcanisation beyond the optimum. These reactions compete with the main reaction in which the sulphur combines with the rubber, and they must therefore be considered as one of the reasons for the retarding action of zinc oxide on the combination of sulphur with the rubber. It is interesting that zinc oxide retards the rate of exchange between ^{35}S and MBT and reduces the degree of exchange, while stearic acid activates it, *i.e.* there is an analogy with the influence of zinc oxide and stearic acid on the combination of sulphur with rubber in the presence of MBT as accelerator.

Zinc oxide alone does not accelerate the formation of cross-linkages in the vulcanisation of mixtures with MBT, but there is a sharp increase in the rate of cross-linking when both zinc oxide and stearic acid are present[76].

There is a linear relationship between the number of cross-linkages and the quantity of sulphur combined with the rubber (organically bound sulphur, *i.e.* the quantity of sulphur in the extracted vulcanisates less the sulphur present as ZnS) up to the point immediately after the vulcanisation optimum (Fig. 14). The slope of the straight lines of Fig. 14 determines the "degree of bridging". Comparison of the slopes shows that stearic acid accelerates the combination of sulphur without increasing the percentage of sulphur present in the cross-linkages. The "degree of bridging" increases sharply when zinc oxide is present in the mixture. The role of zinc oxide as a vulcanisation activator is therefore that of increasing the percentage of sulphur forming cross-linkages in the vulcanisate.

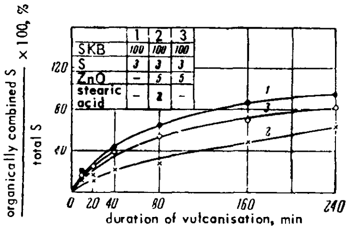


Fig. 13. Kinetics of the combination of sulphur in butadiene rubber (SKB) mixtures without an accelerator. Composition of mixtures in parts by weight.

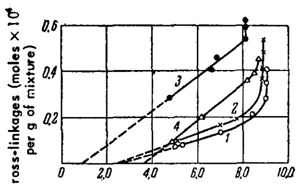
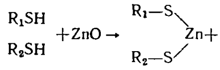


Fig. 14. Number of cross-linkages as a function of the amount of sulphur combined with the rubber during vulcanisation of mixtures of the composition (in parts by weight):

	1	2	3	4
SKB	100	100	100	100
Sulphur	3	3	3	3
ZnO	–	–	5	5
Stearic acid	–	2	2	–
MBT	1	1	1	1

Dogadkin and Beniska's results[74] indicate the following possible mechanism for the role of zinc oxide in the formation of cross-linkages in the vulcanisate: (1) reaction of zinc oxide or salts with thiol polysulphides, producing zinc sulphide and sulphur diradicals which then join molecules of the rubber; (2) oxidation of the thiol groups to form cross-linkages by the reactions

$$2RSH + ZnO + S \rightarrow R—S—S—R + ZnS + H_2O \text{ or}$$

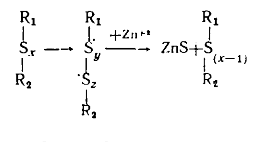


$$\begin{matrix} R_1SH \\ R_2SH \end{matrix} + ZnO \rightarrow \begin{matrix} R_1—S \diagdown \\ \qquad Zn + H_2O; \\ R_2—S \diagup \end{matrix}$$

(3) reaction of zinc oxide or salts with the polysulphide bonds of the vulcanised structure by the reaction:

$$R_1—S_x—R_2 \xrightarrow{+Zn^{+2}} R_1—S_y—R_2 + ZnS.$$

An increase in the number of cross-linkages will be observed only when part of the polysulphide sulphur is liberated as a new diradical $\cdot S_z^{\cdot}$ which can then react with rubber molecules to form a new cross-linkage. The number of cross-linkages will remain the same if the recombination of the radicals occurs at the original site:



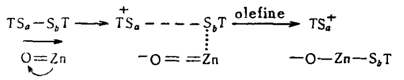
$$\begin{matrix} R_1 \\ | \\ S_x \\ | \\ R_2 \end{matrix} \longrightarrow \begin{matrix} R_1 \\ |\cdot \\ S_y \\ | \\ \cdot S_z \\ | \\ R_2 \end{matrix} \xrightarrow{+Zn^{+2}} ZnS + \begin{matrix} R_1 \\ | \\ S_{(x-1)} \\ | \\ R_2 \end{matrix}$$

The increased number of cross-linkages and the decreased sulphide content thereof in the presence of zinc oxide is shown by the decreased degree of isotope exchange between the extracted vulcanisate (obtained with radioactive sulphur) and elementary non-radioactive sulphur after the vulcanisation optimum, and also by comparison with the vulcanisate obtained in the absence of zinc oxide. Another illustration is the lower rate of stress relaxation, *i.e.* greater thermal stability, of the vulcanisation structures obtained in the presence of zinc oxide (see below).

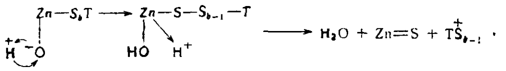
Lorenz and Echte[76] also reported a maximum on the curve of combined polysulphide sulphur against time of vulcanisation.

Bateman and coworkers[53] studied the part played by zinc oxide in the reactions of sulphur with model compounds. In the presence of zinc oxide, the rate of combination of sulphur with a 1,5-diene increases, a greater amount of cyclic sulphides is formed, and the sulphide content of the cross-linkages decreases[74]. In the presence of stearic acid, the rate of this reaction decreases, and equal quantities of cyclic and cross-linked sulphur-containing products are formed. Further addition of MBT increases the rate of reaction and decreases the number of cyclic sulphides.

Great weight is given to the catalytic activity of zinc oxide in the reactions studied. The higher rate of combination of sulphur in the presence of zinc oxide is explained by polarisation of the polysulphide[53] on the ZnO surface:



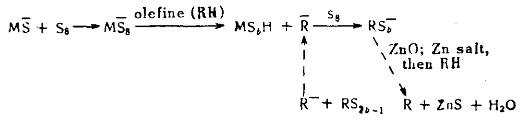
The resulting complex dissociates more easily to give the TS_b^- ion, or a proton adds on, with the formation of water, zinc sulphide, and another polysulphide ion:



The absence of any accelerating activity of zinc oxide in the combination of sulphur in a rubber medium is explained[74] in terms of the weaker adsorption and desorption of protons in a medium of high viscosity, and by the poisoning of the zinc oxide surface by the non-hydrocarbon components of the rubber. The increased number of cross-linkages and the decreased number of cyclic structures in the presence of zinc oxide and stearic acid is explained by the combination of the zinc stearate formed under these conditions with a proton which would otherwise attach itself to a double bond and so form a ring. The action of the zinc salt does not therefore involve the removal of sulphur atoms from the sulphides initially formed.

In the 1,5-diene–sulphur–zinc oxide–stearic acid–MBT system, the rate of combination of sulphur increases and the quantity of sulphur combined as cyclic sulphides noticeably decreases, by comparison with the diene–sulphur system. The actual accelerator, in Bateman's opinion, is the zinc salt of the MBT.

Bateman and coworkers consider that the benzothiazylsulphide anion facilitates the heterolysis of the S–S bond:



The reaction of MS$^-$ or R$^-$ with the sulphur is the rate-limiting step in the whole process, and gives a first-order reaction for the combination of sulphur[31,33-37].

These workers consider that the role of the zinc salts is to stimulate the activity of additional nucleophilic centres. In its turn, the electrophilic reactivity of the labile polysulphide determines the reaction of the sulphur with the unsaturated compounds.

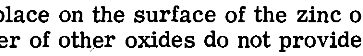
This point of view regarding the catalytic activity of zinc oxide or salts requires further confirmation. As has been reported[72,73], the choice of activator (metal oxide) depends greatly on the type of rubber, and zinc oxide is not always the best choice.

It is interesting to consider the role of activators in vulcanisation with TMTD, since Scheele *et al.*[77] explain the specific role of zinc oxide in this process by its catalytic activity and particular crystalline structure. Direct heating of tetraethylthiuramdisulphide (TETD) with zinc oxide in the range 80°–150° produces in the limit ~90 mole % of Zn DTC based on TETD taken. The formation of gaseous products[78] is clearly due to parallel thermal decomposition of the TETD.

In a vulcanisation system, the limiting conversion of thiuram to Zn DTC is also independent of the initial thiuram and zinc oxide concentrations[79]; however, the rate of accumulation of Zn DTC and the rate of decrease of unchanged thiuram increase with the zinc oxide content of the mixture[78,80]. This has led to the conclusion that vulcanisation takes place on the surface of the zinc oxide crystals, since a number of other oxides do not provide satisfactory vulcanisates. In Scheele's opinion, an intermediate is formed on the surface of the zinc oxide crystals during vulcanisation. This intermediate liberates Zn DTC on decomposition and produces cross-linking in the vulcanisate[81].

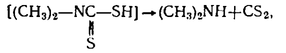
Scheele and his coworkers consider that in the absence of zinc oxide the reaction of thiuram with the rubber proceeds by a completely different mechanism. Dogadkin and Shershnev[14,15,82] have shown that from a chemical point of view the reaction of TMTD with rubber is practically the same in the presence or absence of zinc oxide. Satisfactorily durable thiuram vulcanisates can be obtained without zinc oxide (*e.g.* with 10 parts by wt. of TMTD per 100 parts by wt. of rubber[83]).

The role of the zinc oxide or salts is to combine with the reaction products of the thiuram with the rubber and to suppress destructive oxidation processes in the vulcanisation system[15,82]. In the presence of zinc oxide or salts, the dimethyldithiocarbamic acid formed by the reaction of TMTD with the rubber is taken up as Zn DTC:



$$[(CH_3)_2N\underset{\underset{S}{\|}}{C}{-}SH] \xrightarrow{+ZnO} [(CH_3)_2N\underset{\underset{S}{\|}}{C}{-}S]_2Zn + H_2O.$$

In the absence of metal oxides or salts, or in the presence of magnesium or calcium oxides or salts, this acid decomposes[15] into dimethylamine and carbon disulphide:



$$[(CH_3)_2{-}N\underset{\underset{S}{\|}}{C}{-}SH] \rightarrow (CH_3)_2NH + CS_2,$$

which are volatile and are removed from the vulcanisates. Under these conditions the loss of TMTD sulphur in the vulcanisates reaches 60% of that introduced as TMTD (see Fig. 3). The number of cross-linkages formed in the vulcanisation of mixtures containing zinc oxide or salt on the one hand, and no metal oxide or with magnesium or calcium oxides or salts on the other, is greatly different[15].

In the first case reversion is not observed, but in the second it is very noticeable. The explanation of this was found in experiments on the vulcanisation of these systems in an inert atmosphere[82]; in this case the number of cross-linkages in vulcanisates containing TMTD is practically the same in the absence or presence of zinc or magnesium oxide. Chemically, the process is the same as in air; consequently the reversion of vulcanisation in the case described is due to destructive oxidation processes activated by the decomposition products of the dimethyldithiocarbamic acid. This was confirmed by thermal oxidative aging of thiuram vulcanisates with and without added Zn DTC.[84,85] Zn DTC is an antideteriorant formed during the vulcanisation.

X. CROSS-LINKING (VULCANISATION) OF RUBBER SOLUTIONS AT LOW TEMPERATURES

Vulcanisation by the Peachey process has been considered as taking place by the reaction of the rubber with nascent sulphur formed by reaction between H_2S and SO_2, but Dogadkin and Belyaeva showed[86] that this is not the case. Pure sodium butadiene rubber which has been heated at 80° in nitrogen is not vulcanised by the Peachey process, although sufficient elementary sulphur is formed. The sulphur produced by reaction between DBTD and H_2S by the process $RSSR + H_2S \rightarrow 2RSH + S$ also does not cause agglomeration of rubber solutions, although it reacts with the rubber; in this case the sulphur chemically combined with the rubber is concentrated in a small fraction of the latter (5%), which is not precipitated from solution by methanol; the fraction precipitated by the methanol (90 wt.%) is practically free of combined sulphur. Apparently the hydrogen sulphide and the sulphur formed combine intramolecularly with a small fraction of the rubber to produce cyclic structures by an ionic mechanism similar to that described by Naylor[87] in experiments with di-isoprene. Benzoyl peroxide reacts with hydrogen sulphide to produce benzoic acid and elementary sulphur; however, no agglomeration occurs when this reaction is carried out in a solution of pure rubber. These results show that nascent sulphur does not vulcanise rubber at room temperature.

The DBTD–H_2S system, which liberates sulphur, causes agglomeration (vulcanisation) of rubber when a solution of the latter containing DBTD is irradiated with scattered sunlight or ultra-violet light before being saturated with hydrogen sulphide. The rate of agglomeration depends on the time of irradiation (Fig. 15). There are definite limits to the duration of irradiation which will cause agglomeration; with too little, or after prolonged, irradiation gel formation does not occur. The composition of the gas phase over the solution affects the rate and degree of agglomeration; in nitrogen the ability to form a gel appears after a longer period of irradiation than in air, and persists for a longer period. The resulting gel contains 0.6–0.7% of combined sulphur, evenly distributed throughout its volume. According to spectrographic analysis there is a considerable loss of double bonds (27–60%). This is substantially greater than would correspond to the quantity of combined sulphur, indicating that polymerisation occurs.

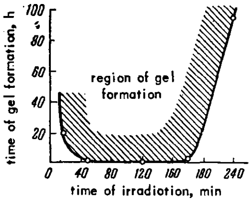


Fig. 15. Time of gel formation of rubber solutions by the action of hydrogen sulphides as a function of the duration of their preliminary ultra-violet irradiation in admixture with DBTD.

The existence of regions of gel formation is apparently due to the presence in solution of rubber radicals, produced by reaction between the rubber and the short-lived benzothiazyl radicals formed by the photochemical dissociation of the disulphide. The formation of a mercaptan can be demonstrated analytically in an irradiated rubber solution containing a disulphide, in accordance with stages 1) and 2) of the mechanism below. These observations, and the inhibiting action of small amounts of hydroquinone, phenyl β-naphthylamine, and other acceptors, suggest the following radical mechanism for the polymerisation:

$$\left.\begin{array}{ll}
1) & R{-}S{-}S{-}R \overset{h\nu}{\rightarrow} 2RS^{\cdot} \\
2) & RS^{\cdot} + Rub \rightarrow Rub^{\cdot} + RSH \\
3) & Rub^{\cdot} + H_2S \rightarrow Rub + HS^{\cdot} \\
4) & Rub + HS^{\cdot} \rightarrow Rub^{\cdot}SH \\
5) & Rub^{\cdot}SH + Rub \rightarrow RubSHRub^{\cdot} \\
6) & RubSHRub^{\cdot} + Rub \rightarrow RubSHRub{-}Rub^{\cdot}\ \text{etc.} \\
7) & Rub + Rub^{\cdot} \rightarrow Rub{-}Rub^{\cdot} \\
8) & Rub{-}Rub^{\cdot} + Rub \rightarrow Rub{-}Rub{-}Rub^{\cdot}\ \text{etc.} \\
9) & Rub^{\cdot} + Rub^{\cdot} \rightarrow Rub{-}Rub
\end{array}\right\}
\begin{array}{l}
\text{initiation} \\ \\ \\ \\ \text{chain growth} \\ \\ \\ \\ \text{chain breaking}
\end{array}$$

Stages 5), 6), 7), 8), and 9) in this mechanism represent the polymerisation steps.

The benzoyl peroxide–hydrogen sulphide system produces polymerisation of rubber solutions in the presence of a definite concentration of an amine, *e.g.* phenyl β-naphthylamine, and the yield of benzoic acid is higher than that expected from the bimolecular reaction:

$$[RO_2]_2 + H_2S \rightarrow 2ROOH + S.$$

These facts indicate that among the initial stage in the sequence of reactions leading to vulcanisation there is a stage in which benzoyl and amine radicals are formed[88,89]:

$$ROOR + R'R''NH \rightarrow [ROOR \ldots R'R''NH] \rightarrow ROOH + RO^{\cdot} + R'R''N^{\cdot}.$$

and these radicals then react with rubber and hydrogen sulphide molecules to form, by analogy with the above mechanism, polymeric and thiol radicals, which initiate polymerisation.

XI. THE REVERSION EFFECT AND OPTIMUM VULCANISATION

Most of the physicochemical properties of rubber change irregularly during vulcanisation, and pass through a maximum or minimum. This kinetic effect gives rise to the technically important reversion effect and vulcanisation optimum. In 1938 Dogadkin[90] suggested that the vulcanisation optimum is due to the operation of a number of factors on the properties of rubber during vulcanisation, of which some are constructive, building up the molecules, and others are destructive. The combined effect of these opposing processes is to produce kinetic curves showing a maximum or minimum, although their individual kinetics are described by smooth curves. This suggestion was later developed experimentally and theoretically[91]. The constructive processes include the action of vulcanising agents, and for some rubbers the action of heat and oxygen; thermal oxidation and thermal degradation are considered to be the destructive processes. From these general considerations, the following kinetic equation has been derived for the change of strength (π) of the vulcanisate[92,93]:

$$\pi = \pi_0 (1 + ax)(1 - by),$$

$$x = \frac{n}{n_{\max}} = 1 - e^{-\alpha t},$$

$$y = \frac{m}{m_{\max}} = 1 - e^{-\beta t},$$

where π is the strength of the mixture at time t, π_0 the strength of the initial mixture, n the number of polymerisation acts in time t, $n_{\max}$ the total maximum number of polymerisation acts, and m and $m_{\max}$ the corresponding values for the destructive acts.

In the simplest case, when polymerisation occurs under the action of sulphur and destruction occurs by thermal oxidative processes, the equation takes the form:

$$\pi = \pi_0 [1 + a(1 - e^{-k_1 t})] [1 - b(1 - e^{k_2 t})],$$

where k_1 is the velocity constant for the combination with sulphur and k_2 the velocity constant for the combination with oxygen.

This equation has been confirmed in many studies of the vulcanisation of natural rubber. It cannot be applied to sodium butadiene or butadiene-styrene rubbers, since with these types of polymer the action of oxygen, even in the early stages, is to cause polymerisation and not degradation.

The effect of oxygen (and compounds containing active oxygen) on the rate of change of properties during vulcanisation has been demonstrated in many experiments. Thus if a natural rubber mixture (with MBT as accelerator) is prepared and vulcanised with strict exclusion of oxygen, the maximum on the strength curve disappears; there is no reduction of strength, because the destructive influence of oxygen is removed (Fig. 16). Since sodium butadiene rubber is polymerised in the same way by sulphur and by oxygen, its strength does not go through a maximum, whether vulcanisation is carried out in nitrogen or in oxygen.

Analogous results were obtained on vulcanisation in a press of mixtures containing tetramethylthiuram sulphide as the vulcanising agent: there was no reversion when the mixture was vulcanised with strict exclusion of oxygen. In this case the oxidative destruction is activated by the decomposition products of the accelerator: carbon disulphide and dimethylamine (see section IX of this review).

It has been suggested[94] that, under technical vulcanisation conditions in a press, oxidation processes do not occur, because direct contact between the vulcanisation mixture and the air is avoided; this cannot be the case, however, since during vulcanisation the rubber reacts with the molecular oxygen and active oxygen-containing compounds introduced into the mixture during plasticising and mixing, and in particular with the ingredients of the mixture. Direct analysis shows that the "free" oxygen content in technical filled mixtures can reach 1.2%. The infra-red spectra of a vulcanisate, recorded after prolonged heating in a press, show the characteristic absorption bands of oxygen compounds.

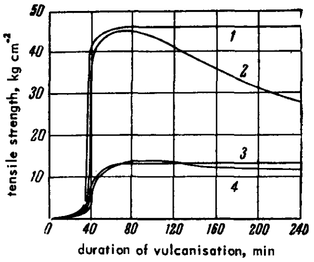


Fig. 16. Change of tensile strength during vulcanisation of mixtures of natural rubber (I) and butadiene rubber (SKB):
1) and 2) I in nitrogen and in air; 3) and 4) SKB in nitrogen and in air.

The influence of thermal oxidative processes on the rate of change of properties during vulcanisation clarifies the part played by certain anti-agers. Thus Tonox, which has practically no effect on the rate of combination of sulphur, markedly increases the strength of a natural rubber mixture. Vulcanisation accelerators or their reaction products have a definite influence on the thermal oxidative processes (Fig. 17).

The thermal rupture and rearrangement of S–S bonds play a very substantial part in reversion and the production of a vulcanisation optimum[95-97]. As already indicated in section IX, in the initial stage the sulphur combines with the rubber to form polysulphide groups, which are then thermally decomposed and rearrange into groups with a smaller number of sulphur atoms. The sulphide bonds can split (a) without or (b) with liberation of sulphur:

$$\text{a) } RS_xR \rightleftarrows RS_{(x-y)}^{\cdot} + R'S_y^{\cdot},$$

$$\text{b) } RS_xR' \rightleftarrows RS_{(x-y-z)}^{\cdot}R'S_y^{\cdot} + {}^{\cdot}S_z^{\cdot}.$$

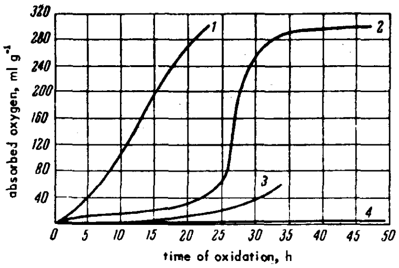


Fig. 17. Influence of accelerators on the absorption of oxygen by rubber:
1) 0.78% Captax; 2) without accelerators; 3) 0.63% diphenylguanidine; 4) 0.7% thiuram.

If the resulting radicals and sulphur can react with the rubber molecules to form new cross-linkages, this process will increase the modulus and decrease the swelling maximum. Such an effect is apparently observed in the vulcanisation of sodium butadiene rubber, which does not show reversion of vulcanisation on prolonged heating; however, the resulting polymeric radicals can be stabilised by combination with the low-molecular compounds present in the vulcanisation mixture (oxygen, accelerators, antioxidants, and their decomposition products). The sulphur formed can combine with the double bonds as thi-irane groups or form intramolecular cyclic structures by the mechanism established[87] for the reaction of sulphur with di-isoprene. The polymeric radicals of type RS_y may be stabilised because of the formation of intramolecular rings. These secondary processes following the thermal decomposition of the sulphide structures lead to a decreased number of cross-linkages or, in other words, to a decrease in the modulus and an increase in the swelling maximum; this is observed in the reversion of vulcanisation in the case of natural rubber and synthetic *cis*-isoprene rubber.

The so-called activators — metal oxides and fatty acids — play a substantial part in the rearrangement of the S–S bonds. Zinc oxide has practically no effect on the rate of combination of sulphur with rubber, but considerably increases the number of cross-linkages in the vulcanisate, by undergoing the series of reactions considered by Dogadkin and Bensika[74]. The most important reactions are those of ZnO with the thiol groups formed in the molecular chains in the reactions referred to in section IX, with sulphur and thiol and perthiol radicals, and with polysulphide linkages, the last by the reaction:

$$RS_xR' \xrightarrow{Zn} ZnS + RS_{(x-1)}R'$$

This reaction increases the ZnS content of the vulcanisate and decreases the amount of sulphur combined with the rubber; the kinetic curve for the accumulation of this sulphur in the vulcanisate (organically bound sulphur) passes through a maximum. The number of sulphur atoms per linkage also decreases, as is demonstrated by the reduced exchange capacity of vulcanisates containing ZnO, as compared with those not containing it (section IX).

An important part in the change of the vulcanisation structures is also played by the compounds produced during the vulcanisation from the accelerators. As already mentioned, during vulcanisation TMTD is reduced to dithiocarbamic acid, which with zinc oxide forms the stable zinc salt. In the absence of ZnO the dithiocarbamic acid decomposes into dimethylamine and carbon disulphide, which facilitate the thermal and particularly the thermal oxidative destruction of the rubber and its sulphur-containing compounds (see section IX).

An unequivocal index of the structural changes during vulcanisation is either the equilibrium modulus or the equilibrium degree of swelling, but not the static strength index. The direct relationship (for one type of polymer) between the strength and the number of cross-linkages holds up to a certain concentration of the latter ($\sim 4 \times \times 10^{19}$ cm^{-3} for natural rubber); further increase of the density of the vulcanisation lattice leads to a decrease in strength, apparently because of steric hindrance to the formation of the limiting orientated crystalline phase of the vulcanisate[98]. The equation given at the beginning of this section can therefore only be used for those vulcanisations in which the number of cross-linkages does not exceed this limit. For mixtures with a higher content of vulcanisation agent, the decreased strength beyond the vulcanisation optimum is due to the limiting density of cross-linking being reached, and not to destructive processes. These cases have been considered by Dogadkin and coworkers and by Gee[99-101].

XII. VULCANISATION STRUCTURES AND THEIR INFLUENCE ON THE STATIC AND DYNAMIC PROPERTIES AND ON THE FATIGUE OF VULCANISATES

As a result of vulcanisation, local chemical bonds and intermolecular (van der Waals) bonds are formed between the molecular chains. In a number of cases the configuration of the chains changes, because of cyclisation and isomerisation. For their effect on the physicochemical properties of the vulcanisates, the most significant of these changes are the chemical vulcanisation bonds — their composition, concentration, and distribution. In use, the vulcanisation structures undergo gradual changes, which is one of the causes of the aging and fatigue of the rubbers. One of the most important tasks of rubber technology is therefore to study the vulcanisation structures, to investigate the factors which affect their formation and change, to correlate the type of structure with the physicochemical properties of the vulcanisates, and to develop vulcanisation conditions which will provide the required vulcanisation structures.

It has been shown[5,75] that the chemical cross-linkages formed on vulcanisation are mainly C–C and $C-S_x-C$ bonds with a variable sulphur content. The carbon–carbon bonds arise by reaction of the polymeric radicals among themselves and with the initial rubber molecules. The polymeric radicals, in their turn, are formed either by physical action (light, ionising radiation) or by reaction with the vulcanising agents or vulcanisation accelerators. This last case has been considered in sections II and IV for vulcanisation with disulphides and sulphenamides.

The $C-S_x-C$ bonds are formed by reaction of the rubber with sulphur diradicals $\cdot S_x^{\cdot}$, and thiol HS· and perthiol $HS_x^{\cdot}$ radicals.

Dogadkin and Tarasova used isotope exchange between the vulcanisates and elementary sulphur or vulcanisation accelerators labelled with ^{35}S to study the nature of the vulcanisation bonds[102]. In the first case the exchange took place between plates of radioactive vulcanisate and elementary inactive ^{32}S, which was introduced in definite amounts by allowing the samples to swell in a saturated solution of sulphur in benzene. In the second case inactive vulcanisate was used, and allowed to exchange with the accelerator containing ^{35}S.

Fig. 18 shows a typical kinetic curve for isotope exchange between elementary sulphur and a vulcanisate from butadiene–styrene rubber. The change of activity passes through a maximum, which is clearly due to combination of the added elementary sulphur taking place on heating the mixture, simultaneously with the exchange (Fig. 18, curve *2*). Since in the last stages the elementary sulphur also becomes active, this combination lessens the apparent decrease of activity of the vulcanisate, so that for comparative evaluation of the exchangeable sulphur content, the activity at the maximum was used.

As Gur'yanova[103] has shown, the kinetics and degree of exchange in the case of low-molecular sulphur-containing compounds depend on the type of radical attached to the

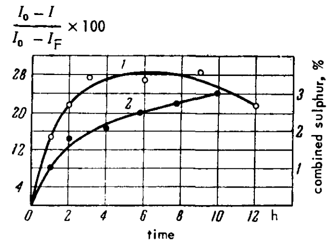


Fig. 18. 1) Kinetics of the exchange between the vulcanisate and elementary sulphur at 120°. 2) Combination of sulphur during the exchange.

sulphur atoms and on the number of sulphur atoms in the sulphide groups. Increasing the number of sulphur atoms in the sulphide group increases the rate and degree of exchange with elementary sulphur, and this has enabled the isotope exchange method to be used for determining the structure of the sulphide bonds in a vulcanisate.

The dependence of the degree of isotope exchange of vulcanisates on the number of sulphur atoms in the sulphide bonds is clearly demonstrated by comparing the rate of exchange with the rate of stress relaxation on heating the vulcanisates at 130° with strict exclusion of oxygen using Dogadkin and Tarasova's procedure[5]. It follows from the theory of high elasticity that the stress (the modulus E_∞) is a linear function of the number of chain segments between the chemical cross-linkages ($E_\infty = \gamma NKT$), so that decomposition of the molecular chains and of the chemical bonds between them leads to a decrease in the stress, which will follow a monomolecular law[104,105]. The velocity constant for the stress relaxation can be used as a measure of the stability of the chemical bonds in the vulcanisate. Fig. 19 shows the correlation between the rate of isotope exchange and the rate of stress relaxation for vulcanisates with various accelerators. The vulcanisate obtained with TMTD (but without sulphur), which due to the mechanism of the accelerator's action will contain mainly C–C and C–S–C bonds, does not exchange with sulphur and shows the lowest rate of relaxation of stress. This vulcanisate, however, exchanges with TMTD itself under the same conditions, indicating the presence in the vulcanisate of combined accelerator groups (radicals). The vulcanisate obtained with DPG and elementary sulphur shows a high rate and degree of exchange with sulphur and the greatest rate of decomposition of vulcanisation bonds under thermomechanical action, indicating that it contains the less stable polysulphide linkages $C-S_x-C$. This is also shown by the reaction of the vulcanisate with sodium sulphite.

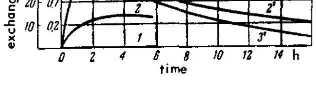


Fig. 19. Kinetics of isotope exchange (1, 2, 3) and stress relaxtion (1′, 2′, 3′) in various vulcanisates: 1) and 1′) TMTD; 2) and 2′) MBT + + S; 3 and 3′) DPG + S.

Isotope exchange and stress relaxation at 130° in an inert atmosphere are good methods for investigating the nature of vulcanisation structures. The results obtained in this way have been amply confirmed by spectroscopic studies: the ultra-violet spectra between 220 and 400 mμ demonstrate the presence of polysulphide bonds at the commencement of vulcanisation, and a decrease in the number of sulphur atoms in these as vulcanisation proceeds[51].

The nature of the bonds in sulphur vulcanisates has recently been considered by Studebaker and Nabors[19], who state that the nature of the bonds can be determined by their proposed mechanism of reaction of lithium aluminium hydride with di- and poly-sulphides:

$$R-S-S-R \xrightarrow[\text{hydrolysis}]{LiAlH_4} 2RSH$$

$$R-S-S_x-S-R \xrightarrow[\text{hydrolysis}]{LiAlH_4} 2RSH + xS^-$$

Monosulphide bonds are shown not to react. Studebaker and Nabors consider that C–C bonds are hardly formed in vulcanisates. The number of monosulphide bonds are taken as the difference between the di- and poly-sulphide bonds, and the total number of bonds determined by the swelling limit. Thiuram vulcanisates contain predominantly monosulphide bonds, and vulcanisates with DPG and sulphur, predominantly polysulphide bonds. These results are essentially in agreement with those of Dogadkin and coworkers described above.

The type and distribution of the vulcanisation linkages have a substantial influence on the fatigue behaviour of the vulcanisates. Since the primary act of destruction of vulcanisates on thermomechanical action (we are not here concerned with the very important action of oxygen) is the mechanical decomposition of the weakest bonds, it is clear that the workability of the vulcanisate, determined by the number of deformations before destruction, will depend on the energy of the bonds and the method of deformation used. With an alternating symmetrical load with bending and rotation, the workability will increase with increase of the energy of the vulcanisation bonds. Fig. 20 shows that vulcanisates with tetramethylthiuram disulphide, which contain predominantly C–C and C–S–C bonds (energy 50–60 kcal mole^{-1}), have a greater workability than vulcanisates with sulphur and diphenylguanidine, which contain more $C-S_x-C$ bonds (energy ~27 kcal mole^{-1}). Radiation vulcanisates, which contain the very stable C–C and C–O–C bonds, are even more stable towards repeated deformation.

Isotope exchange has provided important information on the mechanism of the fatigue of vulcanisates. Fig. 21 shows that fatigue of extracted vulcanisates from butadiene–styrene rubber by alternating bending at room temperature increases the isotope exchange, and decreases the number of cross-linkages between the rubber chains, since the swelling maximum increases. The cause of this interesting effect is not clear. Possibly at low temperatures there is mechanical rupture of the sulphur-containing cyclic structures of the vulcanisate, so increasing the number of exchanging groups. After fatigue at 120°, on the other hand, there is a sharp reduction of isotope exchange and

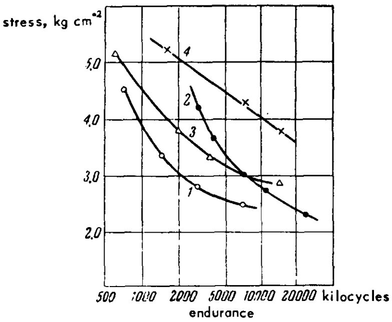


Fig. 20. Endurance of various vulcanisates to alternating symmetrical stress by bending with rotation at 120°:
1) butadiene–styrene rubber SKS–30 with DPG + sulphur; 2) SKS–30 with hexachloroethane; 3) SKS–30 with TMTD; 4) butadiene rubber SKB with DPG + sulphur.

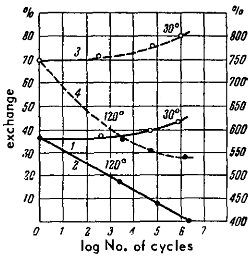
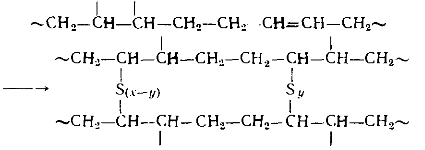


Fig. 21. Change of the degree of exchange (1, 2) and swelling limit (3, 4) during fatigue of vulcanisates at 30° and 120°.

an increase in the number of cross-linkages (the swelling maximum falls and the modulus increases). In this case, therefore, the polysulphide groups decompose to form new bonds, containing less sulphur, between the rubber molecules:



$$\begin{array}{c}\sim CH_2-CH-\overset{|}{C}H-CH_2-CH_2-CH\cdot CH-CH_2\sim\\ |\\ S_x\\ |\\ \sim CH_2-CH-\overset{|}{C}H-CH_2-CH_2\cdot\ \cdot CH{=}CH-CH_2\sim\end{array}\longrightarrow$$

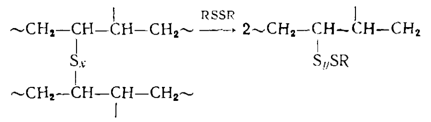
$$\longrightarrow\begin{array}{c}\sim CH_2-CH-\overset{|}{C}H-CH_2-CH_2-CH-\overset{|}{C}H-CH_2\sim\\ |\qquad\qquad\qquad\qquad |\\ S_{(x-y)}\qquad\qquad\qquad S_y\\ |\qquad\qquad\qquad\qquad |\\ \sim CH_2-CH-\underset{|}{C}H-CH_2-CH_2-CH-\underset{|}{C}H-CH_2\sim\end{array}$$

The possibility of forming polymeric radicals by mechanical stress has been demonstrated by plasticising rubber at room temperature in the presence of mercaptobenzothiazole (MBT) labelled in the thiazole ring[106].

The combination of low-molecular substances with radicals of vulcanised rubber, formed by thermomechanical action during fatigue, is observed if *p*-t-butylphenol disulphide (BPD) labelled with ^{35}S in the disulphide bridge is added to the vulcanisate. Table 2 shows that after fatigue, the rubber can combine with more than 1.5% of BPD, which is ~ 50% of the amount added. In this case the combination occurs mainly at the sites of the decomposed sulphide bonds:

TABLE 2. Combination of *p*-t-butylphenol disulphide (BPD) during fatigue of butadiene–styrene rubber vulcanisates at ϵ = 50% and frequency 250 c/min.

Composition of vulcanising group	BPD added, %	Duration of fatigue, h	Temp., °C	Combined BPD as % of rubber	Combined BPD as % of BPD added
1% DPG	3.6	1.5	20	0.35	9.7
2% Sulphur	3.5	5.0	20	1.00	28.6
	3.5	2.5	100	1.55	44.3
3% Thiuram	3.6	2.5	20	0.12	3.34
	3.25	0.5	100	0.20	5.56
	3.25	5.0	100	1.62	50.0



$$\begin{array}{c}\sim CH_2-CH-\overset{|}{C}H-CH_2\sim\\ |\\ S_x\\ |\\ \sim CH_2-CH-\underset{|}{C}H-CH_2\sim\end{array}\xrightarrow{RSSR}2\sim CH_2-\underset{\displaystyle S_ySR}{\underset{|}{C}H}-\overset{|}{C}H-CH_2$$

where R = $C_6H_3OHC(CH_3)_3S$.

The reaction of the polymeric radicals, formed by thermomechanical action causing fatigue in the vulcanisate, with substances able to combine with them, opens up a new approach to the prevention of fatigue in vulcanisates. When the thermomechanical action increases the modulus (*e.g.* in the case of vulcanisates of butadiene–styrene rubber) because of decomposition and rearrangement of the radicals with the formation of new cross-linkages, the introduction of such substances (acceptors) reduces the harmful cross-linking and increases the life of the vulcanisate; this occurs when *p*-t-butylphenol disulphide or hexachloroethane is added to a vulcanisate. However, such substances cannot increase the workability of vulcanisates whose structural changes during fatigue lead to a decrease in the number of cross-linkages (when a decrease in the modulus is observed), *e.g.* vulcanisates from natural or oil-filled butadiene–styrene rubbers.

The nature of the vulcanisation bonds does not only affect the thermomechanical processes of fatigue: Kuz'minskii and coworkers[107,108] have shown that polysulphide bonds reduce the rate of oxidation of vulcanisates. A vulcanisate extracted with acetone is oxidised less rapidly than the same vulcanisate which has been treated with Na_2SO_3 to remove polysulphide sulphur. They consider that the sulphide radicals formed by the decomposition of the polysulphide bonds react with the oxidation chains and so inhibit the oxidation. It is interesting that the stabilities of various vulcanisation structures towards thermal action and radiation (ultra-violet light) are in inverse relationship[109,110].

The influence of vulcanisation structures on the static strength is demonstrated by vulcanisates of carboxylated rubbers[111]. Vulcanisation of this type of rubber with metal oxides gives products of high static strength (up to 200 kg cm^{-2} for butadiene–styrene rubber) but low thermal stability. The velocity constant for the rate of relaxation of stress in vulcanisates with salt bonds is 50–100 times that in sulphur vulcanisates of butadiene–styrene rubbers.

The number of cross-linkages, like the molecular weight of the initial polymer, is practically the same before and after relaxation; this means that thermomechanical action on these vulcanisates causes rupture and rearrangement of the salt bonds as a result of exchange reactions.

If the thermally unstable vulcanisates obtained with calcium hydroxide are irradiated with low doses (5–10 mr) of γ-radiation, they become thermally stable (the relaxation constant at 100° is[1] $\sim 6 \times 10^{-3}$ min, *i.e.* approximately the same as for sulphur vulcanisates of butadiene–styrene rubber with sulphenamide accelerators) and at the same time show a high strength of up to 400 kg cm^{-2}.

A vulcanisate has a high static strength if it contains a dense network (1 bond to about 60 monomeric units) of weak salt bonds and a sparse network (1 bond to 1000 monomeric units) of stable C–C bonds. An increase in the concentration of carbon–carbon bonds decreases the static strength (Fig. 22).

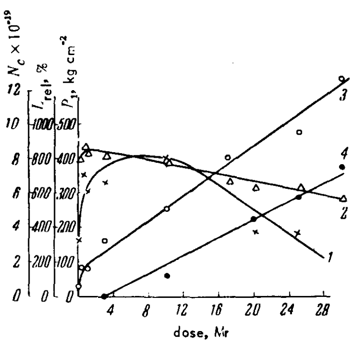


Fig. 22. Properties of a carboxyl-containing rubber (0.65% COOH) vulcanised with calcium hydroxide as a function of the γ-radiation dose: 1) tensile strength (P_1); 2) relative elongation (L_{rel}); 3) total content of cross-linkages (N_c); 4) number of cross-linkages not broken by the action of acid.

The influence of the structure of vulcanisates of carboxyl-containing rubbers on their strength is of general application, and is of undoubted interest in the formulation of the rules determining the strength of polymeric networks[112]. Polymeric networks (vulcanisates) have a high strength when in addition to a relatively sparse and uniform network of stable chemical bonds, they contain a network of less stable and easily rearranged bonds, the redistribution of which relieves the local tensions which give rise to the formation and development of centres of destruction of the polymer. This type of structure provides the conditions for the greatest development, under deformation, of orientation (crystallisation) processes, which are known to be an important factor in increasing the strength of a material.

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SPECTROSCOPIC DETERMINATION OF PEROXY COMPOUNDS DURING PHOTOCHEMICAL OXIDATION

A. V. Karyakin

CONTENTS

1. PHOTOCHEMICAL OXIDATION OF HYDROCARBONS

Many investigations of the thermal and photochemical oxidation of organic compounds indicate that the initial stages involve formation of peroxy compounds — hydroperoxides and photo-oxides — in which two oxygen atoms are linked together[1-5]. The peroxy compounds, containing the –O–O– link, then decompose exothermally forming free atoms and radicals, which are the cause of the chain character of the subsequent stages of the oxidation.

Spectroscopic investigation of the peroxy compounds requires that they should be produced in greater quantities in the reaction mixture, which can be achieved mainly in photochemical oxidation reactions which take place at fairly low temperatures. Thermal oxidation involves a considerably more rapid decomposition of the intermediate reaction products, so that their concentration in the reaction mixture is insignificant. Also, a thermal process does not allow selective supply of energy to one of the reaction components. With activation by light it is possible to raise the oxidisable molecule to an excited state without affecting the intermediate and final reaction products. The photochemical oxidation is initiated by light (principally ultra-violet), which acts either directly on the oxidisable organic molecule or on a sensitiser, the latter oxidising the organic compound under the influence of visible light quanta. The path of the sensitised reaction is naturally of the greatest interest, since reaction is then effected by a small quantum, as in photosynthesis.

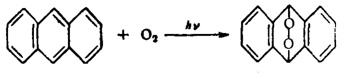
Photochemical oxidation under ultra-violet radiation has been investigated with di- and poly-olefines[6-9], alcohols[10], acetaldehyde[11,12], paraldehyde[13], propionaldehyde[12], butyraldehyde[14], benzaldehyde[15-18], acids[19], the aromatic hydrocarbons toluene[20-23], xylene[20,24], isopropylbenzene[20,25-27], and ethylbenzene[27], decalin, methylcyclohexane, 2,7-dimethyloctane, butylbenzenes and other compounds[5], dioxan[28], cyclohexene[29,30], and terpinolene (*p*-mentha-1,4(8)-diene)[31].

In all these researches the reaction kinetics and the chemical properties of those intermediate and final reaction products isolated were investigated, and on this basis mechanisms were suggested for the oxidation of organic compounds in which the initial stage is assumed to be radical formation by loss of hydrogen from the hydrocarbon. Hydroperoxides are then formed as a result of two bimolecular chain processes:

$$RH + h\nu \rightarrow R + H,$$
$$R + O_2 \rightarrow RO_2,$$
$$RO_2 + RH \rightarrow ROOH + R \text{ etc.}$$

Several organic compounds and dyes, however, absorb oxygen on prolonged or intense illumination of their solutions, peroxides — photo-oxides — being formed[32-50]. The formation of photo-oxides was first noted by Dufraisse and coworkers[32-45] in the case of the bright red hydrocarbon rubrene, solutions of which are rapidly decolorised with loss of fluorescence on exposure to sunlight or artificial light in the presence of oxygen. The colourless photoperoxide, which is deposited on evaporation, decomposes at 180°, giving the original hydrocarbon and oxygen. Photo-oxides of other simple cyclic compounds can be obtained in a similar way. Benzene does not form a photo-oxide, but several furan and thiophen derivatives and terpenes do so, exhibiting great reactivity at the 1,4-positions. The photo-oxides of the simplest heterocyclic compounds are unstable at room temperature, and can be isolated only at low temperatures, *e.g.* the photo-oxide of 1,3-diphenylisobenzofuran.

The most stable photo-oxides are formed by polycyclic aromatic compounds — anthracene, naphthacene, pentacene, and other compounds containing an anthracene nucleus:



Other polycyclic hydrocarbons, containing the naphthalene or phenanthrene nucleus, do not yield photo-oxides. Acridine forms no photo-oxide, but dibenzacridine does, because it contains an anthracene nucleus.

The formation of photo-oxides from polycyclic aromatic compounds is associated with the higher reactivity of the *meso* positions, to which oxygen is added as a bridge lying outside the plane of the molecule (transannular peroxides), the angle between the *meso* carbon atoms and the –O–O– bridge being 118°, which is somewhat larger than in peroxides (100°–105°). There is consequently some strain in transannular peroxides, but it is not very great since the heat of formation of photo-oxides is low.

The reactivity of the *meso* carbon atoms depends on the substituents, especially those in the *meso* position. Thus alkyl or phenyl groups, and especially methoxy groups, facilitate addition of oxygen. Cyano groups, halogens, and oxygen completely suppress it.

The nature of the solvent is of fundamental importance to the formation of photo-oxides. Thus anthracene gives photo-oxides readily in carbon disulphide and chloroform, but only slowly in benzene and hexane, in which anthracene dimers are obtained simultaneously.

All photo-oxides of aromatic compounds decompose on heating, but the amount of oxygen evolved depends on the structure of the original hydrocarbon. The photo-oxides of anthracene and naphthacene decompose explosively at about 120° without liberation of oxygen, but that of 9,10-diphenylanthracene evolves up to 98% of its combined oxygen when heated to 80°. The evolution of oxygen is accompanied by bright luminescence (chemiluminescence). Thermal decomposition of this photo-oxide, as well as that of 1,4-dimethoxyanthracene, apparently takes place by a cyclic electron transfer mechanism[51]:

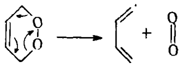


Photo-oxides are not formed in the dark. Their formation requires the action of light, which raises the hydrocarbon molecule first into an excited singlet state, which is then converted, in the presence of oxygen, into a triplet (biradical) state with subsequent addition of the paramagnetic oxygen molecule:

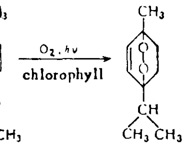
$$A + h\nu \rightarrow A^* \xrightarrow{O_2} \cdot A \cdot$$

$$\cdot A \cdot + \circ O_2 \circ \rightarrow \cdot A \cdot \circ O_2 \circ \rightarrow \cdot A{-}O_2 \circ \cdot$$

Comparatively little work has been done on sensitised oxidation of organic compounds. Photosensitised oxidation of unsaturated hydrocarbons containing the allyl group yields hydroperoxides by a different route from the direct photo-oxidation of mono-olefines.

Similarly, hydroperoxides have been obtained by the photosensitised oxidation of benzaldehyde in the presence of benzophenone, acetophenone, and other substances[52], in the oxidation of tetralin[5,53], ethyl alcohol[54,55], propyl alcohol[55,56], in the presence of benzophenone, anthraquinone and its derivatives as sensitisers, and in the oxidation of cyclohexene, *p*-phenylenediamine, and *p*-tolylenediamine in the presence of various dyes[57,58]. Chlorophyll and its analogues cause photo-oxidation of a variety of compounds — benzidine, carotene, xanthophyll, allylthiourea, amines, phenylhydrazine, pyruvic, oleic, and ascorbic acids, etc. (see the survey in ref. 59 and also refs. 60–65).

Some organic compounds with a conjugated diene structure, such as, for example, ergosterol and various sterol derivatives, form peroxides as well as hydroperoxides on photosensitised oxidation. The sensitisers used are chlorophyll, Eosin, and Methylene Blue[66-71]. This method has been used to synthesise many substances which had not been prepared in other ways. An example is the photosynthesis of ascaridole from α-terpinene (*p*-mentha-1,3-diene):



2. SPECTROSCOPIC INVESTIGATION OF PEROXY COMPOUNDS

Spectroscopic investigations of peroxy compounds have been carried out mainly in the infra-red, as they do not possess any characteristic absorption in the ultra-violet and visible regions.

Up to 1951 there were very few papers on the Raman or infra-red spectra of inorganic or organic peroxides. Frequencies of 870–880 cm^{-1} were ascribed to vibration of the $-O-O-$ link in hydrogen and deuterium peroxides[72-75], and the value 882 cm^{-1} to the peroxy group vibration in five alkyl and acyl peroxides and hydroperoxides[76,77].

These data are clearly insufficient for the detection of organic peroxy compounds in a reaction mixture. Moreover, absorption in the region of 880 cm^{-1} is not an unambiguous indication of the presence of an $-O-O-$ group, but may be caused by vibrations of other atoms, mainly the corresponding vibrations of the molecular skeleton, as the presence of vibrational bands characteristic of the $-O-O-$ group in peroxides has been regarded as improbable. Symmetrical vibrations of the $C-O-O-C$ chain do not produce a great change in the dipole moment, so that the corresponding infra-red bands will be weak. In this chain, furthermore, the masses and the force constants for the $-O-O-$ group are very similar to the values for the $C-O$ and $C-C$ groups, so that appearance of a band typical of the $-O-O-$ group is improbable. However, the definiteness of the characteristic band will depend on the angle between successive bonds in the molecular chain. If it is about 90°, transfer of vibrational energy from one bond to another will not take place, so that the characteristic bands will be clearly defined[78].

X-Ray analysis of hydrogen peroxide and dimethyl peroxide shows that the atoms of the $H-O-O-H$ and $C-O-O-C$ chains do not lie in one plane, and that the $-O-O-$ group forms an angle of 100°–105° with H or C.[72-75,79-81] The $-O-O-$ group may therefore be expected to possess a characteristic band. The presence of the light hydrogen atom at the end of the $C-O-O-H$ chain in hydroperoxides must increase the probability of development of a characteristic band. Theoretical calculation of the vibrations in a model system $X-O-O-X$ with X of different masses [from 15 (CH_3) to infinity] showed that the $X-O$ and $O-O$ vibrational frequencies vary within the comparatively narrow limits 819–985 cm^{-1} for $O-O$, 978–1082 cm^{-1} for $\nu_s(X-O)$ and 824–1044 cm^{-1} for $\nu_a(X-O)$.[81]

In order to establish exact rules governing the effect of the peroxy groups in the $C-O-O-H$ and $C-O-O-C$ chains on the infra-red spectra, the spectra of some organic hydroperoxides and peroxides, and also of related compounds, were studied[82,83]. This analytical procedure is, of course, applicable only to compounds containing many atoms, since otherwise the character of the vibrations will depend greatly on the actual number of atoms. Furthermore, assignment of an absorption band to a definite atomic vibration is to some extent arbitrary, as all the other atoms in the molecule will affect this vibration to different extents.

As an example, let us examine the infra-red absorption spectra of isopropylbenzene hydroperoxide and bisisopropylbenzene peroxide, and also, as compounds of related structure, the spectra of dimethylphenylmethanol and isopropylbenzene (see Figs. 1 and 2). Careful examination of these spectra shows that the hydroperoxide possesses

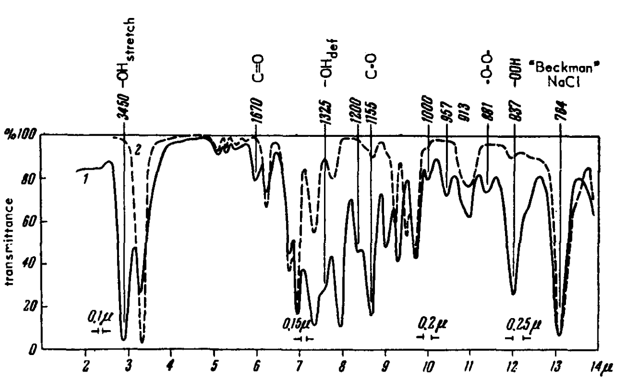


Fig. 1. Infra-red absorption spectra of:
1) isopropylbenzene hydroperoxide (liquid layer 0.02 mm);
2) isopropylbenzene (liquid layer 0.02 mm).

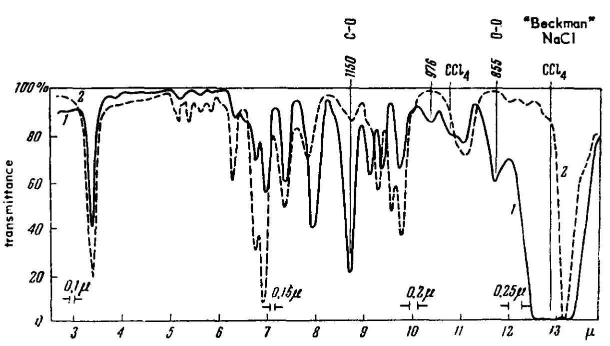
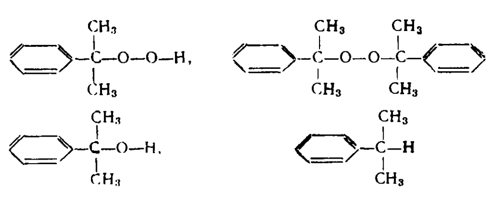


Fig. 2. Infra-red absorption spectra of a saturated solution of bisisopropylbenzene peroxide in CCl_4 and of isopropylbenzene.

an intense absorption band at about 837 cm^{-1}, which is absent in the peroxide.



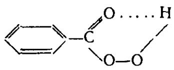
Consequently this band cannot be assigned to the O–O group, but to vibration of the C–O–O–H chain as a whole. The frequencies 855 cm^{-1} for the peroxide and 881 cm^{-1} for the hydroperoxide must be ascribed to the stretching vibration of the O–O group. The first three compounds have a common absorption band at 1150–1160 cm^{-1}, which must be assigned to the ν_{CO} stretching vibration[83]. The hydroperoxide and the alcohol contain an OH group, which has a stretching vibration ν_{OH} at 3450 cm^{-1} and a deformational vibration δ_{OH} at 1325 cm^{-1}.[84] It is difficult to interpret some of the other bands, which are apparently due to vibrations of the $C_6H_5C(CH_3)_2$ nucleus, which depend on the substituents. These conclusions were later confirmed by comparing some synthetic peroxides and hydroperoxides with substances of similar structure[82,83].

The infra-red spectra therefore show clearly several absorption bands due to vibrations of the C–O–O–H chain:

δ_{COOH}	835 cm^{-1},
ν_{O-O}	880 cm^{-1},
ν_{C-O}	1150 cm^{-1},
δ_{OOH}	1325 cm^{-1},
ν_{OH}	3450 cm^{-1}.

The peroxide chain C–O–O–C shows stretching vibration frequencies ν_{O-O} at 855 cm^{-1} and ν_{C-O} at 1150 cm^{-1}.

Benzaldehyde hydroperoxide, which is prepared from benzoyl peroxide[85], shows two new absorption bands in the infra-red spectrum, at 852 and 893 cm^{-1}, which are absent from the spectra of benzaldehyde itself and benzoic acid[86]. These frequencies belong to the C–O–O–H chain. However, the band with a maximum at 852 cm^{-1} is much weaker than with other hydroperoxides. According to experimental[82,83,87] and published data on the presence of an intramolecular hydrogen bond in the hydroperoxides of acids[79,80,88-91], it must be supposed that benzaldehyde hydroperoxide has the following structure



In the infra-red spectra of hydroperoxides, the frequencies relating to the O–O vibration and that of the C–O–O–H chain have not yet been separated. Thus, for example, for four hydroperoxides and two peroxides[91], two absorption bands (a strong one at 840 cm^{-1} and a weak one at 880 cm^{-1}) were assigned to ν_{O-O}. Very similar conclusions were reached in an investigation of the infra-red absorption spectra of tertiary peroxides and hydroperoxides[92,93] and of 32 organic peroxides and hydroperoxides[81]. Absorption at 840 cm^{-1} is due to hydroperoxides, but that at 880 cm^{-1} [81,91-93] and 890 cm^{-1} [94] is due to peroxides. With acyl peroxides 840–842 cm^{-1} is given for ν_{O-O}.[95]

More definite conclusions were reached from an investigation of the infra-red spectra of a homologous series of sixteen alkyl hydroperoxides[96]. All of them were found to give a strong absorption band in the range 810–830 cm^{-1}, while those of normal hydrocarbons containing an odd number of carbon atoms showed one band at 815 cm^{-1}, and those with an even number a double band at 825 and 805 cm^{-1}. Hydroperoxides of secondary and tertiary hydrocarbons contain only one band in the above spectral range. In addition, all the hydroperoxides have a weak band in the range 850–870 cm^{-1}, where some alcohols absorb, but in this case too the absorption due to the hydroperoxide can be distinguished. More precise conclusions confirming the group (ν_{O-O}) and chain ($\delta_{C-O-O-H}$) vibration frequencies were not reached in this work. However, an analysis of all these spectra shows that a quite distinct set of frequencies characteristic of the hydroperoxide and peroxide groupings can be found. The values for the set of vibration frequencies of the C–O–O–H and C–O–O–C chains agree well with our previous conclusions.

Thus on the basis of investigations by the present author and published data it can be accepted that these chains are quite specific in their vibrations and that the corresponding absorption bands must always be situated within a definite spectral range. The C–O–O–H group, which possesses the most characteristic vibrations owing to the presence of a hydrogen atom in the chain, has the following frequencies: 840, 870, 1150, 1325, and 3450 cm^{-1} †.

The characteristic intense band in the range 800–840 cm^{-1} is conventially denoted as $\delta_{C-O-O-H}$, since it is difficult to assign this band to any definite vibration in the chain. It is obviously of interest to examine theoretically the specificity of the above frequencies of the hydroperoxy group. To simplify the problem, we have calculated the vibration frequencies taking as a model for this group a four-atom molecule[97,98] with the structure illustrated in Fig. 3.[79,80] However, this calculation required a knowledge of the vibration frequencies for deuterated hydroperoxides. The infra-red absorption spectrum of the deuterated (70–75%) hydroperoxide of isopropylbenzene showed not only the characteristic bands of the C–O–O–H chain, which, apart from the ν_{O-O} and γ_{C-O} frequencies, were greatly diminished in intensity, but also two new absorption bands at 2550 cm^{-1} (ν_{OD}) and 995 cm^{-1} (δ_{OD}). Owing to the presence of deuterium at the end of the chain, the O–O vibration frequency was somewhat displaced, its value being 885 cm^{-1} instead of 881 cm^{-1}.

Analysis of the above sets of frequencies for the non-linear chains C–O–O–H and C–O–O–D suggests that they are incomplete and should contain six frequencies. The δ_{COO} frequency, which should be about 600 cm^{-1}, is absent. Further examination of isopropylbenzene hydroperoxide in the infra-red between 700 and 400 cm^{-1} showed that it has an intense absorption band at 585 cm^{-1}, which was assigned to δ_{COO}. The intense band at 840 cm^{-1}, which had earlier been identified with δ_{COOH}, must be assigned to oscillation of the dihedral angle κ between the COO and OOH planes.

After the mechanical problem of the vibrations of free COOH and COOD chains had been solved, the vibration frequencies were assigned as shown in Table 1, which includes also the experimental frequencies. The agreement between calculated and observed frequencies is quite good, which again confirms the specificity of the set of frequencies for the hydroperoxide chain. Furthermore, the energy of activation of reactions involving hydroperoxides of benzene derivatives is independent of the length of the radical, indicating that the electron shell of the hydroperoxide chain remains unchanged in structure; this is shown by the constancy of the vibration frequencies.

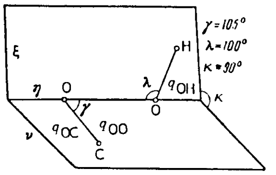


Fig. 3. Geometrical structure of the COOH chain.

TABLE 1. Calculated and observed vibration frequencies of the COOH and COOD chains (cm^{-1}).

COOH			COOD		
bonds and angles	calculated	observed	bonds and angles	calculated	observed
COO	586	585	COO	549	—
κ	834	840	κ	680	—
O — O	886	880	O — O	873	855
C — O	1156	1155	OOD	997	995
OOH	1321	1325	C — O	1156	1155
O — H	3450	3450	O — D	2539	2550

However, no calculation was made of the vibration modes or of the intensity of the absorption bands for the COOH chain, which would make it possible to obtain additional information about its structure and permit a more precise assignment of the observed absorption bands. With this aim the COOH (COOD) frequencies were calculated taking account of the vibration modes and the displacement of all the atoms during them, on the basis of which an approximate estimate of the intensities has been made[98] (see Table 2).

The calculated intensity distribution for the absorption bands in the spectrum of the COOH chain agrees well with the experimental values. This again points to the invariability of structure of the COOH chain in different compounds (constancy of its potential and electrical fields). As regards intensity, the most characteristic vibrations will be those of frequency 1322 cm^{-1} (variation of the OOH angle) and the stretching vibration of the OH bond with a frequency of 3450 cm^{-1}, since they are governed by the change in the λ and q_{OH} parameters, and the corresponding force constants will depend little on the remainder of the COOH chain. The 834 cm^{-1} vibration will be quite characteristic in intensity, giving an absorption band of high intensity due to variation in the dihedral angle κ.

The intensities of the remaining vibrations of the COOH chain will be considerably less characteristic, since they depend on the hydroperoxide radical owing to the fact that the COO angle γ will be determined to a greater extent by the nature of the radical.

The 886 cm^{-1} vibration frequency of the O–O group is characteristic of the COOH chain, since it is dependent not only on the stretching vibration of the O–O group but also

TABLE 2. Frequencies and intensities of vibrations of the COOH chain.

Assignment of bands to corresponding parameters (see Fig. 4)	Frequencies, cm^{-1}	Theoretical intensity	Relative intensity	
			calculated	observed
γ, κ	586	medium	4.3	11
κ	834	strong	9	9.5
γ, q_{OO} κ	886	weak	1.2	1.2
q_{CO} γ	1156	very strong	—	—
λ	1322	strong	9	9.5
q_{OH}	3450	very strong	—	—

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† These values are correct in the absence of an intramolecular hydrogen bond.

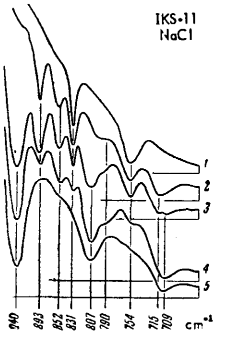

Fig. 4. Infra-red absorption spectra of films at -180°:
1) benzaldehyde; 2) product of photo-oxidation after 40 min at +15° (first fraction, sublimed after 1–2 min); 3) product of photo-oxidation after 40 min at + 15° (second fraction sublimed after 50–60 min); 4) product of photo-oxidation at -50°; 5) benzoic acid.

TABLE 3. Vibration frequencies of the COOC chain in photo-oxides of anthracene and its derivatives from infra-red absorption spectra

Photo-oxide of	Frequency, cm⁻¹	
	—O—O—	C—O (?)
Anthracene	894	1245, 1260
9-Methylanthracene	890	1230, 1246
9, 10-Dimethylanthracene	888	1246, 1258
9, 10-Diphenylanthracene	888	1260

to an equal extent on variation in the parameters γ and κ‡. It will be weak in intensity and not very specific. The intensity of the absorption band at 586 cm^{-1} must be the most sensitive to the hydroperoxide radical, which may explain the considerable discrepancy between the intensity calculated for the COOH chain and that determined experimentally for isopropylbenzene hydroperoxide.

In addition to the peroxy compounds considered above — hydroperoxides and peroxides — other peroxy compounds are known, the photo-oxides or so-called transannular peroxide of polycyclic aromatic hydrocarbons, which were considered earlier. It is supposed that in these compounds the oxygen bridge lies outside the plane of the molecule. It has also been suggested, however, that photo-oxides are hydroperoxides or hydroxy compounds[99]. In order to clarify the structure of photo-oxides and also to discover the frequencies characteristic of the COOC chain, measurements were made at -180° of the infra-red absorption spectra of sublimed films of four photo-oxides of anthracene and its derivatives, and also of the original hydrocarbons[100]. These spectra do not contain the absorption band of the OH group, and hence they are not hydroperoxides or hydroxy compounds. It can be concluded that the photo-oxides contain an oxygen bridge characterised by the COOC chain vibration frequencies given in Table 3.

The presence of an oxygen bridge in photo-oxides is known to affect the ultra-violet absorption spectrum, which is situated at shorter wavelengths than for the hydrocarbon. This is due to the breakdown of conjugation between the two benzene rings. Photo-oxides also show some differences from the hydrocarbons in their infra-red absorption spectra, the bands relating to the corresponding deformation vibrations of the C–H groups of the aromatic ring, for example, being displaced considerably towards higher frequencies in the transannular peroxides. Similarly, the absorption bands of the peroxy group ν_{O-O} and ν_{CO} have rather higher frequencies than those observed with organic peroxides. This increase in frequency must be ascribed to a change in the angle between the O–O group and the plane of the anthracene molecule (118°)[32] compared with that observed in peroxides (100°–105°)[81]. Thus the specific vibrations of the COOC chain are present also in photo-oxides.

3. USE OF INFRA-RED SPECTROSCOPY TO STUDY THE MECHANISM OF PHOTO-OXIDATION

Peroxy compounds are determined by many chemical reactions based on the fact that one oxygen atom (the available oxygen) of the peroxy group takes part in oxidising reactions[5].

The most widely used and most sensitive methods for the quantitative determination of organic hydroperoxides are the iodometric and the stannometric methods. The former is based on the liberation of iodine from acid solutions of potassium iodide by peroxy compounds. In the latter method the quantity of stannous chloride necessary to decompose the peroxide is determined. Chemical methods enable the presence of peroxy compounds in the reaction mixture to be determined with great accuracy, but the peroxides themselves are thereby destroyed.

Infra-red spectroscopy has undoubted advantages over chemical methods for the investigation of photo-oxidation, in spite of its considerably lower sensitivity, since it permits observation of changes in molecular structure during oxidation, and detection of the formation and decomposition of intermediate peroxy products directly in the reaction mixture, without disturbing the normal course of the reaction. We can take as example the photo-oxidation of benzaldehyde[86,101], a reaction which has been most studied by other methods, and also the oxidation of isopropylbenzene.

The photo-oxidation of benzaldehyde has been investigated in the overtone region and in that of the fundamental vibration frequencies; these complement one another very well. The absorption spectra of oxidised benzaldehyde in the near infra-red (as compared with the unoxidised compound) indicate that the aliphatic CH group has disappeared [the absorption bands at 7940 cm^{-1} ($3\nu_{CH\ aliph}$) and 5650 cm^{-1} ($2\nu_{CH\ aliph}$) are missing], and that an OH group has appeared [absorption band at 6920 cm^{-1} ($2\nu_{OH}$) and 6950 cm^{-1} ($2\nu_{OH...}$)]. The bands due to the CH groups of the benzene ring [6020 cm^{-1} ($2\nu_{CH}$) and 8790 cm^{-1} ($3\nu_{CH}$)] do not change. A study was then made of films of products of the photo-oxidation of benzaldehyde (oxidised both at +20° and at -50°) sublimed

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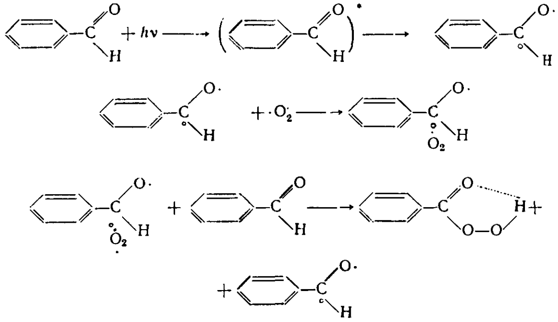
‡ With peroxides, which contain the COOC chain, vibrations of the same frequency will very probably include changes in the O–O bond length and in the COO angles.

on to an aluminised mirror cooled in liquid air. Measurements were made between 700 and 950 cm^{-1}, where there is no overlapping of the absorption bands due to the initial, intermediate, and final reaction products[86].

The photo-oxidation product of benzaldehyde shows a diminution of the bands at 754 and 831 cm^{-1} belonging to benzaldehyde, and the appearance of bands due to the hydroperoxide, κ 852 cm^{-1} and ν_{O-O} 893 cm^{-1}, as well as 715 and 790 cm^{-1} (see Fig. 4). At the same time bands arise with frequencies of 709, 807, and 940 cm^{-1}; these belong to benzoic acid, which is clearly produced in the second fraction of the photoproduct. Hence it can be concluded that the first fraction of the product photo-oxidised at +20° contains benzaldehyde and the hydroperoxide as the most volatile compounds, and that the second fraction contains also benzoic acid. In the photo-oxidation of benzaldehyde at -50° the reaction mixture contains mainly the hydroperoxide, since the absorption bands κ 582 cm^{-1} and ν_{O-O} 893 cm^{-1} are observed.

It was noted earlier that with hydroperoxides containing no intramolecular hydrogen bond the κ absorption band is always more intense than the ν_{O-O} band, whereas the opposite is true with benzaldehyde hydroperoxide, whether prepared from benzoyl peroxide or obtained by photo-oxidation. This indicates that benzaldehyde hydroperoxide contains an intramolecular hydrogen bond. It was also observed that the relative intensities of these absorption bands differ somewhat with specimens prepared by different methods. In fact, the intensity ratio is almost identical for the hydroperoxide prepared from benzoyl peroxide and for that obtained by photo-oxidation at -50°. However, the intensity ratio is considerably larger for the hydroperoxide formed at +20°, indicating a decrease in the proportion of COOH chains while the number of peroxy O–O groups is maintained. It follows that the products of the photo-oxidation of benzaldehyde at +20° contain a peroxide with the COOC chain in addition to the hydroperoxide. This peroxide is very probably a benzaldehyde hydroxyperoxide, formed by reaction between the hydroperoxide and the benzaldehyde.

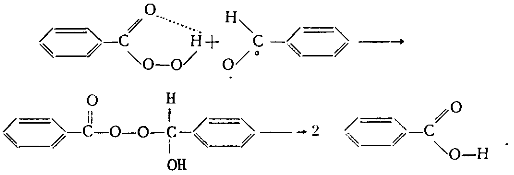
On the basis of the above experimental results and also of published data[15-18,52,102,103], the following mechanism may be suggested for the photo-oxidation of benzaldehyde. A benzaldehyde molecule, after absorbing a quantum of ultra-violet radiation, passes into a reactive (triplet-biradical) state and adds on another valency-saturated molecule, oxygen, to form an active intermediate peroxide (moloxide), which on collision with a normal (unexcited) benzaldehyde molecule is converted into the hydroperoxide with simultaneous formation of an excited benzaldehyde molecule. The resulting chain reaction has a quantum efficiency of 10 000§.[15-18]



The first stage in this scheme is confirmed by the absorption and emission (fluorescence? (Ed. of Translation)] spectra of benzaldehyde[103-105]. Benzaldehyde vapour, and also its solutions at -180°, give a discrete emission spectrum in the visible region, in which the characteristic vibration frequency of the carbonyl group, 1730 cm^{-1}, stands out; this belongs to the ground state of the molecule (1710 cm^{-1} in the infra-red spectrum). If the double bond in the C=O group were retained in the excited benzaldehyde molecule, the ultra-violet absorption spectrum of benzaldehyde vapour should, like the emission spectrum, give a frequency close to 1730 cm^{-1}. Actually, the absorption spectrum of benzaldehyde vapour shows only the frequencies 200, 950, 1200, and 1309 cm^{-1}; the first two are due to the benzene ring, and the latter represent vibration frequencies of the carbonyl group in the excited state[107,108]. Since the vibration frequencies of the CO group in alcohols, ethers, and acids usually have values[84] of 1100–1300 cm^{-1}, the excited carbonyl group of benzaldehyde, with frequencies of 1200 and 1309 cm^{-1}, can be represented as a C=O group with, as it were, one of the bonds broken. This electron transition can be treated more exactly as the transfer of one of the lone pair 2*p* electrons of the oxygen atom to an anti-bonding excited π^* orbital of the $\rangle C=O$ grouping[108-111]. In this way the vibrational structure of benzaldehyde, studied in both absorption and emission, confirms the formation of a biradical after absorption of a quantum of ultra-violet radiation.

The formation of a primary peroxide or moloxide of benzaldehyde with oxygen is proved by a study of the infra-red spectra of benzaldehyde adsorbed on sintered glass[112]. Ultra-violet irradiation in the presence of oxygen leads to increased absorption in the region corresponding to hydrogen bonds between the surface OH groups of the glass and the carbonyl; this is ascribed to formation of the moloxide, the latter possessing strong proton-accepting properties with respect to OH groups.

At room temperature the hydroperoxide reacts readily with the excited benzaldehyde molecules, which are present in excess, to form benzaldehyde hydroxyperoxide[5]; this is an unstable compound decomposing spontaneously to form two molecules of benzoic acid:



An investigation was also made of the sensitisation of the photo-oxidation of benzaldehyde with molecular oxygen, using as sensitisers derivatives of anthraquinone and acridine[100,112] whose optical properties had been studied earlier[113,114]. The changes taking place in the reaction mixture were recorded in the same regions of the infra-red spectrum. With some sensitisers — anthraquinone, 2-aminoanthraquinone, 3-aminoacridine, and 3,6-diaminoacridine — illumination of solutions of benzaldehyde, in the presence of oxygen, with visible light from the part of the spectrum where only the sensitiser absorbs, caused characteristic changes in the infra-red spectrum, indicating that oxidation of benzaldehyde was occurring. No changes in the infra-red absorption spectra were observed on illuminating either pure benzaldehyde solution or solutions containing 1-aminoanthraquinone or 1- or 2-aminoacridine.

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§ Circles and dots denote unpaired electrons with opposite spins.

The sensitising action is thus selective with respect to the anthraquinone and acridine derivatives. Comparison of the sensitisation by the above compounds with the strong quenching of their fluorescence by molecular oxygen and the occurrence in them of delayed fluorescence, indicating their possession of an adjacent triplet level, makes clear the interdependence of these phenomena.

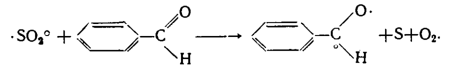
On the above basis the following mechanism may be imagined for the initial stages of the photosensitised oxidation of benzaldehyde[115]. On absorption of a light quantum the sensitiser (dye) passes into an excited state, and then into a metastable (triplet) state under the influence of a paramagnetic O_2 molecule:

$$S \xrightarrow{+h\nu} S^{*} \xrightarrow{O_2} \cdot S \cdot$$

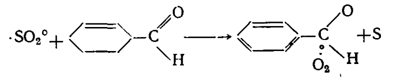
The biradical, *i.e.* the molecule in the triplet state, can add on oxygen, forming an unstable complex having the properties of a biradical:

$$\cdot S \cdot + {}^{\circ}O_2{}^{\circ} \longrightarrow \cdot S \cdot {}^{\circ}O_2{}^{\circ} \longrightarrow \cdot SO_2{}^{\circ} \cdot$$

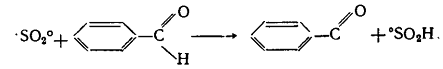
Sensitisation of the photo-oxidation of benzaldehyde is effected by this unstable complex of sensitiser and oxygen, *i.e.* the moloxide¶, which transfers the excitation energy to the oxidisable molecule or even dehydrogenates it[113 117 118] There will be a certain probability of energy transfer if the electronic level of the sensitiser is not lower than that of the oxidisable molecule. Consequently this process can take place only with anthraquinone:



The possibility of the simultaneous transfer of oxygen to the benzaldehyde is not excluded[66]:



where S represents a sensitiser molecule. In the case of derivatives of anthraquinone and acridine, however, dehydrogenation of the benzaldehyde molecule by the $\cdot SO_2{}^{\circ}$ is more probable:



This last process requires that the moloxides, and hence the sensitiser molecule, should possess proton-accepting properties, which is the case with most derivatives of anthraquinone and acridine[119,120].

Spectroscopic study of isopropylbenzene, its photo-oxidation products, and a preparation of its hydroperoxide between 4000 and 700 cm^{-1} shows that the photoproducts exhibit only the characteristic frequencies of the hydroperoxide group (see Fig. 5)[101-103]. Hence isopropylbenzene hydroperoxide is formed initially in the reaction mixture, by the following mechanism.

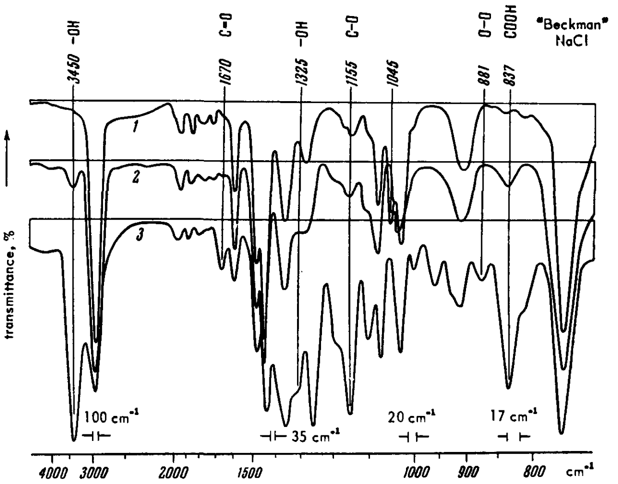
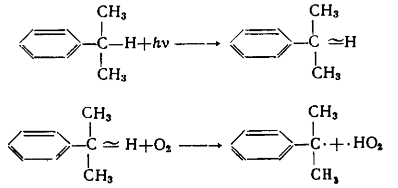


Fig. 5. Infra-red absorption spectra in relation to the photo-oxidation of isopropylbenzene:
1) isopropylbenzene; 2) oxidised isopropylbenzene;
3) isopropylbenzene hydroperoxide.

The first stage in the photo-oxidation of isopropylbenzene is a "loosening" of the C–H bond owing to the increase in vibrational energy due to the absorbed ultra-violet quantum. The direct splitting off of hydrogen atoms under the influence of ultra-violet radiation (the 313 mμ mercury line) is improbable for energetic reasons. Thus after absorption of the quantum, the isopropylbenzene molecule will possess a greater proton-donating tendency, which will aid the splitting off of hydrogen by an oxygen molecule to form radicals, which then propagate the chain oxidation:



Energetically, this reaction mechanism is quite possible. The energy of formation of the HO_2 radical from H + O_2 is equal to 47 kcal[121-124], and hence an additional energy of ~ 50 kcal is necessary for rupture of the CH bond (~ 90 kcal); this can be provided by the storage of vibrational energy in the molecule, rather more than half the energy of the 313 mμ quantum being required.

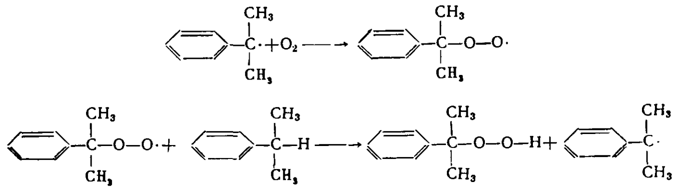


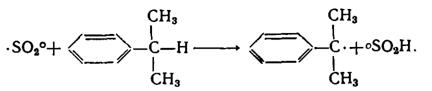
Photo-oxidation of isopropylbenzene sensitised by anthraquinone and 2-aminoanthraquinone also leads to the formation of the hydroperoxide[113]. The moloxide (biradical complex of a sensitiser molecule with oxygen)

¶ A moloxide — an unstable complex of oxygen with a molecule of a substance in the triplet state — is formed also in the quenching of the fluorescence of anthraquinone, acridine, and their derivatives by molecular oxygen[114,115]:

$$A + h\nu \longrightarrow A^{*} \xrightarrow{O_2} \cdot A \cdot$$

$$\cdot A \cdot + {}^{\circ}O_2{}^{\circ} \longrightarrow \cdot A \cdot {}^{\circ}O_2{}^{\circ} \longrightarrow \cdot AO_2{}^{\circ}.$$

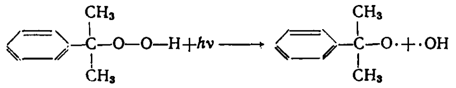
causes dehydrogenation of the hydrocarbon with formation of the corresponding radical, which propagates the chain reaction:



Isopropylbenzene hydroperoxide, being a stable intermediate in the oxidation, may, however, undergo decomposition under the influence of ultra-violet radiation (253.7 mμ) forming the end products of the photochemical reaction.

Measurements between 800 and 3000 cm^{-1} have shown that the photodecomposition products of isopropylbenzene hydroperoxide have an absorption spectrum identical with that of dimethylphenylmethanol[125] (see Fig. 6). It was therefore concluded that this is the main product of the decomposition of the hydroperoxide. The only important difference in the spectra is the appearance of a weak band at 1700 cm^{-1} in that of the photodecomposition product, obviously due to the stretching vibration of the C=O bond of the carbonyl group. The feeble intensity of this band indicates that the concentration of the compound containing the carbonyl group is low; it is apparently a subsidiary product of the photodecomposition.

The first stage in the photodecomposition of the hydroperoxide is the rupture of the weakest O–O bond[5,127,128] with the formation of two radicals:



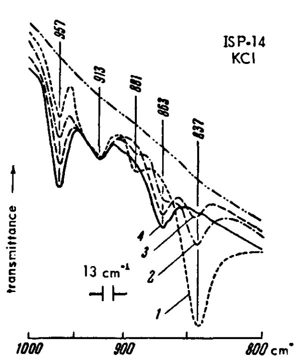
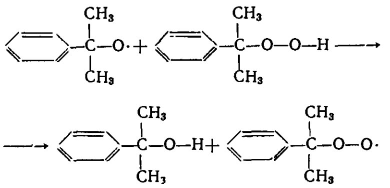
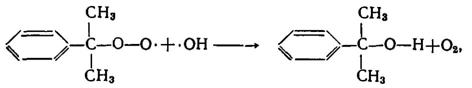


Fig. 6. Change in infra-red spectrum of isopropylbenzene hydroperoxide during photodecomposition:
1) before irradiation; 2)–4) after 3, 10, and 40 min irradiation (881 cm^{-1} relates to γ_{O-O}, 837 cm^{-1} to κ, and 863 cm^{-1} relates to the C–OH group of dimethylphenylmethanol).

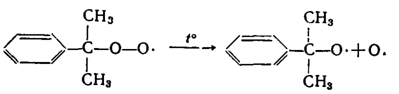
These react with hydroperoxide molecules present in excess, yielding the main product of the photodecomposition, dimethylphenylmethanol:



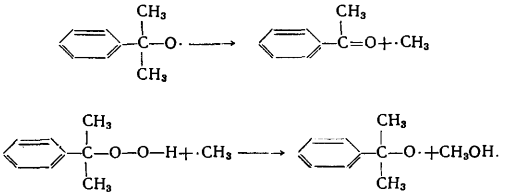
The peroxy radical either reacts with OH radicals (in the liquid phase):



or else liberates atomic oxygen (in the gas phase):



The radicals arising in the first stage can, apart from reacting with hydroperoxide molecules, yield small quantities of subsidiary products[130]:



The sensitised photodecomposition of isopropylbenzene hydroperoxide in the visible region of the spectrum also yields dimethylphenylmethanol, as is proved by the infra-red absorption spectra. However, the initial mechanism of the photodecomposition is different. For instance, the action of ferrocyanide as sensitiser involves an electronic mechanism, *i.e.* electron transfer from the iron cation to the hydroperoxide, leading to rupture of the O–O group[112]. Dye and pigment sensitisers probably dehydrogenate the hydroperoxide molecule with formation of a peroxy radical[112,131].

Thus the infra-red spectra of the reaction mixture in direct and sensitised photo-oxidation of hydrocarbons allow us to assess the changes taking place in molecular structure during the reaction and to detect intermediate peroxy compounds (hydroperoxides) from the appearance of a series of absorption bands having characteristic frequencies. With the unstable hydroperoxides we can also establish the subsequent course of the reaction leading to formation of the final stable products. This applies both to the direct and sensitised photochemical decomposition of hydroperoxides. Spectroscopic data enable the mechanism of the above reactions to be determined more exactly, especially the initial stages, in which radicals and biradicals play the main part.

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STRUCTURE AND REACTIVITY OF ORGANIC COMPOUNDS (QUANTITATIVE LAWS)

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CONTENTS

I. INTRODUCTION

Several quantitative relations have recently been discovered between the reactivities of organic compounds and their structures, and also the nature of the solvent. Analogous quantitative relations exist also between certain physical parameters and the structure or the properties of the solvent. These are not just disconnected, purely empirical relations, but form a single unified whole such that it is not unreasonable to discuss whether we are not dealing here with a basis for an extremely general quantitative theory in this field.

This recalls the idea put forward by a committee report of the Chemical Sciences Section of the Academy of Sciences of the USSR[1]: "The problem of reactivity must be posed as a problem of the *quantitative* study of chemical changes in various systems . . . . The whole of the immense accumulation of experimental results in organic chemistry relating to the problem of reactivity must be examined critically and analysed carefully from this point of view".

This task, of course, cannot be completed in a single paper. Our objective is more limited — to discuss, as far as possible systematically, what are in our opinion the most important successes achieved in developing a quantitative theory of the dependence of the reactivities of organic compounds on their structures and on the nature of the solvent.

It then proves possible to consider most of the existing data from a single point of view, because many of the quantitative relations are based on the rule of the linear relationship between changes in free energy (LFE). This rule, first employed by Brønsted[2] and by Hammett[3,4] on a comparatively restricted scale, can now be regarded as a very general empirical relationship.

The present review does not claim to cover completely all the results available, this applying in particular to section XX, written in collaboration with E. S. Rudakov. We are unable to examine the problems of a quantitative theory of the influence of the solvent on reactivity and other properties with the necessary breadth of view. We can only point out the necessity for a separate detailed review of this problem.

Qualitative aspects of the dependence of reactivity and other properties of organic compounds on their structure will not be considered separately here, but the reader can obtain useful information from the well-known monographs[5-9] and the committee report of the Chemical Sciences Section of the Academy of Sciences of the USSR[1]. We need consider here only a few problems of terminology. The term "resonance", adopted in several original papers, is replaced by "conjugation". In the present state of our knowledge it appears useful to distinguish two forms of conjugation — non-polar and polar. The former refers to what may be called (from a purely formal point of view, of course) a "homolytic" mechanism of interaction between π electrons. Non-polar conjugation takes place, for example, in butadiene, benzene, etc. Polar conjugation represents a "heterolytic" mechanism of interaction between π-electron pairs and atoms, and occurs for example in aniline, nitrobenzene, the carboxyl group, etc.

Substituents having electron-donor properties when polar conjugation occurs are said to be substituents of +C type, the corresponding electron-accepting substituents representing the -C type. The latter must contain an atom possessing either complete or partial co-ordination unsaturation. Examples are the boron atom in the $B(CH_3)_2$ group (complete co-ordination unsaturation) and atoms linked by a π bond to more electronegative atoms such as carbon in the carbonyl group, etc. (partial co-ordination unsaturation).

II. THE LINEAR FREE ENERGY (LFE) RELATIONSHIP

Let us first examine the concept of the reaction series[4,10]. This represents a single type of chemical reaction which a series of compounds X_i—Y can undergo, Y being a reactive centre which is the same for a given series (the part of the molecule which changes as a result of the given reaction), and X_i being some substituent. It is understood that the conditions under which the reaction occurs (temperature, solvent, etc.) remain the same.

If the centre, type, and conditions of the reaction are regarded as variables, a set of reaction series is obtained which in principle embraces all possible organic reactions. The substituent X_i is the variable in each of these series.

In a particular reaction series, the reagent (b_i) and the solvent (s_i) may also serve as variables. In such cases we obtain the following sets of reaction series

$$a + b_i \rightarrow \text{reaction products},$$

$$\text{starting materials} \xrightarrow{s_i} \text{reaction products}.$$

In the case of a given reaction series, a quantitative measure of reactivity is either the free energy of the reaction ΔF_i if equilibrium is being considered, or the free energy of activation $\Delta F_{\neq i}$ if reaction velocity is being considered.

From thermodynamics[11] and the theory of the activated state[12] it is known that

$$\Delta F = -2.303RT \log K$$

and

$$\Delta F_{\neq} = -2.303RT \log k - 2.303RT \log \frac{kT}{n},$$

where K is the equilibrium constant and k the rate constant.

A measure of change in free energy which is convenient from a chemical point of view is thus the logarithm of the equilibrium constant or the rate constant $\log k$.

The LFE is satisfied if a linear relation exists between values of $\log k_i$ for the various reaction series in any of the above three sets:

$$(\log k_i)_m = \alpha + \beta(\log k_i)_n, \qquad (2.1)$$

where m and n denote the reaction series, and α and β are constants.

If k_0 represents the equilibrium or rate constant for some reaction of a given series chosen as standard (standard x_0, a_0, or s_0), the following general expression is obtained for LFE:

$$(\log k_i/k_0)_m = \text{const.}(\log k_i/k_0)_n. \qquad (2.2)$$

The quantity $\log k_i/k_0$ is a measure of the change in free energy of the reaction or of activation on passing from the standard to the i-th reaction in a given reaction series.

An example of the application of the LFE rule in the form (2.1) is Brønsted's law of catalysis, which can be written as follows:

$$\log k = \text{const.} + \beta \log K,$$

where k is the catalytic rate constant for some acid (or base) in a reaction subject to general acid (or base) catalysis, and K is the acid (or basic) dissociation constant of the given acid (or base).

The LFE rule in the form (2.2) was used extensively by Hammett[3,4] to correlate the reactivities of *meta* and *para* derivatives of benzene. Assuming that the constant $\rho \equiv 1$ for the reaction series (dissociation of substituted benzoic acids in water at 25°) selected as the standard of comparison, he gave the relation (2.2) in the following form:

$$\log k_i/k_0 = \rho\sigma_i, \qquad (2.3)$$

where $\sigma_i \equiv \log k_i/k_0$, and k_i and k_0 are the dissociation constants of the substituted and the unsubstituted benzoic acids respectively.

The relation (2.3) is known as Hammett's equation. Its field of application is quite restricted (*meta*- and *para*-substituted derivatives of benzene). As will be shown below, the LFE rule in the form (2.1) or (2.2) is only a particular case of a more general law.

III. EFFECT OF STRUCTURAL FACTORS ON REACTIVITY. FUNDAMENTAL PRINCIPLES

The general problem of the dependence of reactivity on structure was discussed by Hammett[4]. The principles which he introduced have been further developed and received further practical application mainly in the work of Taft[10] and others. These principles are as follows.

Since the magnitude of the equilibrium or rate constant is determined by the *change* in free energy during a reaction or an activation, not all the factors influencing the free energies of the starting materials and of the final reaction products or activated complexes will influence the reactivity as well. Such an effect is observed only if the changes produced in the free energies of the starting materials are not equal to those for the final reaction products or the activated complex. If this is not the case, these changes will cancel out, and will have no effect on the magnitude of ΔF or $\Delta F_{\neq}$.

If, following the theory of the activated state, activated complexes are regarded as analogous to ordinary molecules, calculation of the effect of structural factors on reaction velocity should not differ in principle from the corresponding calculation in the case of equilibrium.

Another important fact is that changes in ΔF or $\Delta F_{\neq}$ produced by different structural factors are mutually independent, and the total change in free energy can be regarded as produced by simple addition of the individual changes[10]. The independence and the additivity of these quantities result from the fact that the changes produced in the magnitude of ΔF by the different structural factors may be treated as small perturbations in the free energies of the reactants and of the final reaction products or activated complexes[10].

Consequently the total change in the free energy of reaction or activation may be expanded into a series of terms representing the different structural factors which affect the reactivity:

$$\log k/k_0 = P + H + G + \psi + S, \qquad (3.1)$$

where k and k_0 are equilibrium or rate constants for the given and the standard compound respectively, and $P = -\Delta\Delta F_p/2.303RT$, etc.; the structural factors are denoted by P = inductive effect, H = hyperconjugation, G = polar conjugation, ψ = non-polar conjugation, and S = steric effects.

Eqn. (3.1) contains no terms corresponding to anchimeric assistance, the field effect, or the effect of an intramolecular hydrogen bond, since few examples are yet available of a quantitative calculation of the influence of these factors on reactivity.

Comparison of (3.1) with (2.2) suggests that the LFE principle really applies, not to the quantity $\log k_i/k_0$, but to the individual terms on the right-hand side of (3.1), *e.g.* to P. If this is so, the successful application of LFE in the form of relations of the type (2.1) or (2.2) indicates that all the remaining terms on the right-hand side of (3.1) are small, with the exception of one or two, which are linked together if only by a very roughly linear relationship. It follows from this that the range of application of the LFE principle may be wider than the limits of application of relations of the type (2.1) and (2.2).

IV. INDUCTIVE CONSTANTS OF SUBSTITUENTS

Several attempts have been made at a quantitative assessment of the influence of the inductive effect of substituents on the reactivity of organic compounds[13-16]. Up to the present the appropriate σ^* constants, introduced by Taft[17], for the various substituents have had the greatest practical application.

On the basis of Ingold's conclusion[18] that conjugation and the steric factor for a substituent X_i in esters (X_i–COOR) have the same effect on the rates of both alkaline and acid hydrolysis, Taft[17] made a quantitative determination of the inductive effect:

$$P_i = (\log k_i/k_0)_B - (\log k_i/k_0)_A, \qquad (4.1)$$

where the subscripts B and A denote alkaline and acid hydrolysis respectively.

Values of P were employed by Taft to construct a quantitative scale of so-called aliphatic polar constants σ^* for different substituents. Values of σ^* are obtained by dividing P by 2.48,[10] the factor 2.48^{-1} being introduced in order to bring the scale of σ^* into line with that of the Hammett constant σ. The methyl group was selected as standard substituent, so that $\sigma^*_{CH_3} \equiv 0$.

Since electronegative substituents accelerate the alkaline hydrolysis of esters, the more electronegative substituents are characterised by more positive values of σ^*, and conversely. As the choice of standard substituents is arbitrary, the numerical values of σ^* and even their sign depend on the standard selected. However, the difference between the values of σ^* for any given pair of substituents is independent of the choice of standard for comparison.

Two simple laws — those of additivity and of the damping of the inductive effect — hold for the dependence of σ^* on the structure of the substituent[10]. The additivity rule can be written as follows:

$$\sigma^*_{(X_1X_2X_3C)} = \sigma^*_{(X_1CH_2)} + \sigma^*_{(X_2CH_2)} + \sigma^*_{(X_2CH_2)} \qquad (4.2)$$

In most cases the additivity rule is obeyed very exactly, but if X_1, X_2, and X_3 are strongly electronegative substituents, such as chloro or fluoro, departures from additivity occur, especially on introduction of a third substituent.

According to the law of the damping of the inductive effect, introduction of carbon (the CH_2 group) between a substituent X and the reactive centre diminishes the influence of the inductive effect of the former on the latter by a factor of 2.8 if X is an electronegative substituent:

$$\sigma^*_{(XCH_2)} = (1/2.78)\sigma^*_{(X)} \pm 0.005. \qquad (4.3)$$

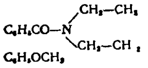
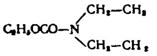
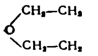
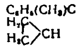
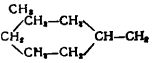
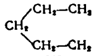
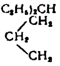
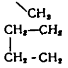
However, if X is hydrogen or a saturated hydrocarbon radical, then

$$\sigma^*_{(XCH_2)} = -0.100 + (1/4.90)\sigma^*_{(X)} \pm 0.01. \qquad (4.4)$$

The factor 2.8 in Eqn. (4.3) is not quite universal. For example, McGowan[15] points out that insertion of a CH_2 group between a substituent and the reactive centre decreases the influence of the inductive effect on the change in free energy to only half.

The inductive constants of substituents are complicated quantities giving a measure of the combined effect of the following factors — the electronegativity of the first atom of the substituent X, the hybridisation of the valency orbitals of this atom, the polar conjugation or polarisation of the π bonds within the substituent X, the field effect in the direction of the σ bonds joining the substituent with the reactive centre (especially if one of the atoms of the substituent other than the first carries a unit charge), the electron density on the first atom (especially if this atom possesses a complete unit charge), and the electronegativity of atoms which are more remote from the reactive centre[10,19]. It

TABLE 1. Taft's polar (inductive) constants σ *.

Substituent	σ*	Ref.
$(CH_3)_3N^+$	+5.3	*
NO_2	+3.9	*
CH_3SO_2	+3.7	*
CN	+3.6	*
F	+3.1	*
Cl	+2.9	*
COOH	+2.9	*
Br	+2.8	*
CCl_3	+2.65	10
CF_3	+2.6	*
C_4H_3O	+2.38	10
I	+2.36	*
F_2CH	+2.05	10
CH_3OCO	+2.00	10
Cl_2CH	+1.940	10
$(CH_3)_3NCH_2^+$	+1.90	10
$O_2N-CH=CH$	+1.704	10
CH_3CO	+1.65	10
HO	+1.55	*
CH_3O	+1.45	*
$C_6H_5-C\equiv C$	+1.35	10
$R-C\equiv C$	+1.30	20
$CH_3SO_2CH_2$	+1.32	10
$NCCH_2$	+1.300	10
$Cl_3C-CH=CH$	+1.188	10
FCH_2	+1.10	10
$HOOCCH_2$	+1.05	*
$ClCH_2$	+1.05	10
$HOOC-CH=CH$	+1.012	21
$BrCH_2$	+1.000	10
CF_3CH_2	+0.92	10
$Cl-CH=CH_2$	+0.900	21
$Cl_2CH-CH=CH_2$	+0.882	21
 $C_6H_5CO-N\begin{matrix}CH_2-CH_3\\CH_2-CH_3\end{matrix}$	+0.86	22
$C_6H_5OCH_2$	+0.850	10
ICH_2	+0.85	10
$N\equiv C-(CH_2)_2$	+0.80	24
$C_6H_5(OH)CH$	+0.765	10
$CH_2=CH$**	+0.653	21
 $C_6H_5OCO-N\begin{matrix}CH_2-CH_3\\CH_2-CH_3\end{matrix}$	+0.70	22
 $O\begin{matrix}CH_2-CH_3\\CH_2-CH_3\end{matrix}$	+0.67	22
$CH_3-CO-CH_2$	+0.60	10
C_6H_5	+0.600	10
$HOCH_2$	+0.555	10
CH_3OCH_2	+0.520	10
$O_2N(CH_2)_2$	+0.50	10
H	+0.490	10
$C_6H_5CH=CH$	+0.410	10
$(C_6H_5)_2CH$	+0.405	10
$Cl(CH_2)_3$	+0.385	10
$CH_3CH=CH$	+0.360	10
$CF_3(CH_2)_2$	+0.32	10
$NC(CH_2)_3$	+0.30	24
$C_6H_5CH_2$	+0.215	10
$CH_3CH=CH-CH_2$	+0.13	10
$CF_3(CH_2)_3$	+0.12	10
$C_6H_5(CH_3)CH$	+0.11	10
 $\begin{matrix}H_2C\\H_2C\end{matrix}CH$	+0.11	25
$C_6H_5(CH_2)_2$	+0.080	10
$NC(CH_2)_4$	+0.06	24
$C_6H_5(C_2H_5)CH$	+0.04	10
$C_6H_5(CH_2)_3$	+0.02	10
CH_3	+0.000	10
 $CH_2\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}CH-CH_2$	−0.06	10
$CN(CH_3)_3$	−0,06	24
C_2H_5	−0.100	10
$n-C_3H_7$	−0.115	10
$n-C_4H_9$	−0.125	10
$n-C_4H_9$	−0.130	10
Cyclohexyl	−0.15	10
$(CH_3)_3C-CH_2$	−0.165	10
 $CH_2\begin{matrix}CH_2-CH_3\\CH_2-CH_3\end{matrix}$	−0.18	22
$(CH_3)_2CH$	−0.190	10
Cyclopentyl	−0.200	10
$C_2H_5(CH_3)CH$	−0.210	10
$(C_2H_5)_2CH$	−0.225	10
 $CH_2\begin{matrix}CH_3\\CH_3\end{matrix}$	−0.24	22
 $\begin{matrix}CH_2-CH_2\\ \vert \\CH_2-CH_2\end{matrix}$	−0.26	22
$(CH_3)_3SiCH_2$	−0.26	10
$(CH_3)_3C-(CH_3)CH$	−0.28	10
$(CH_3)_3C$	−0.300	10

* Calculated from the formula: $\sigma^*_{(X)} = 2.8\sigma^*_{XCH_2}$.

** The value +0.653 for the substituent CH_2:CH is evidently rather too high. If σ* is calculated for this substituent by combining the rules of damping and additivity of the inductive effect, a value of +0.40 is obtained.

is the combined effect of these factors which in the classical electronic theory has been termed the inductive effect of the substituent.

Values of σ* for different substituents are given in Table 1, from which it can be seen that the sequence of the substituents according to decreasing values of σ* is the same as that indicated by qualitative ideas about the inductive effect[6,7,9].

V. GENERAL APPLICABILITY OF INDUCTIVE CONSTANTS OF SUBSTITUENTS

At the end of section III it was noted that the simplest form of LFE, as represented by the Hammett equation, is to be expected when all terms on the right-hand side of Eqn. (3.1), other than the first, can be neglected. When only the inductive effect is responsible for the change in reactivity, the following relation[26] holds:

$$\log k/k_0 = \rho^*\sigma^*, \qquad (5.1)$$

or, if the reactive centre is linked with several substituents,

$$\log k/k_0 = \rho^*\Sigma\sigma^*, \qquad (5.2)$$

where k and k_0 are rate or equilibrium constants for compounds X−Y and X_0−Y respectively, σ* is the inductive constant of the substituent X, and ρ* is a constant representing sensitivity to the inductive effect in the given reaction series. The summation in Eqn. (5.2) covers values of σ* for all substituents combined with the reactive centre.

The expression (5.1) can be termed "Taft's special equation", since it takes account only of the inductive effect. With reaction series in which the terms other than P on the right-hand side of Eqn. (3.1) are not small, Taft's special equation is written in the form[26]

$$P = \rho^*\sigma^*. \qquad (5.3)$$

Taft and his collaborators[26-32], as well as several other workers[16,20-22,33-39] have shown that Eqns. (5.1)−(5.3) are applicable to a great variety of reaction series. Positive values of ρ* are characteristic of reactions facilitated by electronegative substituents. Negative values of ρ* are found when electronegative substituents tend to inhibit the reaction.

It must be stressed that the same values of σ* characterise the effects of substituents on the reactivities of organic compounds in a very great variety of chemical processes, and also give a quantitative measure of their effect on several physical constants of organic compounds. Among these are the infra-red absorption frequencies corresponding to the stretching vibrations of several groups[10,25,26,39,40], the infra-red absorption coefficients of aliphatic alcohols[41], and dipole moments[10,26].

From the above facts Taft concludes that the σ* values are universal parameters characteristic of the corresponding substituents alone, and are independent of the structure of the rest of the molecule or of the chemical or physical properties under consideration. The laws of the dependence of σ* on the structure of the substituent indicate that we are dealing with a quantitative expression of the phenomenon which has been termed the inductive effect[10,26]. The general applicability of relation (5.3), and especially the validity of Eqns. (5.1) and (5.2), make it possible to determine values of σ* from a great variety of reaction series. In principle, the actual origin of the σ* determinations is immaterial and does not affect their magnitude. The values of σ* for various substituents given in Table 1 were obtained from various reaction series. In the case of substituents whose σ* values can be calculated from several reaction series, mean values are quoted.

The extremely important problem of the application of Taft's equation to reactions involving heterogeneous catalysis has not yet been discussed in the literature. If data for the dehydrogenation of the alcohols X_1X_2CHOH are treated[42] in the appropriate manner, ρ*Σσ* correlation is maintained satisfactorily only for five out of eight alcohols. The observed deviations cannot be ascribed to the steric effect.

It can now be regarded as established that the quantities σ^* are only roughly of general applicability. Apparently this is true especially of compounds in which the reactive centre is separated from the substituent by an atom not of carbon but of some other element, silicon for example[16].

VI. STERIC CONSTANTS OF SUBSTITUENTS FROM KINETIC DATA ON THE ACID HYDROLYSIS OF ESTERS

It was pointed out in section IV that, in the acid hydrolysis of esters, $P \simeq 0$ or, what is equivalent, $\rho^* \simeq 0$. Consequently, the quantity $(\log k/k_0)_A$ depends on the steric factor and on conjugation. In the case of esters of α,β-unsaturated carboxylic acids, non-polar conjugation also is absent, and the reactivity will then depend only on the steric factor and on hyperconjugation. Neglecting the latter too, Taft[17,10] utilised data on the kinetics of the acid hydrolysis of esters in order to construct a quantitative scale of steric constants of substituents, on the assumption that

$$(\log k/k_0)_A \equiv S \equiv E_S. \qquad (6.1)$$

The methyl group was chosen as standard substituent, so that $E_{S(CH_3)} \equiv 0$. Since activation of an ester involves the conversion of the carbon of the carbonyl group from the second to the first valency state, it is accompanied by a "contraction" of the substituents. As a result of this, bulky radicals retard the reaction, and values of E_S are negative for all substituents larger than the methyl group.

The laws governing the dependence of E_S on the structure of the substituents have nothing in common with those operating in the case of the inductive constants of the substituents. At the same time, the character of these laws confirms the steric nature of the E_S values.

It is interesting that substituents have a rather greater effect on E_S when introduced into the β than into the α position. Substitution in the γ position has practically no effect on E_S. It must also be stressed that the additivity rule, valid in the case of the inductive constants σ^*, cannot be applied to the steric constants of substituents. Introduction of a second and a third substituent into the α or β position has a far greater effect on the magnitude of E_S than has introduction of the first substituent[10].

Taft and his coworkers[10,17,31,32] have shown that the quantities E_S are not only characteristic of the corresponding substituents in the acid hydrolysis of esters. In the case of some other reaction series, for which $\rho^* \simeq 0$, the following relation is observed:

$$\log k/k_0 = \delta E_S, \qquad (6.2)$$

where δ is a constant representing sensitivity to the steric effect of the substituent in the given reaction series.

In some cases in which the inductive effect cannot be ignored, the following relation holds[17,32]:

$$\log k/k_0 = \rho^*\sigma^* + \delta E_S. \qquad (6.3)$$

Eqns. (6.2) and (6.3) are essentially examples of the application of the LFE rule to the steric term on the right-hand side of (3.1):

$$S = \delta E_S. \qquad (6.4)$$

The question of the generality and limits of applicability of Eqn. (6.4) cannot yet be regarded as solved, because of the inadequacy of the experimental data available. A relation of type (6.2) does not hold for the acid hydrolysis of thiolacetates $CH_3-CO.S-X$.[10] In some cases the inapplicability of Eqn. (6.4) may be due to additional steric effects, such as steric hindrance to conjugation, as in the alkaline hydrolysis of anilides[43].

Steric effects in the hydrolysis of ketals are discussed by Glasstone *et al.*[12]

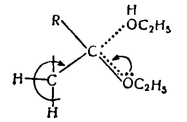
Although few quantitative data are yet available on the steric effects of substituents on reactivity, some important conclusions can nevertheless be drawn. On the one hand, it can be accepted as proved that the LFE rule is applicable to the steric term of (3.1) if the reaction series under consideration are analogous with respect to the steric changes occurring about the reactive centre during the reaction or activation. On the other hand, there is apparently no universal scale of steric constants of substituents analogous to that of the σ^* values. It is possible that calculation of the steric effects of substituents in different types of reaction series may require the use of a definite set of steric constants for each substituent.

The influence of steric factors on reactivity may be regarded as the net effect of two factors — steric strain and steric hindrance to movement[10,44].

Another approach to a quantitative treatment of the steric effect is given by De la Mare *et al.*[45] The values of E_S are shown to include, besides the steric effect, the so-called "ponderal" effect (effect of a change in mass of the substituent on the vibration frequencies and the partition function).

VII. QUANTITATIVE CALCULATION OF THE HYPERCONJUGATION EFFECT

Kreevoy and Taft[28] have shown that change in the hyperconjugation of the substituents with the reactive centre during activation or reaction in the acid hydrolysis of acetals and ketals leads to considerable departures from a relation of type (5.1) or (5.2). In an actual case of this reaction, hyperconjugation is absent in the original acetals and ketals, but arises in the activated state owing to the appearance of a carbon atom showing partial co-ordination unsaturation in the carbonyl group which is formed†:



The hyperconjugation component in (3.1) was shown[28] to be the sum of quantities representing the hyperconjugation of the individual C–H bonds with the reactive centre:

$$H = (\Delta n)h, \qquad (7.1)$$

where h is a parameter characteristic of the given reaction series and $\Delta n = n - n_0$, n being the number of C–H bonds involved in hyperconjugation in the given substituents, and n_0 the corresponding quantity for the standard substituents. The methyl group, for which $n = 3$, was chosen as standard.

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† The mechanism of the acid hydrolysis of acetals and ketals is discussed by Kreevoy and Taft[46].

The rates of acid hydrolysis of acetals and ketals are correlated by the equation[28]:

$$\log k/k_0 = \rho^*\Sigma\sigma^* + (\Delta n)h. \qquad (7.2)$$

The relation (7.1) describes quantitatively the effect of hyperconjugation on reactivity for several other series of reactions as well — the hydrogenation of aldehydes and ketones[26], the hydrogenation of *trans*-substituted ethylenes[26], etc.

Developing these ideas further, Taft and Lewis[47] concluded that more accurate results can be obtained by also taking into account the part played by C–C bonds (α-carbon atoms) in hyperconjugation. The hyperconjugation term can then be represented by

$$H = n_H h_H + n_C h_C, \qquad (7.3)$$

where n_H and n_C are the numbers of C–H and C–C bonds respectively, taking part in the hyperconjugation. In this case hydrogen was chosen as standard substituent ($n_H = n = 0$). The ratio h_H/h_C is 1.3 ± 0.1 for *p*-alkyl substituents in benzene derivatives, and ~ 2.5 in aliphatic compounds, independently of the reaction series.

An attempt has been made[48,49] to calculate h_H and h_C by the method of molecular orbitals, hyperconjugation being regarded, by analogy with anchimeric assistance (see section XV), as the result of the "overlapping" of an *s* orbital of hydrogen by a π orbital of the second carbon atom in $H-C^1-C^2$, *i.e.* as resulting from the presence of an "α-hydrogen" bond. Semi-quantitative agreement with the experimental data was obtained.

Consideration of hyperconjugation from this point of view leads to the conclusion that this phenomenon (the Baker–Nathan effect) is not to be classed with those combined under the term conjugation.

The problem of steric hindrance to hyperconjugation is considered by Jaffe and Roberts[50].

VIII. QUANTITATIVE CALCULATION OF CONJUGATION BETWEEN π BONDS

If compounds containing α,β-unsaturated substituents are included in reaction series in which a correlation of the type (7.2) is applicable, Eqn. (3.1) becomes[30]

$$\Delta\Delta F \text{ (or } \Delta\Delta H) = \rho^*\Sigma\sigma^* + (\Delta n)h + \Delta\Delta E_\psi. \qquad (8.1)$$

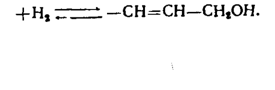
Hence the energy of conjugation $\Delta\Delta E_\psi$ can be calculated by means of the formula:

$$\Delta\Delta E_\psi = \Delta\Delta F \text{ (or } \Delta\Delta H) - \rho^*\Sigma\sigma^* - (\Delta n)h. \qquad (8.2)$$

If the experimental data relate to reaction velocities (*e.g.* in the acid hydrolysis of acetals and ketals), the free energy of conjugation is calculated from the equation[30]:

$$\Delta\Delta F_\psi = -2.303RT[\log k/k_0 - \rho^*\Sigma\sigma^* - (\Delta n)h]. \qquad (8.3)$$

Kreevoy and Taft[30] calculated values of $\Delta\Delta E_\psi$ for a series of *trans*-substituted ethylenes and unsaturated aldehydes starting from the heats and the free energies of equilibrium respectively. Both these reaction series are distinguished by the absence from the final reaction product of the conjugation present in the initial molecule:



$$\text{(H)(X}_1\text{)C=C(H)–CH=CH–} + H_2 \longrightarrow X–CH_2–CH_2–CH=CH–CH=CH–CH=O$$
$$+H_2 \rightleftharpoons –CH=CH–CH_2OH.$$

Kreevoy and Taft[30] also give values of $\Delta\Delta F_\psi$ for the acid hydrolysis of acetals and ketals. Kreevoy[20] calculated values of $\Delta\Delta F_\psi$ for conjugated substituted acetylenes from the heats of hydrogenation of these compounds.

In all these cases[20,30] the energy of conjugation of the π bond (forming part of a double or a triple bond) with some system of π bonds (in the simplest case with a double bond) remains constant in a given reaction series, within the limits of accidental fluctuations, which seldom exceed ±1 kcal. Furthermore, the conjugation of two $>C=C<$ bonds is energetically equivalent to that between $>C=C<$ and $>C=O$ bonds. Only non-polar conjugation is present in the former case, but in the latter polar conjugation is present also, since the carbonyl group is a -C type of substituent. From the equality of the energies of conjugation in the two cases it follows that the polar conjugation component is small compared with the energy of non-polar conjugation. It can therefore be stated that the quantities considered in this section relate to non-polar conjugation.

The conjugation energy is additive in the sense that the value of $\Delta\Delta E_\psi$ is approximately twice as great for compounds in which a given double or triple bond is conjugated with two systems of π bonds as for singly conjugated systems.

Taft and Kreevoy emphasise[30] that the so-called "experimental resonance energies" quoted by Wheland[51] were obtained without allowing for the inductive effect. Neglect of this factor leads to such large errors that the data obtained in this way are of no practical value.

The good agreement with experimental data of the conjugation energies calculated by the molecular-orbital method must be specially emphasised[30].

The changes in the energy of conjugation of the carboxyl group with the benzene nucleus during formation of the activated complex in the catalytic decomposition of diphenyldiazomethane by benzoic acid[52] and in the dissociation of benzoic acid[26] are ~ 0.5 kcal. In both cases the change in conjugation energy is associated with the conversion of carboxyl into a carboxylate anion. In this process the valency state of the carbonyl carbon remains unchanged, and the non-polar conjugation is obviously maintained. However, the capacity of the carboxyl group for polar conjugation must be greatly diminished by the appearance of a negative charge on the group. Thus there are grounds for ascribing the above 0.5 kcal to a decrease in (or the disappearance of) the polar conjugation of the carbonyl group with the benzene nucleus. This supports the above conclusion that the energy of non-polar conjugation of a polar double bond of the type $>C=O$ with a π-electron system is considerably greater than the energy of the corresponding polar conjugation.

The general conclusion is that the energy of non-polar conjugation of a double bond with a system of π bonds varies between 5 and 7 kcal. A value of 6 kcal can be used for rough calculations.

The value of the parameter h for the hydrolysis of esters was estimated from the empirical rule that the energy of hyperconjugation is about one-tenth of the energy of conjugation[30]. The resulting value of h = 0.5 kcal mole^{-1} indicates that the steric constants of substituents contain an appreciable hyperconjugation term of $0.35\Delta n$. In the case of hydrogen, for example, $E_S = +1.24$, $\Delta n = -3$, and

$0.35\Delta n = +1.05$. Consequently, the so-called "steric" constant of hydrogen is mainly of the nature of hyperconjugation.

IX. POLAR EFFECTS OF NUCLEAR SUBSTITUENTS ON THE REACTIVITY OF AROMATIC COMPOUNDS. HAMMETT'S EQUATION

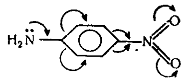
A detailed review of existing data on the use, accuracy, and limits of applicability of Hammett's equation was published by Jaffe[53] in 1953. This paper contained valuable standard data in the shape of values of ρ and of $\log K_0$ for 218 reaction series. In the present section only a few of the main points discussed by this author will be considered, since many ideas in this field have been considerably improved in the ensuing period of rapid development of the underlying theory.

As stated above, Hammett's equation served as a model for many other attempts at applying LFE to organic reactions. This was because this equation, like Eqn. (5.1), is the most simple form in which LFE is satisfied, when there is no need to expand $\Delta\Delta F$ into its components. This is also omitted with Taft's special equation, since this equation applies only to reaction series in which all factors other than the inductive effect can be neglected. Such is not the case with Hammett's equation, however. Right from the start it was clear that the effect of polar conjugation cannot be neglected in this case, at least with *para*-substituted benzene derivatives. Thus Hammett's equation describes the combined effect of two factors — the inductive effect and polar conjugation[41]. The analysis of problems associated with the application of Hammett's equation is therefore more complicated.

As already noted in section II, Hammett's equation is

$$\log k/k_0 = \rho\sigma. \qquad (9.1)$$

Originally only one set of constants σ, based on the dissociation constants of the substituted benzoic acids, was used for the substituents (standard reaction series, $\rho = 1$). Values of the σ constants were determined for many different substituents and were used to calculate values of ρ for a large number of reaction series[4,53]. In some cases Eqn. (9.1) fitted the experimental data with great accuracy (Fig. 1), but there were also examples of departures from the equation (Fig. 2), which were sometimes considerable (Fig. 3). Thus values of σ for such substituents as NO_2, COOH, CHO, CN, $COCH_3$, etc., determined from the dissociation constants of the benzoic acids, cannot be used to study the acid dissociation of *meta*- and *para*-substituted phenols or the basic dissociation constants of *meta*- and *para*-substituted anilines[4,54-56]. Since all these substituents possess considerable negative polar conjugation effects, the above phenomenon was explained in terms of direct conjugation between a -C type of substituent and a +C type of reactive centre[4].



New, so-called "dualistic" values σ^- of the constants for *para*-substituents of -C type were introduced for reaction series in which this type of conjugation is present‡.

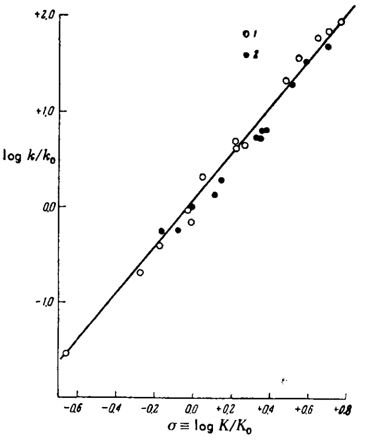


Fig. 1. Linear dependence of values of $\log k/k_0$ for the alkaline hydrolysis of *meta*- and *para*-substituted ethyl benzoates in 60% aqueous acetone at 25° on Hammett σ values determined from the dissociation constants of the benzoic acids: 1) *meta*-substituents; 2) *para*-substituents.

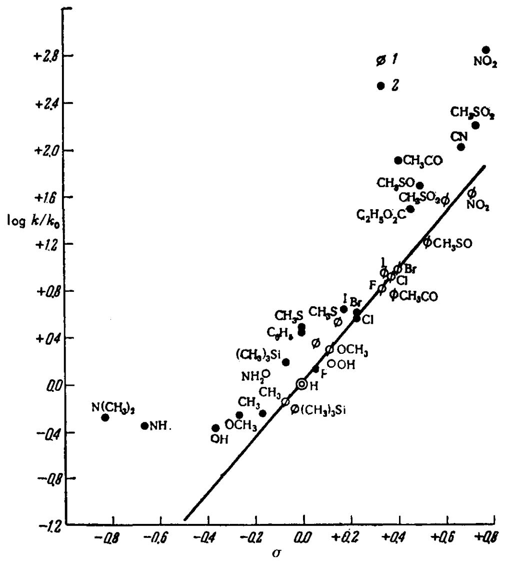


Fig. 2. Departures from Hammett's equation for the acid dissociation of *meta*- and *para*-substituted phenols at 25°: 1) *meta*-substituents; 2) *para*-substituents.

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‡ The symbol $\sigma_p{}^*$ was employed formerly[4,43,53] instead of σ^-.

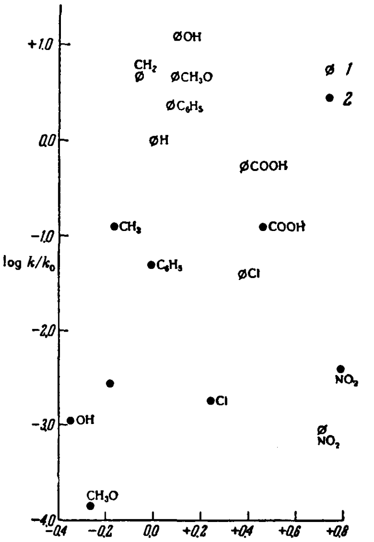
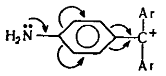


Fig. 3. Failure of the Hammett equation for the decomposition of ***meta***- and ***para***-substituted benzenediazonium chlorides in water at 29°: 1) ***meta***-substituents; 2) ***para***-substituents.

A comparable situation arises if a +C type of substituent enters into direct polar conjugation with a -C type of reactive centre. An example is provided by reactions in which triarylcarbonium ions either take part or are formed:



New constants σ^+, taking account of the ability of a given substituent to enter into direct polar conjugation with a -C type of reactive centre, were introduced[57-65] for such reaction series. Since the -C type includes also the carboxyl group, which is directly combined with the benzene nucleus in substituted benzoic acids, and can enter into direct conjugation with a +C type of substituent, the "normal" σ values for *para*-substituents of this type have in fact already made some allowance for their capacity for direct polar conjugation[57-66].

Since direct polar conjugation always intensifies the polarisation of the reactive centre produced by the substituent, $\sigma^- > \sigma$ and $\sigma^+ < \sigma$.

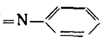
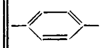
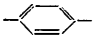
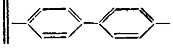
If the reactive centre can undergo direct polar conjugation with both +C and -C substituents, σ^+ constants are employed with the first type, and σ^- with the second[67].

The interrelationships between the quantities σ and σ^- were also analysed by the molecular-orbital method. The changes in electron density in the *meta* positions are proportional to the corresponding values of σ. Changes in the energy of localisation in the *meta* positions are proportional to the values of σ, and those in the *para* position to values of σ^-.[68]

The values of σ, σ^+, and σ^- do not remain constant if different reaction series are used to determine them. Consequently the substituent constants in Hammett's equation are not completely general parameters. For example, the value of σ^- calculated for CH_3SO_2 from data for the dissociation of substituted anilinium ions is +0.98, whereas the value calculated from data for the dissociation of phenols[55] is +1.13, etc. It is for this reason that it has been necessary to introduce σ^+ constants for some reaction series. Thus the "normal" σ values for substituents of +C type, determined from the dissociation constants of benzoic acids, are by definition also constants of σ^+ type. Therefore values of σ calculated for +C substituents from experimental data for reaction series in which the reactive centre is of +C type or is separated from the benzene nucleus by a saturated side-chain, have considerably larger positive values than the "normal" σ values[57].

The values of σ can change within wide limits on passing from one reaction series to another, even in the absence of direct conjugation of the substituent with the reactive centre[57].

The dependence of the reaction constant ρ on the nature of the reaction, the structure of the reagent, and the solvent is of no less interest. This constant has positive values for all reactions facilitated by electronegative substituents. Reactions favoured by electron-donating substituents are characterised by negative values of ρ. The numerical value of ρ measures the "sensitivity" of a given reaction to polar effects, and the ability of the atomic grouping linking the benzene nucleus with the reactive centre to transmit the polar effects of the nuclear substituents. The insertion of a group of atoms Z between the aromatic nucleus and the reactive centre results in a diminution in ρ, which may be expressed quantitatively by a factor π′ independent of the nature of the reactive centre and of the reaction and the conditions under which it occurs[53,70,71]. Values of π′ calculated by the molecular-orbital method[53] agree with the experimental results, as can be seen from the data below.

Z	π′		Z	π′	
	expt.	calc.		expt.	calc.
$—CH_2$	0.410∓0.084	—	—N=N—  —	0.145∓0.015	0.136
$—CH_2—CH_2$	0.206∓0.009	—	—CH=CH—CO	0.035	—0.010
—CH=CH—	0.508∓0.038	0.683		— —	—0.013
	0.303∓0.040	0.177		0.25	—

In the case of reaction series representing the dissociation of acids in which the functional acid group is directly linked to a benzene nucleus, the magnitude of ρ depends on the polarisability of the central atom [*e.g.* in $B(OH)_2$] of the functional group. The value of ρ increases with the ionic refraction of the ion obtained by filling the valency shell of this atom to complete its octet[53,72].

Jaffe, on the basis of his statistical investigation covering 336 reaction series[73], concluded that $\rho_m = \rho_p$. This result is not surprising, since the values of σ_{meta} and σ_{para} which he employed had been calculated on the assumption that $\rho_{meta} = \rho_{para}$. The result obtained by Jaffe therefore bears no relation to the actual constants representing sensitivity to the polar effects of substituents in the *meta* and *para* positions of the benzene nucleus. Hine[74] in considering this problem rules out the postulate that the two sensitivity constants are equal, and concludes that ρ_m and ρ_p should differ appreciably. This is quite understandable in view of the rapid damping of the influence of the inductive effect as the distance between substituent and reactive centre increases.

There are several examples of empirical relations linking ρ for a given reaction with the composition of a mixed solvent[75] or with the dielectric constant of the medium[76].

As regards the range of applicability of Hammett's equation, it covers a great variety of reaction series, both heterolytic and homolytic[53].

Hammett's equation allows several physical properties of substituted aromatic and heterocyclic compounds to be correlated, for example the infra-red absorption frequencies corresponding to some stretching vibrations[53,77-83].

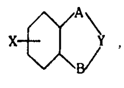
A few additivity rules are important in practice[53]. If a benzene nucleus contains more than one substituent in the *meta* and *para* positions, or if several benzene nuclei are linked symmetrically with the reactive centre, the following relation can be employed:

$$\log k/k_0 = \rho\Sigma\sigma. \tag{9.2}$$

If several benzene nuclei are linked unsymmetrically with the reactive centre,

$$\log k/k_0 = \Sigma\rho\sigma. \tag{9.3}$$

In the case of compounds of the type



the following formula can be used[84]:

$$\log k/k_0 = \rho_1\sigma_m + \rho_2\sigma_p. \tag{9.4}$$

Since values of σ_p measure the combined influence of the inductive effect and polar conjugation, they can also be used with the corresponding unsaturated aliphatic systems. The acidity of *trans*-3-substituted acrylic acids is represented by the usual Hammett equation[85]. The inductive constants of substituents of the type *trans*-X–CH = CH– are related to values of σ_p for X by the following relation[86]:

$$\sigma^* = 0.60 + 1.60\sigma_p. \tag{9.5}$$

Application of Hammett's equation to heterocyclic compounds is of very great interest and has several aspects. Examples are known of the usual Hammett $\sigma-\rho$ correlation when the heteroatom is the reactive centre, as with the basic dissociation constants of 3- and 4-substituted pyridines and the corresponding oxides[87]. On the other hand, replacement of a =CH– group in the benzene nucleus by =N–, $\overset{\diagdown}{\underset{\diagup}{N}}\rightarrow O$, and $\overset{\diagdown}{\underset{\diagup}{N}}H^+$ groups can be regarded as analogous to the replacement of hydrogen in the *meta* or *para* position, and appropriate values of σ_3 and σ_4 can be assigned to these groups[87-89]. There are indications, however, that the values of σ_3 and σ_4 for =N– do not remain constant on passing from one reaction series to another[90].

A Hammett type of equation

$$\log k/k_0 = \rho\sigma, \tag{9.6}$$

where σ represents the logarithm of the ratio of the dissociation constants of substituted and unsubstituted carboxylic acids of a given series, is applicable to several substituted derivatives of thiophen, furan, thiazole, and pyridine. In the case of thiophen and furan derivatives ρ has about the same value as with benzene derivatives (with the exception of one reaction series), but this does not apply to thiazole and pyridine derivatives[91].

In these cases the Hammett equation does not imply proportionality between the quantities $\log k/k_0$ and σ determined from the dissociation constants of substituted benzoic acids. Therefore the values of σ in (9.6) are not necessarily equal to the Hammett σ constant [*i.e.* not when ρ in (9.6) is not equal to ρ in the Hammett equation for the benzene series]. Relations like (9.6) and cases of LFE in general are often combined under the general term "Hammett equation". Such a broad interpretation of this term and the identification of the Hammett equation with the LFE principle are hardly desirable at the present time.

The Hammett equation, like the Taft equation, can be successfully employed in the study of reaction mechanisms[4,10,53,72,92-95].

Values of the constants σ, σ^-, and σ^+ for various substituents are given in Table 2.

TABLE 2. Hammett constants for various substituents.

Values quoted from Jaffe[53] calculated by statistical averaging of data for all reaction series for which experimental results were available by 1953; values from McDaniel and Brown[96] obtained from the dissociation constants of substituted benzoic acids or from data for reaction series for which ρ had been determined by the use of values of σ calculated from the dissociation constants of benzoic acids; and individual values quoted by other authors from data on some reaction series for which the value of ρ was known.

Substituent	σ_m			σ_p			σ^-	σ^+	
	ref. 53	ref. 96	other refs.	ref. 53	ref. 96	other refs.		*meta*	*para*
CH_3	−0.069	−0.069		−0.170	−0.170	from −0.080[95] to −0.170		−0.066[65]	−0.311[65]
C_2H_5	−0.043	−0.07		−0.151	−0.151			−0.064[65]	−0.295[65]
C_3H_7	—	—		−0.126	—				
$CH(CH_3)_2$	—	—		−0.151	−0.151			−0.060[65]	−0.280[65]

TABLE 2 (contd.)

Substituent	σ_m			σ_p			σ^-	σ^+	
	ref. 53	ref. 96	other refs.	ref. 53	ref. 96	other refs.		*meta*	*para*
C_4H_9	—	—		−0.161	—				
$CH_2CH(CH_3)_2$	—	—		−0.115	—				
$CH(CH_3)C_2H_5$	—	—		−0.123					
$C(CH_3)_3$	−0.120	−0.10		−0.197	−0.197			−0.059[65]	−0.256[65]
$(CH_2)_2CH(CH_3)_2$	—	—		−0.225	—				
$C(CH_3)_2C_2H_5$	—	—		−0.190					
CF_3	+0.415	+0.43		+0.551	+0.54			+0.520[62]	+0.612[62]
CCl_3	—	—	+0.407[21]	—	—	+0.454[21]		—	—
CH_2Cl	—	—	—	+0.184	—	—	—	+0.14[65]	+0.01[65]
$CHCl_2$	—	—	+0.185[21]	—	—	+0.212[21]		—	—
CH_2CN	—	—		+0.007	—			—	—
CH_2CH_2COOH	−0.027	—		−0.066	—			—	—
OH	−0.002	+0.121		−0.357	−0.37			—	−0.92[65]
OCH_3	+0.115	+0.115		−0.268	−0.268	−0.361[98]		+0.047[65]	−0.778[65]
OC_2H_5	+0.150	+0.1		−0.250	−0.24			—	—
OC_3H_7	—	+0.1		−0.268	−0.25			—	—
$OCH(CH_3)_2$	—	+0.1		−0.286	−0.45			—	—
OC_4H_9	—	+0.1		−0.320	−0.32			—	—
OC_5H_{11}	—	+0.1		−0.340	−0.34			—	—
$O(CH_2)_2CH(CH_3)_2$	—	—		−0.265	—			—	—
$OCH_2C_6H_5$	—	—		−0.415	—			—	—
OC_6H_5	—	+0.252		−0.028	−0.320			—	−0.5[65]
O^-	−0.708	—		−0.519				—	—
$OCOCH_3$	—	+0.39		—	+0.31			—	—
NH_2	−0.161	−0.16		−0.660	−0.66			−0.16[65]	−1.3[65]
$NHCH_3$	−0.302	—		−0.592	−0.84				
NHC_2H_5	−0.240	—		—					
NHC_4H_9	−0.344	—		—					
$N(CH_3)_2$	−0.211	—		−0.600	−0.83			—	−1.7[65]
$NHCOCH_3$	—	+0.21		−0.015	0.00				−0.6[65]
$NHCOC_6H_5$	+0.217	—		+0.078					−0.6[65]
$NHNH_2$	−0.020	—		−0.550					
NHOH	−0.044	—		−0.339					
NH_3^+	+0.634	—		—					
$NH_2CH_3^+$	+0.958	—		—					
$NH_2C_2H_5^+$	+0.958	—		—					
$N(CH_3)_3^+$	+0.904	+0.88	+0.67[64] +1.02	+0.859	+0.82	0.66—1.11[64]	—	+0.359[65]	+0.408[65]
N_2^+	—	—	+1.7[99]	—	—	+1.8 ±0.5[99]			
COOH	+0.355	(+0.37)		+0.265	(+0.45)		+0.728[53]	+0.322[62]	+0.421[62]
$COOCH_3$	+0.315	—	—	—	—	+0.436[100]	+0.636[53]	+0.368[62]	+0.489[62]
$COOC_2H_5$	+0.398	+0.37		+0.522	+0.45		+0.678[53]	+0.366[62]	+0.482[62]
$COOC_4H_9$	—	—		—			+0.674[53]		
$COOCH_2C_6H_5$	—	—					+0.667[53]		
$CONH_2$	+0.280	—		—			+0.627[53]		
CHO	+0.355	—	+0.382[101]	+0.216			+0.126[53]		
$COCH_3$	+0.306	+0.376	+0.306[101]	+0.516	+0.502		+0.874[53]		
COC_6H_5	—	—		+0.459			—		
CN	+0.678	+0.56	+0.52[101]	+0.628	+0.660	+0.65[101]	+1.000[53]	+0.562[62]	+0.659[62]
COO^-	+0.104	−0.1		+0.132	0.0	—	—	−0.028[65]	−0.023[65]
$C_2H_5OCOCH_2$	—	—		—	—	—	—	−0.01[65]	−0.164[65]
NO_2	+0.710	+0.710		+0.778	+0.778	—	+1.270[53]	+0.710[62]	+0.790[62]
NO	—	—		+0.123					
F	+0.337	+0.337		+0.062	+0.062			+0.352[65]	−0.073[65]
Cl	+0.373	+0.373		+0.227	+0.227			+0.399[65]	−0.114[65]
Br	+0.391	+0.391		+0.232	+0.232			+0.405[65]	+0.150[65]
I	+0.352	+0.352		+0.276	+0.18	+0.27[102]		+0.359[65]	+0.135[65]
IO_2	(+0.70)	+0.70		(+0.76)	+0.76				
SCH_3	+0.144	+0.15		−0.047	0.0			+0.158[65]	−0.604[65]
$SOCH_3$	+0.551	+0.52		+0.567	+0.49	+0.73[103]			
SO_2CH_3	+0.647	+0.60	+0.56[101]	+0.728	+0.72	+0.68[101]	+1.049[53]		
SCN	—	—		+0.699	+0.52				
SeCN	—			+0.664					
$B(OH)_2$	+0.006			+0.454					
$Si(CH_3)_3$	−0.121			−0.072	−0.07			+0.011[65]	+0.021[65]
$Si(C_2H_5)_3$	—	—		—	0.0				
$CH_2Si(CH_3)_3$	—	−0.16		—	−0.21				
C_6H_5	+0.218	+0.06		+0.009	−0.01			+0.109[65]	−0.179[65]
$N{=}N{-}C_6H_5$	—			+0.640	—				
$C_6H_4N{=}NC_6H_5$	—			—	—		+1.088[53]		
$CH{=}CH{-}C_6H_5$	+0.141				—		+0.619[53]		
AsO_3H^-	—			−0.019	−0.02		—		
PO_3H^-	+0.228	+0.2		+0.238	+0.26		—		
SO_2	—			+0.381	—		—		
SO_2NH_2	—	+0.46	+0.55[101]	+0.621	+0.57	+0.62[101]	+0.94[101]		
SO_3^-	—	+0.05	+0.31[101]	—	+0.09	+0.37[101]	+0.58[101]		
3,4-$(CH_2)_3$	—			−0.259	—				
3,4-$(CH_2)_4$	—			−0.477	—				
3,4-$(CH)_4$	—	—		+0.170	+0.042				−0.135[65]
3,4-CH_2O_2	—			−0.159					
$Ge(CH_3)_3$	—	—		—	−0.0				
$Ge(C_2H_5)_3$	—	—		—	−0.0				
$Sn(CH_3)_3$	—	—		—	−0.0				
$Sn(C_2H_5)_3$	—	—		—	−0.0				
$SeCH_3$	—	+0.1		—	+0.0				
SC_2H_5	—	—		—	+0.03				
$SCH(CH_3)_2$	—	—		—	+0.07				
SH	—	+0.25		—	+0.15				
$SCOCH_3$	—	+0.34		—	+0.44				
$S(CH_3)_2^+$	—	+1.0		—	+0.90				
2-$CH_3C_6H_4$	—	—	—	—	—	−0.016			
2-HOC_6H_4	—	—	—	—	—	+0.003			
2-$CH_3OC_6H_4$	—	—	—	—	—	+0.012			
2-ClC_6H_4	—	—	—	—	—	+0.047			
$HC{\equiv}C^-$	—	—	—	—	—	+0.281			
$CH_3C{\equiv}C{-}$	—	—	—	—	—	+0.087			
$CH_3CH{=}CH{-}$	—	—	—	—	—	−0.043			
$>N^+H$	—	—	+2.1[87]	—	—	+2.3[87]	4.0[87]		
$>NO^+H$	—	—	+2.3[87]	—	—	—	3.9[87]		

X. POLAR AND STERIC CONSTANTS OF *ortho*-SUBSTITUENTS

The Hammett equation is usually inapplicable to *ortho*-substituted benzene derivatives[53], the "anomalous" behaviour of these compounds being known as the "*ortho* effect". The anomaly is ascribed to steric effects, including steric hindrance to conjugation between the reactive centre and the aromatic nucleus, the field effect, and intramolecular hydrogen bonding[53,72].

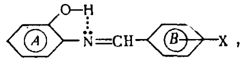
Taft[10,17,26] attempted to discuss *ortho*-substituted benzene derivatives by analogy with aliphatic compounds. He calculated the polar constants σ_o^* for *ortho*-substituents from data on the rates of alkaline and acid hydrolysis of *ortho*-substituted benzoates by means of Eqn.(4.1), hydrogen being taken as standard substituent. The "aromatic" polar constants σ_o^* thus obtained for the substituents were analogous in physical significance to the Hammett σ constants, since they represent the combined influence of an inductive effect and polar conjugation. They will therefore be denoted, in what follows, by σ_o. The values of σ_o for different substituents are similar in magnitude to the Hammett σ_p constants.

Several reaction series are known in which the steric effect of *ortho*-substituents on the reactive centre is insignificant, and the Hammett–Taft equation[10,17,26] is applicable:

$$\log k/k_0 = \rho_o\sigma_o. \qquad (10.1)$$

The quantity ρ_o is usually close to ρ in the Hammett equation for the given reaction series, but this is not always the case[10]. Eqn. (10.1) cannot be applied with *ortho*-substituents which can form an intramolecular hydrogen bond with the reactive centre[10].

Values of the polar constants for *ortho*-substituents were determined also by Baker and Shulgin[77] from a study of the changes in infra-red absorption frequency of a hydroxyl group forming an intramolecular hydrogen bond in Schiff bases of the type



produced by substitution in nucleus B. In this case there is good agreement with the Hammett equation $\Delta\nu = \rho\sigma$. These workers calculated values of σ_o for the *ortho*-substituents by substituting in this equation the value of ρ obtained from data for *meta*- and *para*-substituents. In view of the considerable distance of the B ring from the hydrogen bond, the resulting values of σ_o should represent only the combination of inductive effect and polar conjugation, if the component due to the field effect is disregarded. Except for the nitro group, values of σ_o determined in this way differ little from Taft's σ_o^*.

Apparently because of the superimposition of the field effect, the Taft and Baker–Shulgin σ_o constants are not so generally applicable as the Hammett σ values. As an example, although the infra-red absorption frequencies for the carboxyl group in *ortho*-substituted benzoic acids, acetanilides, and several other benzene derivatives vary in the same direction as the Taft σ_o values, this variation is not linear[104].

With fourteen reaction series involving compounds of the type o-X–C_6H_4–Z–Y, where Z is an "isolating" chain consisting of two or more atoms (Z = –CH=CH–, –CH_2–CH_2–, –O–CH_2–, etc.), Charton[105] has shown that the Hammett equation can be applied in the form (10.1), and Hammett's σ_p can be used instead of σ_o values. From this he concludes that the failure of Hammett's equation to hold for *ortho*-substituted benzene derivatives is in general a consequence of steric interaction between the substituent and the reactive centre, or else of the formation of a hydrogen bond between them.

Introduction of a substituent into the *ortho* position does not disturb the Hammett $\sigma-\rho$ correlations for a given series of *meta*- and *para*-substituted compounds[54,106]. It follows that *meta*- and *para*-substituents do not affect the magnitude of the *ortho* effect.

Values of "aromatic" steric constants have been calculated for several substituents from data on the kinetics of the acid hydrolysis of *ortho*-substituted benzoates[17,10]. One example is known of the application of the LFE principle to values of E_S for *ortho*-substituents[10].

E_S values for *ortho*-substituents vary in the same sense as the van der Waals radii of the substituents[10].

XI. PROBLEM OF THE QUANTITATIVE SEPARATION OF INDUCTIVE AND POLAR CONJUGATIVE EFFECTS

As noted above, the Hammett σ values characterise the combined influence of the inductive effect and the polar conjugation inherent in a given substituent. This is the reason for the fundamental inaccuracy of the Hammett equation. Numerous attempts have therefore been made to determine quantitatively the several effects of these factors. Various approaches may be made to this problem.

Roberts and Moreland[107] and later Taft[10] tried to evaluate the inductive term in the Hammett σ values. The former used model compounds in the shape of 4-substituted bicyclo[2,2,2]octane-1-carboxylic acids and their ethyl esters. Three reaction series involving these compounds exhibit LFE behaviour as represented by the Hammett equation:

$$\log k/k_0 = \rho_I\sigma_I, \qquad (11.1)$$

where $\sigma_I = [\log(k/k_0)]/1.464$, k and k_0 being the dissociation constants of the 4-substituted and the unsubstituted bicyclo[2,2,2]octane-1-carboxylic acids respectively in 50 vol.% ethanol at 25°, and 1.464 being the value of ρ in the Hammett equation for the dissociation of substituted benzoic acids in 50% ethanol at 25°. Values of ρ_I in Eqn. (11.1) are similar to those of ρ in the Hammett equation for the corresponding reaction series. The above workers therefore concluded that values of σ_I are practically equal to the inductive component in the Hammett σ constants for the appropriate substituents.

Taft[111] has shown that the quantity $\sigma_{I(X)}/\sigma^*_{(X-CH_2)}$ has a constant value of +0.450 for different substituents. It follows that the σ_I and σ^* scales of inductive effects are fundamentally equivalent, and that values of σ_I can be obtained from the corresponding values of σ^* by means of the formula:

$$\sigma_{I(X)} = 0.450\sigma^*_{(X-CH_2)}. \qquad (11.2)$$

The inductive components in the σ values can be found also by determining the Hammett constants for groups whose conjugation with the benzene nucleus is completely destroyed by steric hindrance[10,108-110]. The results obtained agree with the σ_I values.

The σ_I values have been used to separate the inductive and resonance (polar conjugation) components in the Hammett equation. Values of σ_I are given in Table 3.

TABLE 3. Aromatic polar substituent constants: σ°, σ_I, σ°_C, σ_C, σ^-_C, σ^+_C, $\Delta\sigma^+_C$.

Substituent	σ° [111]		σ_I [112]	σ°_c [113]	σ_c [114]	σ_c [114]	σ^+_c [115]	$\Delta\sigma^+_c$ [116]
	meta	*para*						
H	(0.00)	(0,00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)
CH_3	−0.07	−0.15	−0,05	−0.10	−0.13	—	−0.26	−0,131
C_2H_5	—	—	−0.05	—	—	—	—	−0,141
$(CH_3)_2CH$	—	—	—	—	—	—	—	−0.125
$(CH_3)_3C$	—	—	−0.07	—	—	—		−0.053
$(CH_3)_3Si$	—	—	−0.12	—	+0.11	—	−0.07	
C_6H_5	—	0,00[113]	+0.10	−0.10	−0.09	—	−0,22	−0.200
$C_6H_5CH_2$	—	—	+0.04	—	—	—	—	—
CH_2Cl	—	—	+0.17	—	—	—	(−0.11)	—
CF_3	—	—	+0,41	—	+0.14	—	—	—
F	+0.35	+0.17	+0.52	−0.35	−0.44	—	−0.57	−0.130
Cl	+0.37	+0,27	+0.47	−0.20	−0.24	—	−0.36	−0,106
Br	+0.38	+0.26	+0.45	−0.19	−0,22	—	−0.30	−0.081
I	+0.35	+0.27	+0.39	−0.12	−0,10	—	−0.25	−0.144
OH	+0.04[c]	−0,13[c]	+0,25	−0.37[a]	−0.50	—	(−1.07)	−0.56
	+0.13[a]	−0.12[a]		−0.41[b]			−0.99	−0.496
OCH_3	+0.06[b]	−0.16[b]	+0.25	−0.41[b]	−0.50	—	—	−0.494
C_2H_5	—	−0.123*	—	—	—	—	—	−0.51
OC_6H_5	—		+0,38	—	−0.41	—	—	—
OCF_3	—	—	+0.48	—	−0.11	—	—	—
SH	—	—	+0.25	—	—	—	—	—
SCH_3	—	—	+0.25	—	−0.24	—	—	—
SC_2H_5	—	−0.025*	—	—	—	—	—	—
SCF_3	—	—	+0.43	—	−0.05	—	—	—
$COCH_3$	+0,34	+0.46[d]	+0,28	+0.18[d]	+0.25	+0.60	—	—
		+0.40[c]		+0.12[c]				
COOH,COOR	+0.36	+0.46[d]	+0.30	+0.16[d]	+0.20	+0.36	—	—
COO^-	+0.08*	+0.08*	—	—	—	—	—	—
CN	+0.62	+0.69[d]	+0,58	+0.11[d]	+0.07	+0,41	—	—
		+0.63[c]		+0.05[c]				
NH_2	−0.14	−0.38	+0.10	−0.48	−0.76	—	−1.31	−1.00
$NHCH_3$	−0.22*	−0.42*	—	—	—	—	—	—
NHC_2H_5	−0.18*	—	—	—	—	—	—	—
NHC_4H_9	−0.24*	—	—	—	—	—	—	—
$N(CH_3)_2$	−0.15	−0.44	+0.10	−0.54	—	—	(−1.89)	−0.74
$NH{-}NH_2$	+0.02*	−0.40	—	—	—	—	—	—
$NH_2(CH_3)^+$	+1.00*	—	—	—	—	—	—	—
$NH_2(C_2H_5)^+$	+1.00*	—	—	—	—	—	—	—
$NH(CH_3)_2^+$	—	1.00*	—	—	—	—	—	—
$N(CH_3)_3^+$	—	—	+0.86	0.00	—	—	—	—
$NH(COCH_3)$	—	+0.03[113]	+0.28	−0.25	—	—	—	−0.58
NO_2	+0.70	+0.82[d]	+0,63	+0.19[d]	+0.15	+0.64	—	—
		+0.73[c]		+0.10[c]				
$SOCH_3$	—	—	+0.52	—	—	—	—	—
SO_2CH_3	—	—	+0.59	—	+0.14	+0.46	—	—
SO_2NH_2	—	+0.62	—	—	—	—	—	—
SO_2CF_3	—	—	+0.84**	—	+0.19**	—	—	—

* Calculated from Eqn. (14.2).

** Taken from ref. 117.

[a] Values only for pure aqueous solutions.

[b] Values for non-hydroxylic solvents and for most mixtures of water with organic solvents.

[c] Values only for non-hydroxylic solvents.

[d] Values for aqueous solutions and most mixtures of water with organic solvents.

Taft[111] notes that values of σ_I (and hence σ^*), Branch and Calvin's[14] inductive constants I_a, and Pauling's[5] electronegativities agree well with the Periodic Table.

It is further assumed that the effects of *meta*- and *para*-substituents on the reactivity and other properties of aromatic compounds should theoretically be represented by the following equations[112,114,118]:

$$\log k_p/k_0 = \rho^p_I\sigma_I + C_p, \tag{11.3}$$

$$\log k_m/k_0 = \rho^m_I\sigma_I + C_m, \tag{11.4}$$

where C_p and C_m represent the effects of polar conjugation for a given substituent in the *meta* and *para* positions respectively. Although there is no direct conjugation of a substituent with the *meta* position of the benzene nucleus, polar conjugation has nevertheless an indirect influence on such positions too[107,118]. The nature of this effect will be clear if it is assumed that charges induced in the *ortho* and *para* positions by polar conjugation cause like charges to appear in the *meta* positions owing to electrostatic repulsion or attraction of electrons along σ bonds (secondary inductive effect).

It has been suggested[114] that C_p and C_m should be divided into factors analogous to ρ_I and σ_I (application of LFE principle): $C_p = \rho^p_c\sigma_c$ and $C_m = \rho^m_c\sigma_c$. Eqns. (11.3) and (11.4) can then be rewritten as follows:

$$\log k_p/k_0 = \rho^p_I\sigma_I + \rho^p_c\sigma_c, \tag{11.5}$$

$$\log k_m/k_0 = \rho^m_I\sigma_I + \rho^m_c\sigma_c. \tag{11.6}$$

If $\rho^p_I = \rho^p_c = \rho$, the quantities ρ^m_I/ρ and ρ^p_I/ρ are constant for all reaction series, and σ_c is a universal constant for a given substituent, Eqns. (11.5) and (11.6) reduce to the Hammett equation:

$$\log k_p/k_0 = \rho\sigma_p \text{ and } \log k_m/k_0 = \rho\sigma_m,$$

where $\sigma_p = \sigma_I + \sigma_c$ and $\sigma_m = \dfrac{\rho^m_I\sigma_I + \rho^m_c\sigma_c}{\rho}$.

The above restrictions are necessary for the Hammett equation to be applicable. Clearly, this condition is not always observed, and consequently the Hammett equation is in principle not exact.

If $\rho^p_I = \rho^p_C = \rho$, then $\sigma_I + \sigma_C = \sigma_p$, and values of σ_C can be calculated from the formula[107,112,114]

$$\sigma_C = \sigma_p - \sigma_I. \tag{11.7}$$

The quantities σ^-_C and σ^+_C, characterising the direct conjugation between a reactive centre and a substituent of type -C and +C respectively, are determined in a similar manner[114]:

$$\sigma^-_C = \sigma^-_p - \sigma_I, \tag{11.8}$$

$$\sigma^+_C = \sigma^+_p - \sigma_I. \tag{11.9}$$

Values of σ_C, σ^-_C, and σ^+_C are given in Table 3.

Among examples of the practical application of these quantities, the chemical shifts in nuclear magnetic resonance for ^{19}F in *meta*- and *para*-substituted fluorobenzenes are well represented by the equations:

$$\delta^p_{^{19}F} = \rho_I\sigma_I + \rho_C\sigma_C, \tag{11.10}$$

$$\delta^m_{^{19}F} = \rho_I\sigma_I, \tag{11.11}$$

where $\rho_I \neq \rho_C$. A similar relation holds also for chemical shifts in nuclear magnetic resonance for H in substituted benzenes[95]. Values of σ^- have been used also to correlate rates of acid dissociation of substituted methanes in water[119]. For the use of σ^-_C and σ^+_C in the correlation of dipole moments, see section XIX. The quantities σ_I and σ_C may perhaps be related by[120]: $\sigma_I = 0.570 + 0.603\sigma_C$.

Taft *et al.*[113,118] tried to determine the inductive component by eliminating C_p and C_m from Eqns. (11.3) and (11.4). They assumed at first, following Roberts and Moreland[107], that $\rho_C^p = \alpha = 0.33$. It was also assumed[112] that, in the case of direct conjugation between a *para*-substituent and the reactive centre, $\alpha = 0.1$. Roberts and Jaffe[121] then demonstrated that α is not a universal constant for all reaction series. This was allowed for by Taft and Lewis[118], who calculated values of α for 88 reaction series. By eliminating C from the equations

$$\log k_p/k_0 = \rho_I\sigma_I + C, \quad (11.12)$$

$$\log k_m/k_0 = \rho_I\sigma_I + \alpha C, \quad (11.13)$$

they obtained the following relationship

$$\log k_m/k_0 - \alpha \log k_p/k_0 = (1 - \alpha)\rho_I\sigma_I. \quad (11.14)$$

In the derivation of (11.14) it is assumed that $\rho_I^p = \rho_I^m$. This is not altogether obvious.

In all cases examined a quite good linear dependence of the left-hand side of (11.14) on σ_I was found[118]. This was regarded as yet a further proof of the general applicability of the inductive constants of the substituents.

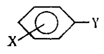
The differences $\log k/k_0 - \rho_I\sigma_I$ were used to calculate values of C_m and C_p, and, on the assumption that $\rho_C = \rho_I$, also σ_C^m and σ_C^p. The values of σ_C^p obtained for the same substituents from data for different reaction series were found to fluctuate extremely widely, and in several cases even changed their sign[118].

Moreover, it can be shown that the quantity α is not even roughly constant in a single reaction series. Division of Eqn. (11.14) by σ_I yields

$$(1/\sigma_I) \log k_m/k_0 = (1 - \alpha)\rho_I + \alpha(1/\sigma_I) \log k_p/k_0. \quad (11.15)$$

Thus, if α is constant, the quantity $\sigma_I^{-1} \log k_m/k_0$ should vary linearly with $\sigma_I^{-1} \log k_p/k_0$. A check carried out here has shown that in most cases no such linear dependence exists. Consequently the values of C_p and C_m given by Taft and Lewis[118] cannot be accepted as correct, although it is stated there that σ_C^p values are universal constants.

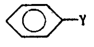
In principle the problem of determining the magnitude of the influence of the inductive effect and of polar conjugation can be approached from two directions[111]. If Y is regarded as the reactive centre in compounds of the type



the interaction of the substituent $X.C_6H_4$ with Y along the Ar–Y bond results from superposition of the inductive effect of this substituent and the conjugation between it and the reactive centre Y. In such a case C_6H_5 is regarded as the standard substituent. Consequently the Hammett σ constants are parameters characterising the inductive effects of $X.C_6H_4$ substituents. Since the σ values are determined from the dissociation constants of substituted benzoic acids, they already contain, in the case of X substituents of +C type, some component due to conjugation between $X.C_6H_4$ and Y. As a result, the scale of Hammett σ values is not altogether suitable for quantitative examination of the problem.

In this case all departures from the Hammett equation must be ascribed to some quantity ψ which is a measure of the polar conjugation between $X.C_6H_4$ and Y. The task of making the Hammett equation more exact then reduces to finding the dependence of ψ on the structure of the $X.C_6H_4$ substituent and on the specific character of the reaction series.

Another possible approach is to take the



group as the reactive centre. We must now consider the interaction of substituent X with this reaction centre along the X–Ar bond. This interaction is made up of the following three factors: (1) the inductive effect of the substituent X, (2) the polar conjugation of substituent X with the aromatic nucleus, leading to a corresponding charge distribution at the different positions in the nucleus, and (3) direct polar conjugation between the substituent X and the reactive centre Y. The problem is reduced to finding the dependence of quantities characterising these factors on the structure of the X substituents and the nature of the reaction series.

It is easily observed that these two approaches are not mutually contradictory. The inductive effect of the $X.C_6H_4$ substituent can be equated to the overall effect of factors 1 and 2, and the polar conjugation between $X.C_6H_4$ and Y should be equivalent to the direct conjugation between X and Y (factor 3), since conjugation between Y and the benzene nucleus is excluded from consideration by taking phenyl as the standard substituent.

We have already seen that the second approach to a solution of the problem involves considerable difficulties. In addition, the σ_I values are only an approximate measure of the inductive effect in the case of the standard reaction series, since the bicyclo[2,2,2]octane ring is not exactly equivalent to the benzene ring in its ability to transmit the inductive effect, and also since the individual deviations from the relationship (11.2) are quite large[10].

The feasibility of solving the problem by the first method was examined by Taft *et al.*[113,118] and also by Wepster *et al.*[66] Taft's starting point was that, if conjugation cannot occur between the reactive centre and the benzene ring or especially the substituent, the constants for the substituents will definitely contain no component representing the effect of polar conjugation with the reactive centre. The corresponding new constants for the substituents are denoted by σ^0 and are normalised in such a way that the scale of the Hammett σ values is maintained. This is easily done, since with substituents of +C type, especially in the *meta* position, $\sigma^0 = \sigma$. Then for some arbitrary reaction series the Hammett equation can be modified as follows:

$$\log k_p/k_0 = \rho\sigma_p^0 + \Delta C_p, \quad (11.16)$$

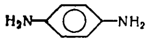
$$\log k_m/k_0 = \rho\sigma_m^0. \quad (11.17)$$

The quantity ΔC_p in Eqn. (11.16) represents direct polar conjugation and polarisation interaction between the substituent and the reactive centre, and can be readily found by substituting in (11.16) the appropriate experimental data and the value of ρ obtained from data for *meta*-substituted compounds and those *para*-substituted compounds in which there is no direct interaction between the substituent and the reactive centre[111-113].

Values are also given for $\sigma_C^0 = \sigma_p^0 - \sigma_I$, it being noted[111,113] that $\sigma_C^0 = 2\sigma_C^m$, where σ_C^m is the mean value of $\sigma_m - \sigma_I$. Owing to the inaccuracies noted above, produced in bringing the σ_I values to the same scale as the σ values, the values thus obtained for σ_C^0 cannot be regarded as completely reliable.

Furthermore, with several substituents the magnitude of σ^0 depends on the type of solvent[66].

In principle, Wepster[66] starts from the same premises as Taft. However, the "normal" values (*i.e.* free from any component for polar conjugation with the reactive centre) which he obtained for σ^n are not equal to Taft's σ^0 values. The calculation of σ^n was also based on such reaction series as the dissociation of phenols and anilinium ions (in the case of +C substituents). This leads to distortions owing to the so-called saturation effect[66] in compounds of the type



Here the polar conjugation of both amino groups with the aromatic nucleus is less intense than, for example, in aniline. As a consequence, greater positive values of σ^p are obtained for +C substituents compared with the corresponding σ^0 values.

Yukawa and Tsuno[116] made a detailed investigation of the divergence of the experimental data from the Brown–Okamoto modification of the Hammett equation:

$$\log k/k_0 = \rho\sigma^+, \tag{11.18}$$

where σ^+ are electrophilic constants of the substituents[65,122]. They concluded that, when the number of series examined is sufficient, the relation (11.18) often leads to considerable differences between calculated and experimental values of the constants for *para*-substituents.

Yukawa and Tsuno[116,123] also showed that the differences $\sigma^+_p - \sigma_p$ determined from data for different reaction series (*A* and *B*) are proportional to one another:

$$(\sigma^*_A - \sigma) = r(\sigma^+_B - \sigma), \tag{11.19}$$

where σ is the Hammett constant for the substituent, determined from data on the dissociation of substituted benzoic acids.

Taking the solvolysis of *meta*- and *para*-substituted α,α-dimethylbenzyl chlorides in 98% aqueous acetone at 25° as the standard reaction series ($r = 1$), these workers introduced a new scale of $\Delta\sigma^+_C$ values measuring the ability of +C substituents to undergo direct polar conjugation with a -C type of reactive centre:

$$\Delta\sigma^+_C = \sigma^+ - \sigma, \tag{11.20}$$

where the σ^+ are the Brown–Okamoto electrophilic constants of the substituents[65,122].

The modified Hammett equation is then obtained in the following form:

$$\log k_p/k_0 = \rho(\sigma + r\Delta\sigma^+_C), \tag{11.21}$$

where ρ and r are parameters characteristic of the reaction series, and σ and $\Delta\sigma^+_C$ are characteristic of a given substituent.

The relations (11.19) and (11.21) are obtained by application of the LFE principle to the direct conjugation of substituents with the reactive centre.

Values of $\Delta\sigma^*_C$ for various substituents are given in Table 3.

Yukawa and Tsuno made a statistical test of Eqn. (11.21) for 35 reaction series. Good results were obtained in all cases, and the accuracy of correlation was considerably greater when the Yukawa–Tsuno equation was used than with Eqn. (11.18).

An attempt has also been made to separate the inductive effect from polar conjugation by calculations based on the method of molecular orbitals[124].

XII. GENERALISATION OF THE CONCEPT OF POLAR CONSTANTS OF SUBSTITUENTS

Hine[74,86,124] demonstrated that when a Hammett type of equation holds for equilibrium we have

$$\rho = \tau(\sigma_{Y_2} - \sigma_{Y_1}), \tag{12.1}$$

where τ is a universal constant depending on the structure of the "skeleton" of the molecule, to which the substituent and the reactive centre are joined, and σ_{Y_1} and σ_{Y_2} are the polar constants of the substituent with the reactive centre in its initial and final states respectively.

Hine also showed[124] that relation (12.1), as well as the Hammett and Taft equations, can be derived on the assumption that the free energy of the polar interaction of any pair of substituents X and Y is proportional to the product of quantities termed the polar constants of the substituents, σ_X and σ_Y:

$$F_{X,Y} = \tau\sigma_X\sigma_Y. \tag{12.2}$$

Hine examined specifically various reaction series involving *meta*- or *para*-substituted benzene derivatives, including some involving direct polar conjugation between the reaction centre and the substituent. The free energy of direct conjugation between the latter is regarded as analogous to ordinary polar interaction, and the capacity of substituents for polar conjugation is characterised by appropriate constants σ^C. The final equation is

$$\log k/k_0 = \tau[\sigma_X(\sigma_{Y_2} - \sigma_{Y_1}) + \sigma^C_X\sigma^C_{Y_1} - \sigma^C_X\sigma^C_{Y_2}]. \tag{12.3}$$

In the derivation it is also assumed that τ does not depend on whether "ordinary" polar interaction or direct conjugation between X and Y is being considered. By definition, the products $\sigma^C_X\sigma^C_Y$ vanish if σ^C_X and σ^C_Y have the same sign, since there can be no polar conjugation between two substituents of type +C (or -C).

In the case of an equilibrium, σ_{Y_2} in (12.3) relates to the reaction centre in the product of the reaction. If k/k_0 is a ratio of velocity constants, σ_{Y_2} then represents the state of the reaction centre in the activated complex. Therefore the σ_{Y_2} values cannot be defined here in the usual way, since a reaction centre in an activated state cannot fill the role of substituent in some other reaction series. Eqn. (12.3) was therefore modified as follows for application to reaction velocities:

$$\log k/k_0 = \rho\sigma_X + \rho^C\sigma^C_X, \tag{12.4}$$

where $\rho = \tau(\sigma_{Y_1} - \sigma_{Y_2})$ and $\rho^C = \tau(\sigma^C_{Y_1} - \sigma^C_{Y_2})$.

Hine gives values which he has calculated for σ_m, σ_p, and σ^C_p for several substituents, τ_m and τ_p for aqueous solutions at 25°, and ρ_m, ρ_p, and ρ^C for some reaction series. The quantity τ is normalised on the basis that $\tau(\sigma_{COOH} - \sigma_{COO^-}) \equiv 1$ for *meta*- and *para*-substituted benzoic acids.

Eqns. (12.1) and (12.4) enable σ_{Y_2} to be calculated for a reaction centre in an activated state, which is important for the investigation of reaction mechanisms.

The definition of the polar constants of substituents in Eqn. (12.2) is more general than those given earlier. Both substituent and reactive centre are regarded from the same point of view. In deriving the formulae, Hine notes their similarity to Kirkwood's formula[13] for the free energy of interaction between two dipoles. This may perhaps provide a theoretical basis for applying the LFE principle in cases of polar interaction, which would be of fundamental importance.

XIII. USE OF THE LFE PRINCIPLE TO OBTAIN SPECIAL CORRELATION EQUATIONS HAVING A LIMITED RANGE OF APPLICATION

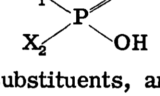
Section XI has confirmed that the Hammett equation is a purely empirical relationship in the sense that the inductive effect and the effect of polar conjugation are not separated, and only those cases are covered (though, of course, they are numerous) in which the conditions indicated in section XI are satisfied, albeit very roughly. However, this defect (from the viewpoint of a more rigorous theory) of the Hammett equation is offset by an important practical advantage, since it is possible with this equation to apply the LFE principle to the gross ΔF values, in spite of the fact that several factors are influencing the reactivity at the same time. In general, the existence of the Hammett equation indicates the possibility of making an overall quantitative allowance for the effect of several factors when either the substituents possess in some sense similar structural features (*meta*- and *para*-substituted phenyls) or else similar reaction series are being considered. In this respect the Hammett equation can be regarded as an example of the use of the LFE principle to obtain an approximate correlation equation having a limited range of application. In this sense the Hammett equation does not form an exception, and has several analogues. Some examples will be given below.

Taft's equation[125] for the hydrolysis of esters $X_1.COOX_2$ or o-$X_3.C_6H_4.COOX_2$ and the esterification of the corresponding acids by the alcohols X_2OH:

$$\log k/k_0 = fA, \tag{13.1}$$

where k and k_0 are rate constants for the given ester and the standard ester (acid or alcohol) respectively (methyl being the standard substituent), A is a constant for the substituent X depending on whether it is in positions 1, 2, or 3 and on the type of catalysis (acid or alkaline), and f is a parameter characteristic of the reaction series (only one X substituent varies in the given series). The constant A is an approximate measure of the overall effect of the inductive and the steric factors of the X substituents.

Kabachnik's equation[126-128] for the dissociation constants of substituted phosphinic acids of the type



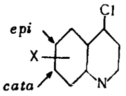
where X_1 and X_2 are substituents, and Z is an atom of oxygen or sulphur. This equation is of the form

$$\log k/k_0 = \rho_\Phi \Sigma\sigma_\Phi. \tag{13.2}$$

The σ_Φ values are characteristic of the substituents X_1 and X_2, and ρ_Φ of the reaction series§. Hydrogen is selected as standard substituent, and the standard reaction series is the dissociation of X_1X_2POOH acids in water at 25°.

The σ_Φ values may be a quantitative measure of the joint influence of the inductive effect and the field effect (see section XIV).

Hammett equation for quinoline derivatives. Baciocchi *et al.*[129] have shown that the basic dissociation constants K_a of 6- and 7-substituted 4-chloroquinolines



and the rate constants k_2 of the nucleophilic replacement of chlorine in these compounds by reaction with CH_3O^- in methanol at 75° are related by the formula:

$$\log k_2 = 1.02 \log K_a + 0.12. \tag{13.3}$$

Since the basic dissociation constants of β- and γ-substituted pyridines are represented by a Hammett equation having "normal" σ values[130], the Hammett σ_{epi} and σ_{cata} were calculated from the known value of ρ.

Rate constants for the formation of semicarbazones k_{sem} and oximes k_{ox} from various ketones are related as follows[131]:

$$\log k_{sem} = a + b \log k_{ox}. \tag{13.4}$$

Zahradnik's correlation scheme[132,133] establishes proportionality between values of $\log k/k_0$ for the following reaction series: (1) $X.NCS + OH \rightarrow X.NH.CO.S^-$ in water containing 2% of dioxan; (2) the same reaction in alcohol and water (50% by volume); (3) $X.NCS + n\text{-}C_4H_9NH_2 \rightarrow X.NH.CS.NH.C_4H_9$ in water containing 2% of dioxan; and (4) $CH_3.NCS + X.NH_2 \rightarrow CH_3.NH.CS.NH.X$ in 50% alcohol.

With these reactions, proportionality between $\log k/k_0$ and Taft's σ^* is observed only with a few substituents[133], although the steric factor is absent.

Salomaa's correlation scheme[134] establishes proportionality between values of $\log k/k_0$ for the following reaction series: (1) rate of the acid hydrolysis of dialkoxymethanes $CH_2(OX)_2$ in 0.13 M aqueous HCl; (2) rate of the ethanolysis of alkoxymethyl chlorides $XOCH_2Cl$ in absolute ethanol; (3) this reaction in 53.5% ethanol; and (4) rate of the acid hydrolysis of alkoxymethyl acetates CH_3COOCH_2OX and alkoxymethyl formates $HCOOCH_2OX$ in 0.1–0.15 M aqueous HCl. The steric factor is also absent from these reactions. Correlation with the Taft σ^* values gives a poor result, since the point for $X = ClCH_2CH_2$ falls markedly out of line, this being the only substituent with $\sigma^* > 0$ for which experimental data exist. Salomaa therefore introduced new polar constants for the substituents: $\overline{\sigma}^* \equiv \log k/k_0 = (2.76 \pm 0.36)\sigma^*$, where k and k_0 relate to reaction series 3.

These last two correlation schemes are apparently of the same type. In both cases the substituent X is linked with the reactive centre *via* a heteroatom possessing a lone pair of electrons and therefore capable of polar conjugation both with the reactive centre and with the substituent X if the latter has a suitable structure. It is significant that the reactivity of amines $X.NH_2$ in Zahradnik's reactions correlates not with Taft's inductive constants for the X substituents but with values of $\log k/k_0$ for Zahradnik's

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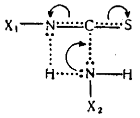
§ The symbols σ and ρ in the original have been replaced by σ_Φ and ρ_Φ to avoid confusion with Hammett's σ and ρ.

reaction series (1). This suggests that the two nitrogen atoms in the activated complex occupy analogous positions:



Zahradnik's $\log k/k_0$ and Salomaa's σ^* values form quantitative measures of the inductive effect and the capacity for polar conjugation, with a -C type of reactive centre, of $X-\ddot{N}<$ and $X-\ddot{\underset{\cdot\cdot}{O}}-$ substituents respectively. The intensity of transmission of the inductive effect through the nitrogen and oxygen atoms may vary with the nature of the substituent X.

Relation between partial rate and selectivity factors. With electrophilic substitution reactions in the benzene nucleus, the following relation has been shown to exist between the partial rate and the selectivity factors[135,136]

$$\log pf = b \log Sf, \tag{13.5}$$

where $S_f = pf/mf$ is the selectivity factor, pf and mf being the relative rates of substitution in the *para* and *meta* positions respectively if the reaction velocity with unsubstituted benzene is taken as unity:

$$pf = k_p/k_0 \text{ and } mf = k_m/k_0.$$

The relation (13.5) is a direct consequence of the applicability of the Hammett equation to these reactions[137-140], since

$$\log pf = \sigma_p/\sigma_m \log mf \text{ or } \log pf = \sigma_p^+/\sigma_m \log mf,$$

and hence

$$b = \frac{\sigma_p}{\sigma_p - \sigma_m} \text{ or } b = \frac{\sigma_p^+}{\sigma_p^+ - \sigma_m^+}.$$

A more detailed review of this question will be found in the monograph by Shatenshtein[141].

Among other correlations having a limited range of application may be mentioned the linear relationship between the infra-red absorption frequencies of the carbonyl group in ketones and the half-wave potentials of the polarographic reduction of the latter[142], the relation between conformational equilibrium and dissociation constants in the case of cyclohexanecarboxylic acids[143], the linear relation between values of $\log K$ for the first and second instability constants of the chelate complexes of di-isobutyl ketone and acetylacetone with various metals[144], and the application of the LFE principle to the reactivity of *trans*-4-substituted-cyclohexanecarboxylic acids and the corresponding methyl esters[144].

XIV. THE PROBLEM OF CALCULATING THE FIELD EFFECT

By the field effect is meant electrostatic interaction between substituent and reactive centre occurring directly through space. It was pointed out in section IV that Taft's σ^* value may contain a term due to the field effect. Apparently partly for this reason, Taft himself terms these quantities aliphatic polar constants of the substituents, in contrast to the Hammett aromatic polar constants σ. However, he also argues that the orientation of the substituent X in space has no effect on the corresponding σ^* value, and hence that this quantity is not associated to any appreciable extent with the field effect[52].

On the other hand, Roberts and Carboni[145] concluded, from a study of the reactivity of substituted (with NO_2 and Cl) phenylpropiolic acids and their ethyl esters, that the field effect forms a considerable proportion of the Hammett σ values. These workers consider that, with a given substituent in the *meta* and *para* positions, internal compensation of the overall influence of the inductive effect and the field effect occurs, since in virtue of the latter effect a *para*-substituent strengthens the inductive effect, while a *meta*-substituent weakens it. In the *ortho* position the relative proportion contributed by each of the above factors varies from one reaction to another (depending, for example, on the distance between the reactive centre and the *ortho*-substituent), which is one of the causes of the "*ortho* effect". A similar view is held by Smith and Larson[146].

Since the literature contains few data on the quantitative separation of the inductive and field effects, Kabachnik's σ_Φ values (see section XIII) are, in the opinion of the present reviewer, of special interest. In the case of aromatic substituents $X.C_6H_4$, the σ_Φ values vary linearly with Taft's σ^0 (see Fig. 4):

$$\sigma_\Phi = -0.48 + 0.78\sigma^0. \tag{14.1}$$

The linear dependence on the Hammett σ value is not nearly as good owing to positive deviations in the case of *C*-substituents. Thus in the case of aromatic substituents the σ_Φ values are equivalent to σ^0 constants and are a measure of the inductive effects of $X.C_6H_4$ substituents, hydrogen being chosen as the standard substituent. Since values

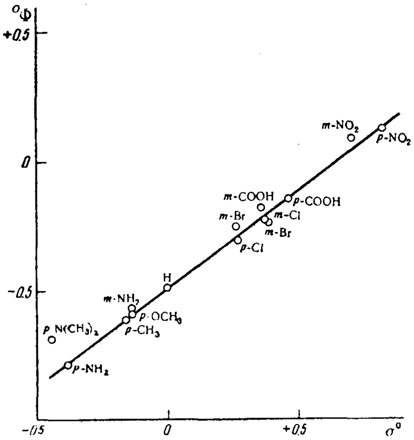


Fig. 4. Linear relation between Kabachnik's σ_Φ values and Taft's σ^0 values for *meta*- and *para*-substituted phenyl compounds.

of σ_Φ are known for a greater number of substituents than are the σ^0 constants, the former can be used to calculate the latter by means of the equation:

$$\sigma^0 = 1.28(\sigma_\Phi + 0.48). \qquad (14.2)$$

Conditions are more complicated with non-aromatic substituents. Values of σ_Φ for hydrogen and all hydrocarbon radicals are related to Taft's σ^* values by the formula (see Fig. 5):

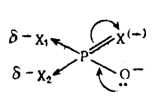
$$\sigma_\Phi = 0.965 + 1.97\sigma^*. \qquad (14.3)$$

Consequently the σ_Φ constants for these substituents also provide a measure of the inherent inductive effect of the latter. The points for all the remaining substituents (OH, CH_2OH, OCH_3, OC_6H_5, CH_2Cl, CH_2Br, CH_2I, $CHCl_2$, CCl_3, CF_3), however, give a poor fit on the straight line representing Eqn. (14.3) (see Fig. 5). The σ_Φ values for these substituents are considerably lower than would be expected from the corresponding σ^* values.

With the phenyl radical, and hence with all the remaining aromatic substituents, there is a marked discrepancy between the aliphatic (σ^*) and the aromatic (σ^0) scales of inductive effects, although the scales have been brought to a common basis. The slopes of the straight lines (14.1) and (14.3) also differ, by a factor of about 2.5, although they should be the same in view of the above identical basis for the σ^* and σ^0 values.

These deviations are of great interest. The possibility of direct conjugation with the reactive centre is excluded because relation (14.1) is obeyed well. Steric effects are also excluded, for otherwise relation (14.3) would not be satisfied for hydrocarbon radicals which have very different values of the steric constants E_S. Steric hindrance, and in most cases the actual nature of the substituents, also exclude the possibility of an intramolecular bond being formed. Among factors known to affect reactivity only the development of a field effect can be invoked to account for these deviations. It is also noteworthy that all substituents for which the σ_Φ values diverge from the "norm" are more electronegative than the methyl group.

In view of all the above, there are grounds for suggesting that these "abnormalities" are caused by electrostatic repulsion of electronegative substituents from negatively charged atoms of oxygen (or sulphur) in anions of acids of the class under consideration:



Such repulsion should act to decrease the stability of these anions, leading to a decrease in the dissociation constant of the acids and in the value of σ_Φ. This does in fact occur.

If this hypothesis is correct, Kabachnik's σ_Φ values are a measure of the combined inductive and field effects inherent in the substituents. Since the σ_Φ values for hydrogen and hydrocarbon radicals obey Eqn. (14.3) very exactly, it follows that no field effect is present with these substituents. Thus in these cases the σ_Φ values are a measure of the inductive effect alone, and Eqn. (14.3) can be used to calculate the inductive components σ_Φ^i in the σ_Φ values for all the remaining substituents. The component σ_Φ^F, due to the field effect, can be found by difference:

$$\sigma_\Phi^F = \sigma_\Phi - \sigma_\Phi^i = \sigma_\Phi + 0.965 - 1.97\sigma^*. \qquad (14.4)$$

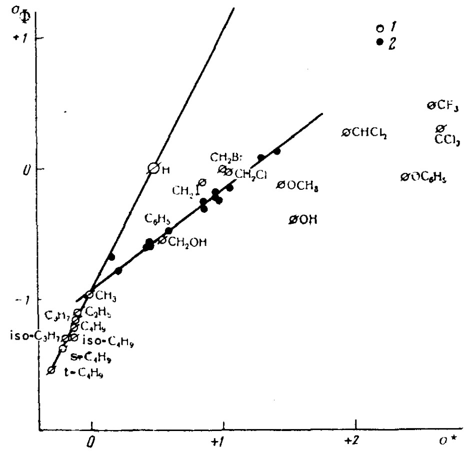


Fig. 5. Relation between Kabachnik's σ_Φ and Taft's σ^* values: ● *meta-* or *para*-substituted phenyl compounds.

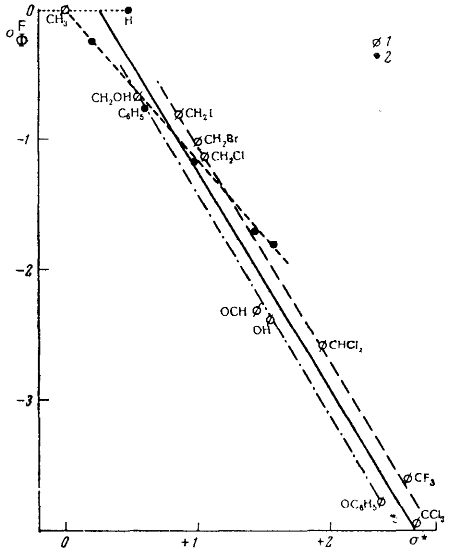


Fig. 6. Variation of the field effect component σ_Φ^F in Kabachnik's σ_Φ values with Taft's σ^* values: ● aromatic substituents.

In absolute magnitude σ_Φ^F is comparable with, and in several cases even greater than, σ_Φ^i.

Fig. 6 shows the variation of σ_Φ^F with Taft's σ^* values, the latter being calculated for aromatic substituents by means of the formula $\sigma^* = 0.600 + \sigma^0$. The first point of interest is the approximate linear relation between σ_Φ^F and σ^*:

$$\sigma_\Phi^F = (+0.40 - 1.63\sigma^*) \pm 0.25. \qquad (14.5)$$

Although all the σ_Φ^F values are grouped about this straight line (the continuous line in Fig. 6), it is obvious that the substituents can be divided into three separate groups — (1) mono-, di-, and tri-halogenated methyls, (2) oxygen-containing substituents (OH, OCH_3, OC_6H_5, and CH_2OH), and (3) aromatic substituents. Within each of these groups there is a very exact linear relation between σ_Φ^F and σ^* (broken lines in Fig. 6). The straight lines for the two groups of aliphatic substituents are parallel and their slope is 1.63, as in Eqn. (14.5). The slope for the aromatic substituents has a lower numerical value of 1.18, and also the line passes through the origin.

To these three groups of substituents should be added a fourth, comprising hydrogen and hydrocarbon radicals, for which σ_Φ^F is zero.

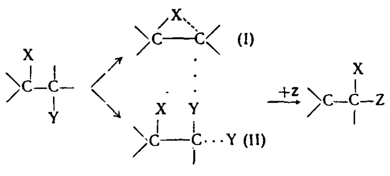
On the basis of the above, the following rules can be formulated as a working hypothesis, and can be usefully borne in mind in considering the problem of the field effect.

1. The influence of the field effect on reactivity may be comparable in magnitude with that of the inductive effect.
2. Hydrogen and hydrocarbon radicals do not interact with the reactive centre by the mechanism of the field effect.
3. The ability of substituents to interact with the reactive centre by the field effect mechanism can be measured quantitatively by Taft's σ^* or σ^0 values, or perhaps by other polar constants of the substituents. All substituents can then be divided into several groups each having its own linear relationship between field effect and σ^*, σ^0, etc.
4. In many cases, therefore, Taft's relations (5.1) and (5.3) and the Hammett equation can evidently take account also of the field effect.
5. These rules can yield far reaching conclusions. It follows from points 2 and 3 that Taft's σ^* values may be on different scales for hydrogen and hydrocarbon radicals on the one hand, and for all electronegative substituents on the other. Different laws are therefore to be expected for these two groups of substituents, as was noted in connection with the damping of the inductive effect (see section IV).

The conclusions reached in this section require to be checked against more extensive experimental results. However, the suggestion that the component due to the field effect can often make a very substantial contribution to the value of $\Delta\Delta F$ is evidently correct.

XV. ANCHIMERIC ASSISTANCE

The term anchimeric assistance¶ denotes the effect exerted on reaction velocity by a substituent X attached to an α-carbon atom relative to the reactive centre:



Anchimeric assistance is observed if the activated complex has structure (I), but is absent from the activated complex (II). A qualitative and semi-quantitative theory of this effect was worked out by Winstein and his collaborators[147,148] and by others. The quantity L' is taken as a measure of this effect:

$$L' = RT \log k/k_c, \qquad (15.1)$$

where k and k_c are rate constants in the presence and in the absence respectively, of anchimeric assistance. Because no exact allowance is made for the inductive effect, estimates of L' given by Winstein are at best semi-quantitative and will not be considered here.

Streitwieser[149] investigated the kinetics of the solvolysis of a series of esters of p-bromobenzenesulphonic acid of the type $X_1X_2CH.O.SO_2.C_6H_4.Br$, *trans*-2-X-cyclohexyl-p-bromobenzenesulphonates, and tertiary alkyl halides. Taft's Eqn. (5.2) applies to all these reactions. Streitwieser was therefore able to determine the magnitude of L' by means of the formula:

$$L' - \log k/k_0 - \rho^*\Sigma\sigma^*. \qquad (15.2)$$

Since anchimeric assistance stabilises the activated complex, L' is always greater than zero. Substituents for which $L' = 0$ do not exhibit anchimeric assistance.

XVI. CORRELATION SCHEMES WITH A VARIABLE REACTIVE CENTRE

The correlation schemes considered so far have been characterised by the fact that only the substituent X in X–Y varied in a given reaction series, while the reaction centre P remained constant. The present section will give correlation equations for reaction series in which the reactive centre varies, while the structure of the substituent can also change. These correlation equations have also been obtained by the use of the LFE.

Formally the Grunwald–Winstein equation[150,151], which served in some sense as a prototype for relationships of analogous form, also belongs to this type. Since this equation represents in essence the dependence of reactivity on the nature of the solvent, it will be considered in section XX. Only cases of bimolecular interaction between reactants will be given here.

The Swain – Scott equation[152] relates to the S_N1 type of nucleophilic substitution reactions in the aliphatic series. A substrate S, capable of undergoing substitution, is attacked by the nucleophilic reagent N. The LFE principle is of the form:

$$\log k_{ij}/k_{ip} = S_i \log k_{0j}/k_{00}, \qquad (16.1)$$

where k_{ij} is the rate constant for reaction between S_i and N_j, k_{i0}, k_{0j}, and k_{00} have an analogous significance, S_0 and N_0 are the standard substrate and standard nucleophilic reagent respectively, and S_i is a constant characterising the sensitivity of the substrate to nucleophilic attack. Denoting $\log k_{0j}/k_{00}$ by n_j, we can write (16.1) as follows:

$$\log k_{ij}/k_{i0} = S_i n_j, \qquad (16.2)$$

where n_j is a constant characterising the nucleophilic character of reagent N_j relative to the standard N_0.

The Swain–Scott equation is not generally applicable, and the degree of nucleophilic character of a reagent N may change on passing from one group of substrates S to another[152].

¶ The term "anchimeric assistance" is used in the American literature[98,124] and is translated into Russian as "immediate proximity effect".

Edwards' equation[153] for the S_N2 type of reaction evidently has a considerably wider range of application. It can also be used to calculate the equilibrium constants of reactions involving the formation of a new covalent bond. The equation is

$$\log k_{ij}/k_{i0} = \alpha E_n + \beta H, \qquad (16.3)$$

where k_{ij} and k_{i0} are velocity or equilibrium constants for the given and the standard nucleophilic reagents respectively, E_n and H are the nucleophilic constant and the relative basic strength respectively of the attacking reagent (electron donor), and α and β are constants characteristic of the substrate.

Values of H are obtained from the basic strengths on the pK_a scale (K_a being the dissociation constant of the corresponding conjugate acid in water) by means of the formula

$$H = pK_a + 1.74, \qquad (16.4)$$

where 1.74 is the value of pK_a for water.

Values of E_n are obtained from the oxidation potentials E_0 of the reagents N by means of the equation

$$E_n = E_0 + 2.60, \qquad (16.5)$$

where 2.60 is the electrode potential of the cell†:

$$2H_2O \rightleftharpoons H_4O_2^{2+} + 2e.$$

Eqns. (16.4) and (16.5) mean that water is regarded as the standard nucleophilic reagent.

Eqn. (16.3) was used by Edwards[153] to correlate the rates of S_N2 reactions at a carbon atom, the rates of substitution reactions at a halogen atom, equilibrium in the formation of complex ions, solubility product, equilibrium in complex formation by iodine with various compounds, and several other reactions. All equilibria are regarded as the substitution of water, co-ordinated with the substrate, by reaction with the nucleophilic reagent.

The nature of E_n is discussed by Edwards[154]. The nucleophilic character of an electron donor depends on the polarisability of its reactive centre and on its basic strength:

$$E_n = aP + bH, \qquad (16.6)$$

where $P \equiv \log R_{\sim}/R_{H_2O}$, $R_{\sim}$ and R_{H_2O} being the molar refractions of the reactive centre of the electron donor and of water respectively, H is given by Eqn. (16.4), $a = 3.60$, and $b = 0.0624$.

Differences between values of E_n calculated by means of Eqn. (16.6) for anions (F^-, Cl^-, Br^-, OH^-, I^-, and S^{2-}) and those obtained from electrode potentials do not exceed 0.06 E_n unit.

Eqn. (16.3) can therefore be transformed as follows:

$$\log k_{ij}/k_{i0} = AP + BH, \qquad (16.7)$$

where $A = 3.60$ and $B = 0.0624\alpha + \beta$.

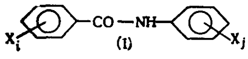
Substantial deviations from the Swain–Scott and Edwards equations are found in reactions between p-nitrophenyl acetate and nucleophilic reagents[155].

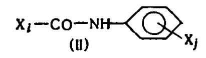
Exner – Horak equation[156,157]. These workers showed that the infra-red absorption frequency of the carbonyl group ν_{CO} in derivatives of carboxylic acids of the type R.CO.Y is given by the formula:

$$\nu_{CO} = kx + q, \qquad (16.8)$$

where k is a constant characteristic of the substituent R, and x is constant for a given class of compounds. Change in the functional group Y in this case corresponds to a change in the reactive centre.

Exner[83] showed that, for compounds of types (I) and (II)


(I)


(II)

the values of k and x vary linearly with the Hammett σ and Taft σ^* constants of the substituents.

With compounds of type (I) the following relations hold:

$$k_i = k_0 + \rho_1\sigma_i^+, \qquad (16.9)$$

$$x_j = x_0 + \rho_2\sigma_j, \qquad (16.10)$$

In the case of compounds of type (II) x_j can be represented by Eqn. (16.10) and

$$k_i = k_0^* + \rho^*\sigma_i^*. \qquad (16.11)$$

Hence with compounds of type (I)

$$\nu_{CO} = (q + k_0x_0) + x_0\rho_1, \ \sigma_i^+ + k_0\rho_2\sigma_j + \rho_1\rho_2\sigma_i^+\sigma_j, \qquad (16.12)$$

where $(q + k_0x_0) = 1678.2$; $x_0\rho_1 = 7.5$; $k_0\rho_2 = 15$; and $\rho_1\rho_2 = 0.7$.

In the case of compounds of type (II)

$$\nu_{CO} = (q + k_0^*x_0) + x_0\rho^*\sigma_i^* + k_0^*\rho_2\sigma_j + \rho^*\rho_2\sigma_i^*\sigma_j, \qquad (16.13)$$

where $(q + k_0^*x_0) = 1697$; $x_0\rho^* = 39.1$; $k_0^*\rho_2 = 16.7$; and $\rho^*\rho_2 = 3.5$ (all frequencies in cm^{-1}).

If the quantity $q + k_0x_0$ is denoted by ν_{CO}^0, it becomes obvious that Eqns. (16.12) and (16.13) represent a particular case of the second solution of (16.12) for cross-correlations having $m = 2$ (see section XXII).

XVII. CORRELATION OF POLAROGRAPHIC HALF-WAVE POTENTIALS

Zuman[158-161] has recently shown that, for many series of organic compounds of the type X–Y (where X is the substituent and Y the electronically active group), the dependence of reactivity on structure is the same for heterogeneous electrode reactions as for homogeneous reactions. A measure of reactivity in this case is the half-wave potential $E_{\frac{1}{2}}$ of polarographic reduction or oxidation. With reversible and irreversible electrode processes $E_{\frac{1}{2}}$ is a measure of the free energy of reaction and of activation respectively.

The general form of the dependence of $\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}} - E_0$ (where E_0 refers to the standard substituent) on structure is written as follows[160]

$$\Delta E_{\frac{1}{2}} = P + M + S. \qquad (17.1)$$

Eqn. (17.1) is a particular case of the relation (3.1), where M represents the effect of various forms of conjugation. The quantity P can be represented by the usual relation $\rho\sigma$, $\rho_I\sigma_I$, or $\rho^*\sigma^*$ according to Hammett or Taft. This applies also to heterocyclic compounds[159,161].

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† This quantity was estimated indirectly by Edwards, using his proposed method of correlation by means of Eqn. (16.3).

In the case of *para*-substituted benzene derivatives the quantity M can be roughly calculated by using the σ^+ or σ^- constants of the substituents.

The dependence of S on structure is given by the equation $S = SE_S$, where E_S represents Taft's steric constants (see section VI). With *meta*- and *para*-substituted benzene derivatives a linear relation is found[160] to exist between the values of E_0 for the unsubstituted benzene derivatives and the corresponding value of ρ, which enables values of $E_{\frac{1}{2}}$ for the substituted derivatives to be estimated from the value of E_0 alone.

These regularities, apart from their great theoretical importance, may serve as a basis for working out the least laborious, and yet reliable, methods for determining new values of constants for substituents.

With NH_2 and NH_3^+ it was necessary to introduce new "polarographic" values of the Hammett σ constants[160].

XVIII. USE OF THE LFE PRINCIPLE FOR RADICAL REACTIONS

A particular case of the LFE principle, known as the Polanyi–Evans rule[162], can be applied to radical reactions, thus establishing a linear relation between energy of activation and heat of reaction in a reaction series of the type

$$R\cdot + X_iY \rightarrow \text{reaction products.}$$

Problems of the application of this rule have been examined in greater detail by Semenov[163].

Several aspects of the application of the LFE rule to reactions involving free radicals were investigated by Bamford *et al.*[164], who subdivided all radical reactions into the following three types:

1. Reactions involving transfer of an atom (or a group) at the same time as electron transfer:

$$R\cdot + XQ \rightarrow RX + Q,$$

where R· is a free radical, and X a hydrogen, halogen, etc. atom.

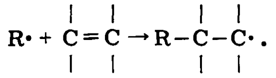
2. Reactions involving electron transfer alone (oxidation–reduction reactions):

$$R\cdot + M^{z+} \rightarrow R^+ + M^{(z-1)+},$$

$$R\cdot + M^{z-} \rightarrow R^- + M^{(z-1)-},$$

where M^z are any ions (metallic or otherwise).

3. Addition of a radical to a double bond:



$$R\cdot + \underset{|}{\overset{|}{C}}{=}\underset{|}{\overset{|}{C}} \rightarrow R{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}\cdot.$$

If XQ is a hydrocarbon in reactions of class 1, only non-polar interaction takes place, and it is necessary to take into account only the non-polar reactivity of the radical R· and the reagent XQ, including the non-polar conjugation in R· and in Q. In all the remaining cases the polar component (induction effect and polar conjugation) also must be allowed for.

The non-polar reactivity of free radicals is characterised by the rate constant $k_{3_1\mathrm{T}}$ for their reaction with toluene at 60° (standard reaction series). The velocity constant $k_{3_1\mathrm{HC}}$ for reaction of a given radical with any other hydrocarbon can then be obtained by simple application of the LFE principle to the overall value $\Delta\Delta F$:

$$\log k_{3_1\mathrm{HC}} = \log\gamma + b\,\log k_{3_1\mathrm{T}}. \qquad (18.1)$$

Since $b = 1$ always, Eqn. (18.1) simplifies to

$$\log k_{3_1\mathrm{HC}}/k_{3_1\mathrm{T}} = \log\gamma \text{ or } k_{3_1\mathrm{HC}} = \gamma k_{3_1\mathrm{T}}. \qquad (18.2)$$

The relationships (18.1) and (18.2) can be regarded as a particular case of the correlation equation for a scheme involving a variable reactive centre. Each free radical is characterised by a $k_{3_1\mathrm{T}}$ value, and each hydrocarbon by $\log\gamma$, which is a measure of its non-polar reactivity. In most cases the accuracy of the correlation does not exceed ±20%, the maximum deviations resulting in an error not exceeding a factor of 3, whilst the range of variation of $k_{3_1\mathrm{HC}}$ exceeds a factor of 10^6.

When the polar component in the value of $\Delta\Delta F$ (induction effect and polar conjugation) must also be taken into account, the velocity constant k_3 for reactions of classes 1 and 3 is given by the formula

$$\log k_3 = \log k_{3_1\mathrm{T}} + \alpha\sigma_p + \beta, \qquad (18.3)$$

where α and β are constants characteristic of the reagent attacked by the free radical, and σ_p is the Hammett *para* constant for the substituent in the free radical. Eqn. (18.1) is a particular case of (18.3) when $\alpha = 0$. Hence $\beta = \log\gamma$. Values of $\log k_{3_1\mathrm{T}}$ are regarded as a measure of the energy of dissociation at the R–X bond, and β as a measure of the energy of dissociation at the Q–X bond.

Bamford's equation (18.3) confirms that the principle of the independence and the additivity of the individual components in $\Delta\Delta F$ and the LFE rule are valid also in radical reactions.

Reference must also be made to the equation of Levy and Szwarc[165]: $\log k_{ij} = n\,\log k_{0j}$, where i and j relate to the free radical and the hydrocarbon respectively (for details see ref. 166).

XIX. CORRELATION OF DIPOLE MOMENTS

The correlation of dipole moments by means of the various polar constants of substituents is of great theoretical value for an understanding of the physical meaning of these constants. Taft[10] managed to correlate the dipole moments of compounds of the type R–Y, where R is a hydrocarbon radical or hydrogen, by means of the equation $\mu - \mu_0 = \rho^*\Sigma\sigma^*$. Not altogether successful attempts were also made to correlate the dipole moments of aromatic compounds with the Hammett σ parameters[167,168]. As Exner[115] has shown, simple correlation of dipole moments with σ values is not justified, since the latter take into account only variation in charge (electron density) on the atom or group Y, whereas the dipole moment also depends to a considerable extent on the distance between charges of opposite sign. By allowing for the distance d between the charges, Exner[115] showed the possibility of a satisfactory linear correlation between the values of μ/d and Taft's σ^* constants for the substituents X in the series X–Cl, where X should not possess an appreciable internal dipole moment. He showed a similar correlation for μ/d and the corresponding σ_I in the series $X{-}CH_3$ and $X{-}C_6H_5$.

In the case of various aromatic compounds of the type $X{-}C_6H_5$, where X is any substituent, the component of the dipole moment due to polar conjugation, μ_c, is connected with the constants of the substituents by the relation:

$$\mu_c/d_c = \rho\sigma_c^{+,-}. \qquad (19.1)$$

The symbol $\sigma_c^{+,-}$ means that σ_c^+ values must be used in the case of +C substituents, and σ_c^- values in the case of -C substituents. Values of μ_c are given by the difference $\mu_c = \mu_{Ar} - \mu_{Alk}$, where the μ_{Ar} are the dipole moments of the $X-C_6H_5$ compounds, and the μ_{Alk} those of the $X-CH_3$ compounds.

Exner suggested the following general formula for the dependence of dipole moments on the polar constants of substituents:

$$\vec{\mu} = \vec{\mu}_0 + \rho_I\overrightarrow{d_I}\sigma_I + \rho_c\overrightarrow{d_c}\sigma_c^{+,-}, \qquad (19.2)$$

where d_I is the distance between the charges due to the inductive effect (usually the length of the X–Y bond) and d_c the distance between those due to polar conjugation.

Since the dipole moments of molecules are solely a function of the charge distribution in the latter, Exner's equations given in this chapter indicate that the σ^*, σ_I, σ_c^+, and σ_c^- values define quantitatively the ability of the corresponding substituents to acquire a negative or a positive charge. Hence these parameters have in fact the physical meaning which is ascribed to them.

XX. SOME QUANTITATIVE ASPECTS OF THE DEPENDENCE OF REACTIVITY ON THE NATURE OF THE SOLVENT

The preceding sections have discussed the dependence of the reactivity of organic compounds on their structure. The problem of the dependence of reactivity on the medium in which the reaction takes place is of no less importance, as was pointed out at an early date by Menshutkin[169,170].

The dependence of rates and equilibria on the nature of the solvent will be examined below only for reactions for which the mechanism is independent of the solvent. The problem is then reduced to finding the dependence of the activity coefficients of the activated complex (or reaction products) and of the initial compounds on the properties of the solvent. Only the appropriate activity coefficient ratios need to be known[12].

The influence of the solvent on the activity coefficient of a solute can be of two types. On the one hand, dissolved species interact with the electrostatic field of the surrounding solvent molecules, without preferential interaction with any of the latter (the field, of course, is produced mainly by the neighbouring solvent molecules, but this is not what is meant). Such interaction is termed a non-specific solvation effect, of which polar and non-polar types must be distinguished. The former is purely electrostatic in nature, and involves interaction of electric charges existing on polar solvent and solute molecules (dipole–dipole or ion–dipole interaction). The latter type is based on interaction of dispersion forces between non-polar components of the solution.

In addition to non-specific solvation there can also be specific interaction between solvent molecules and solute species — formation of hydrogen bonds, complex formation, unbalanced fluctuations in concentration of the components of a mixed solvent around solute species, etc.

The problem of the quantitative assessment of non-specific polar interaction between solvent and solute will be discussed below. The main results have been obtained for nucleophilic substitution reactions of type S_N1, and are based on the work of Ingold, Hughes, and their collaborators[171-175] on the mechanism of this class of reactions.

The Grunwald – Winstein activity postulate[150,151,176-178]. These workers found that the following form of the LFE rule can be applied to solvolysis reactions occurring by an S_N1 mechanism in different solvents:

$$\log k_{ij}/k_{i0} = m_i \log k_{0j}/k_{00}, \qquad (20.1)$$

where k_{ij} is the velocity constant for solvolysis of the i-th solute in the j-th solvent, the subscripts 0 denoting the standard solute (t-butyl chloride) and the standard solvent (80% ethanol by volume), and m_i is a constant depending solely on the nature of the i-th solute. The value of $\log k_{0j}/k_{00}$ for t-butyl chloride is denoted by Y_j. Remembering that $k_{ij}/k_{i0} = \gamma_{ij}/\gamma_{\neq ij}$, where γ_{ij} and $\gamma_{\neq ij}$ are the activity coefficients of the i-th reactant and the corresponding activated complex respectively in the j-th solvent, and taking a solution in 80% ethanol as the standard state, we can write the Grunwald–Winstein equation as follows:

$$\log k_{ij}/k_{i0} = \log\gamma_{ij}/\gamma_{\neq ij} = m_iY_j. \qquad (20.2)$$

This relationship represents the so-called activity postulate, since it establishes the form of the dependence of the activity coefficient ratio on the nature of the solvent. This last is characterised by the parameter Y, termed the "ionising power" of the solvent. The reactant is characterised by the parameter m.

It is clear from the standard conditions that in 80% ethanol $Y \equiv 0$, and for t-butyl chloride $m = 1$. The value of Y for some one solvent other than the standard can be chosen arbitrarily.

Eqn. (20.2) is satisfied by the alkyl halides. The deviations observed in several cases, especially with alkyl fluorides and derivatives containing phenyl groups, were explained by the formation of hydrogen bonds with the solvent molecules and by the effect of "reassociation of ion pairs"[178]. Owing to this effect the true rate of ionisation by the S_N1 mechanism found from formula (20.2) is greater than the measured "titration" reaction velocity.

The choice of $(CH_3)_3CCl$ as basis for the scale of Y values is linked with Winstein and Grunwald's view that the solvolysis of this compound is truly unimolecular. In this case the "titration" velocity coincides with the rate of ionisation[172].

There is no definite relation between the Y values and the dielectric constants of the solvents[146].

Reference must be made to the work of Kosower[179-181], who showed that the quantity $Z = h\nu_{max}$, where ν_{max} is the absorption frequency for a solution of a very polar compound (*e.g.* pyridine oxide), varies linearly with the Y values for the corresponding solvents.

The activity postulate was used also to obtain the quantitative dependence of dissociation constants of acids on the nature of the solvent[182-184]. "Activity functions" Y_0 and Y_- were introduced. With the carboxylic type of acids (charge on conjugate base $Z = -1$)

$$pK_{AH}^S - pK_{AH}^0 = \log f_H^S + m_{A^-} - Y_-. \qquad (20.3)$$

With acids of the type of substituted ammonium ions (charge on conjugate base $Z = 0$)

$$pK_{BH^+}^S - pK_{BH}^0 = \log f_H^S + m_BY_0. \qquad (20.4)$$

The symbols S and 0 indicate the given solvent and the standard solvent respectively, f_H^S is the degenerate activity coefficient of the proton in the given solvent, m_{A^-} and m_B are constants characteristic of the given acids, and Y_- and Y_0 are constants characteristic of the given solvent. It must be stressed that

$$\log \gamma_{A^-}/\gamma_{AH} = m_{A^-}Y_- \text{ and } \log \gamma_B/\gamma_{BH^+} = m_B Y_0. \quad (20.5)$$

In media to which Hammett's acidity function is applicable, both activity functions vanish:

$$Y_- = Y_0 = 0; \quad (20.6)$$

since water is selected as standard solvent, condition (20.6) is assumed for it.

The values of m_{A^-} for *meta*- and *para*-substituted benzoic acids, and of m_B for *meta*- and *para*-substituted anilines have been shown to be related linearly with the Hammett σ values[182,183]. From this were obtained the following relations between Hammett's ρ values and Y_0 and Y_-

$$\rho = \rho_0 + \beta_0 Y_0; \quad \rho = \rho_0 + \beta_- Y_-, \quad (20.7)$$

where ρ_0 is the value of ρ in the standard solvent (water), β_0 and β_- are constants having very similar numerical values for substituted benzoic acids and substituted anilines (+0.628 and -0.57 respectively).

Brownstein[185] showed that a somewhat modified Grunwald–Winstein equation was of wide application. His equation is

$$\log k_{ij}/k_{i0} \text{ (or } \nu_{ij} - \nu_{i0}) = S_j R_i, \quad (20.8)$$

where the k terms are velocity or equilibrium constants, the ν terms are ultra-violet or infra-red absorption frequencies, and i and j denote the compound and the solvent respectively. Absolute ethanol was selected as standard solvent ($R \equiv 0$), the standard compound being 1-methyl-4-methoxycarbonylpyridinium iodide (ultra-violet absorption $S \equiv 1$).

Swain's equation. In the opinion of Swain and his collaborators, a definite borderline cannot be drawn between S_N1 and S_N2 mechanisms[186-190]. They therefore regard Eqn. (20.2) as a particular case. With different types of reagents it would be necessary to introduce several scales of Y values for the same solvents[152,191]. A more general equation[152,192] containing four parameters is therefore proposed:

$$\log k/k_0 = Sn + S'e \quad (20.9)$$

or

$$\log k/k_0 = c_1 d_1 + c_2 d_2,$$

where k is the velocity constant of the reaction in the presence of the given nucleophilic (N) and electrophilic (E) reagents, k_0 is the rate constant in the presence of the standard nucleophilic (N_0) and electrophilic (E_0) reagents, n and e (d_1 and d_2) are constants measuring the nucleophilic character of N and the electrophilic character of E respectively, and S and S' (or c_1 and c_2) are constants representing, according to the authors' treatment, the "sensitivity" of the reagent to the action of nucleophilic and electrophilic reagents respectively. When Sn is constant,

$$\log k/k_0 = S'e, \quad (20.10)$$

and, assuming that $S' = m$ and $e = Y$, Eqn. (20.9) reduces to (20.2). If $S'e$ is constant (when, for example, water present in excess acts as the electrophilic reagent), Eqn. (20.9) reduces to (16.2).

Swain and Dittmer[193] proposed a special equation containing two parameters for the rates of solvolysis of organic chlorides or bromides:

$$\log k_{ij}/k_{i0} - \log k_{0j}/k_{00} = a_i b_j, \quad (20.11)$$

where the subscript i refers to the reagent, j to the solvent, and 0 to the standard reagent (methyl bromide) and the standard solvent (80% ethanol).

Swain's views on the S_N type of reaction mechanism, including the termolecular character of reactions previously assigned to the S_N class, have been critically analysed by Hughes and Ingold and their collaborators[194,195] and by Winstein *et al.*[178] These workers discovered errors in the experimental data quoted by Swain and in his treatment of the data, and on the basis of additional experimental results they showed several of his conclusions to be incorrect. Eqn. (20.9) is apparently a purely empirical formula, and no concrete physical meaning can be ascribed to the parameters on its right-hand side.

The problem of the interrelationship between the polarity of a solution and its dielectric constant was examined in greater detail by Rudakov[196]. He has shown that the dielectric constant D is not a universal measure of the polarity of a solvent. For this purpose he proposes another empirically defined quantity D_0, which is equal to D only in the case of alcohols and water.

Reference must also be made to correlation equations obtained in using the theory of regular solutions[197] to calculate activity coefficients.

McGowan's equation[198]. This is

$$\log f_2/f_1 = \log c_2/c_1 = k_M P, \quad (20.12)$$

where f_2 and f_1 are the activity coefficients of the solute in the immiscible solvents 2 and 1 respectively, the concentration ratio c_2/c_1 is equal to the partition coefficient of the solute between these solvents, k_M is a constant characteristic of the given pair of solvents, and P is the parachor of the solute, taken as a measure of its molecular volume. Eqn. (20.12) allows for the non-polar non-specific (dispersion) interaction between solvent and solute.

Deno and Berkheimer[199] tested Eqn. (20.12) with a number of compounds. The molar concentration of a given pure substance "in itself" was taken as c_1, while c_2 represented the concentration of a saturated solution of this substance in water. Eqn. (20.12) proved to be applicable to liquid aromatic and aliphatic, solid aromatic, and gaseous aliphatic hydrocarbons, as well as to halogenated aliphatic and aromatic hydrocarbons. With all these compounds and water as the second component, k_M had a value of ~0.0130 at 25°.

In the presence of some specific interaction between the solute and water (for example, a hydrogen bond), a term $E_A = E_H/2.3RT$, where E_H is the energy of the specific interaction, must be added to the right-hand side of Eqn. (20.12):

$$\log c_2/c_1 = k_M P + E_A. \quad (20.13)$$

The above value of k_M is retained. It is also found that E_A has an approximately constant value for compounds having the same functional group.

Eqn. (20.13) is applicable to ethers and esters, aldehydes and ketones (apart from the lower members), nitriles and nitro compounds[199]. With all these classes of compounds, it is apparently no longer possible to neglect the polar non-specific interaction: in this connection, the applicability of

Eqn. (20.13) with the value of k_M unchanged is not altogether easy to understand. Perhaps the term E_A roughly takes into account also the energy of polar interaction.

Rudakov's equation[200,201]. This worker gives fresh proofs that solvolysis of t-butyl chloride is a truly unimolecular reaction, and that its mechanism does not undergo substantial changes on passing from such a polar solvent as water to the gas phase. The influence of solvents on the velocity of this reaction (the change in rate on passing from water to the gas phase amounts to a factor of $10^{19.5 \pm 2}$) may be considered a result of polar non-specific interaction of the reagent and the activated complex with the solvent.

From the theory of regular solutions, the activity coefficient of a dissolved substance, *e.g.* $(CH_3)_3CCl$, can be expressed as follows[199,200]:

$$RT \ln\gamma_1 = V_1^{2/3}(\Pi_1 - \Pi_C)^2, \qquad (20.14)$$

$$\Pi_1 = E_1^{1/2}V_1^{-1/3}; \quad \Pi_C = E_C^{1/2}V_C^{-1/3},$$

where V_1 is the molar volume of the solute in the pure state, E_1 is the molar energy of the pure solvent, and V_C and E_C are the corresponding quantities for the dissolved substance.

The quantities Π_1 and Π_C are called polarity factors.

An expression analogous to (20.14) is assumed for the activated complex:

$$RT \ln\gamma_{\neq} = V_{\neq}^{2/3}(\Pi_{\neq} - \Pi_C)^2. \qquad (20.15)$$

Eqns. (20.14) and (20.15) give values of γ_1 and $\gamma_{\neq}$ referred to the corresponding pure liquids[‡] as standard states. If a solution in some solvent is chosen as the standard state, the activity coefficients relative to this new standard are given by the following expressions:

$$2.3RT \log\gamma_1^0 = V_1^{2/3}[2\Pi_1(\Pi_0 - \Pi_C) + \Pi_C^2 - \Pi_0^2] \qquad (20.16)$$

and

$$2.3RT \log\gamma_{\neq}^0 = V_{\neq}^{2/3}[2\Pi_{\neq}(\Pi_0 - \Pi_C) + \Pi_C^2 - \Pi_0^2], \qquad (20.17)$$

where Π_0 is the polarity factor of the standard solvent.

In the case of a unimolecular reaction, the velocity constant k_C in an arbitrary solvent is connected with the velocity constant k_0 in the standard solvent by the relation[12]

$$k_C/k_0 = \gamma_1^0/\gamma_{\neq}^0. \qquad (20.18)$$

On substituting γ_1^0 and $\gamma_{\neq}^0$ from (20.16) and (20.17) in (20.18) and assuming that $V_1 = V_{\neq}$ (such equality is approximately true in the case of t-butyl chloride[200]), we have

$$\log k_C/k_0 = V_1^{2/3}/2.3RT(\Pi_{\neq} - \Pi_1)(\Pi_C - \Pi_0) \qquad (20.19)$$

Eqn. (20.19) represents in essence the Grunwald–Winstein equation (20.2) deduced theoretically: Y_C is given by the expression (20.19), and

$$m_i = V_i^{2/3}(\Pi_{\neq i} - \Pi_i)V^{2/3}(\Pi_{\neq} - \Pi_1)$$

if the subscript 1 refers to t-butyl chloride, and the subscript 0 to 80% ethanol.

If the gas phase is taken as the standard medium, the quantity Π_0 becomes zero. It follows from this that the polarity factor Π_C is the natural absolute measure of the intensity of polar interaction in a pure liquid.

Using experimental rate constants for the solvolysis of t-butyl chloride, Rudakov calculated values of Π_C for various pure liquids and also values of Π_1 and Π for t-butyl chloride[200,201].

Values of Π_C for water and alcohols of general formula X–OH show very good linear dependence on Taft's σ^* values for the substituents X (see Fig. 7):

$$\Pi_C = 0.740 + 0.480\sigma^*. \qquad (20.20)$$

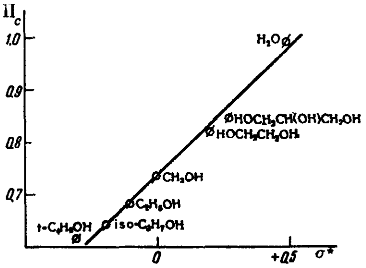


Fig. 7. Linear relation between Rudakov's polarity factors Π_C for alcohols X–OH and Taft's σ^* values for the substituents X.

This confirms the physical significance of the Π_C values as a measure of the capacity of a substance for polar non-specific interaction. It also gives grounds for hoping that the dependence of Π_C on the structure of the corresponding compounds can be considered on the basis of the principles which have been applied to the dependence of reactivity on structure, which is of great practical importance.

A universal scale for the effect of solvents on the electronic spectra of organic compounds has been given by Zhmyreva *et al.*[23]

XXI. FREE ENERGY AS THE SOLE UNIVERSAL MEASURE OF REACTIVITY

In the preceding sections the free energy ΔF of activation or reaction has been considered in nearly every case as the measure of reactivity. ΔF is a complicated quantity depending on the enthalpy ΔH and the entropy ΔS of activation or reaction: $\Delta F = \Delta H - T\Delta S$. Alternatively, ΔF can be regarded as a sum of terms representing the changes in potential energy (ΔEp) and in kinetic energy ($R \ln \Pi Q$) during activation or reaction.

The quantities ΔH and ΔS are in principle different in character, and should depend in different ways on the structure of the reactants.

[‡] $\gamma_{\neq} = 1$ in a hypothetical liquid consisting entirely of activated complexes.

Hammett himself[4] pointed out that the inductive effect and the various forms of conjugation should affect reactivity, producing corresponding changes in the energetic factor (energy of activation or heat of reaction). The experimental results, however, disproved this§ [4]. Hammett attempted to find a way out by referring to the frequently observed empirical rule[4,202-204] of a linear relation between ΔH and ΔS. Recently[205] a theoretical basis has also been given to this rule in the case of condensed systems. Taft[10] suggests that this rule is widely applicable also in the aliphatic series.

However, data are now available suggesting that in many cases the changes in reactivity are caused mainly by changes in the entropy factor, the linear relation between ΔS and ΔH being absent[37,206,207]. The correlation equations of Taft and of Hammett remain applicable.

Ingold[7] and also Taft[10] consider that electronic effects influence the magnitude of $\Delta\Delta Ep$, which in most cases cannot be measured. Taft concludes that $\Delta\Delta F$ is a better measure of $\Delta\Delta Ep$ than is $\Delta\Delta H$.

The fact that the Arrhenius activation energy frequently has no definite physical meaning was pointed out as early as 1939 by Selivanova and Syrkin[208].

The factual material which has accumulated by now suggests strongly that it is to the free energies that the correlation equations examined above are applicable, as is postulated by the LFE principle, independently of how ΔH and ΔS vary individually, and of the relation existing between these quantities. It is impossible by considering ΔH and ΔS separately to obtain quantitative relations having such a wide range of application as has the LFE rule.

From the above it can be concluded that at the present time the only universal measure of reactivity which can serve as a basis for a quantitative theory in organic chemistry is the value of ΔF (in practice, $\log k$). This statement does not, of course, mean that determinations of energy of activation or enthalpy of reaction and entropy of activation or reaction are not of great importance. It is emphasised merely that, so far, it is impossible to base a quantitative theory on independent (or even interdependent) correlation schemes involving either only energetic or only entropic terms. In view of this, it must always be remembered that electronic "effects" are as much "entropic" as they are "energetic".

The above principles can evidently be extended to the theory of the dependence of reactivity on the nature of the solvent[209].

XXII. PRACTICAL EFFICIENCY OF LINEAR CORRELATION EQUATIONS

All the main correlation equations examined above can be written in the form

$$A_{ij} = A_{0j} + \sum_k \alpha_{jk}\beta_{ik}, \tag{22.1}$$

where $A_{ij} = \log k_{ij}$ or some physical parameter of the given compound, A_{0j} is a similar function for the standard compound in a given series, β_{ik} are parameters characteristic of the i-th compound (constants of the substituents), j represents the reaction series, and k the factor influencing the reactivity (inductive effect, etc.).

An equation of type (22.1) can always be converted to the form

$$\sum_k A_{ijk} = \sum_k (A_{0jk} + \alpha_{jk}\beta_{ik}). \tag{22.2}$$

Instead of (22.2) we can write a series of independent equations

$$A_{ijk} = A_{0jk} + \alpha_{jk}\beta_{ik}. \tag{22.3}$$

Study of the properties of Eqn. (22.1) can therefore be reduced to that of the properties of (22.3). The latter is similar in form to the Taft equation (5.1) or the Hammett equation (9.1). Below, therefore, we shall consider only an equation of the Hammett type

$$\log k_{ij}/k_{0j} = \rho_j\sigma_i. \tag{22.4}$$

In this section the properties of an equation of the type (22.4) will be examined to assess the practical possibility of including a sufficiently large number of organic reactions with the correlation equations discussed in the preceding sections.

The chief problem which arises here is the practically unlimited number of possible organic reactions. Consequently, the number of velocity and equilibrium constants which must be known for a quantitative characterisation of these reactions is also unlimited.

In this connection the most relevant property of an equation of the type (22.4) is that the experimental determination of a certain number N_0 of parameters for certain compounds of a given series (velocity constants, etc.) makes it possible to calculate an even larger number N of analogous parameters for other compounds in this series, providing that the appropriate σ values are known. The greater the ratio N/N_0 the greater the practical usefulness of the correlation. The quantity $N/N_0 = \varphi$ can be termed the efficiency of the correlation. Clearly, if N is a very large number, φ too must be quite large, so that the task of the experimental determination of N_0 parameters should not go beyond the bounds of practical possibility.

The position will be different in this respect if reaction series of a different type are considered. In this case the reaction series is characterised by the number m of independent substituents X_i whose structure can be varied without leaving the given reaction series. In this sense the simplest case is provided by reaction series for which $m = 1$, of the type

$$X_i - Y_i + a \rightarrow \text{reaction products.}$$

To this belong all unimolecular reactions (a absent) and those bimolecular processes in which the structure of one of the reactants remains unchanged, *e.g.* $a = Cl^-$, etc. In this case the number of quantities to be correlated ($\log k_{ij}$) is equal to the number n of substituents having known σ_i constants, which are universal parameters, and for the present will not be included in the assessment of φ. Hence $N = n$, $N_0 = 2$ (ρ and $\log k_{0j}$), and $\varphi = \frac{1}{2}n$. For correlation it is necessary to know two specific parameters for each reaction series and n universal parameters; n should be sufficiently large to cover all substituents which are in practice met relatively often.

The problem of cross correlations investigated by Miller[210] is more complicated. He uses graphical analysis to solve the general problem of the superposition of

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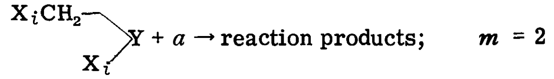
§ The widely held view that the applicability of the Hammett equation is explained by constancy of the entropy factor is erroneous.

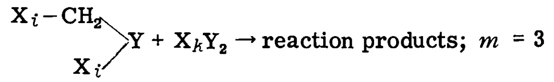
several correlation equations. The essentials of the final formulae which he obtained will be given below, but solutions will be obtained analytically, which will make it easier to understand the physical meaning of the parameters in these formulae.

With such reaction series, $m > 1$, for example

$$X_i - Y_1 + X_j - Y_2 \rightarrow \text{reaction products}; \quad m = 2$$



$$(X_iCH_2)(X_i)Y + a \rightarrow \text{reaction products}; \quad m = 2$$



$$(X_i{-}CH_2)(X_i)Y + X_kY_2 \rightarrow \text{reaction products}; \quad m = 3$$

etc.

If $m = 2$, we have

$$\log k_{ij}/k_{0j} = \rho_{(-j)}\sigma_i, \qquad (22.5)$$

$$\log k_{ij}/k_{j0} = \rho_{(i-)}\sigma_i. \qquad (22.6)$$

Eqns. (22.5) and (22.6) cover every possible k_{ij} if all k_{0j} and $\rho_{(-j)}$ ($j = 0, 1, \ldots, n$) or all k_{i0} and $\rho_{(i-)}$ ($i = 0, 1, \ldots, n$) are known. In other words, a complicated reaction series can be divided into n simple reaction series. It would appear at first sight that $2n$ specific and n universal parameters would have to be known for correlation, φ retaining the same value as in the case of a simple reaction series in which $m = 1$. Actually, however, the value of φ is considerably larger owing to the overlapping of the two equations (22.5) and (22.6). On combining these in a different sequence we obtain

$$\log k_{ij}/k_{00} = \rho_{(-j)}\sigma_i + \rho_{(0-)}\sigma_j = \rho_{(-0)}\sigma_i + \rho_{(i-)}\sigma_j. \qquad (22.7)$$

This equation has two solutions, the first of which is

$$\rho_{(-j)} = \rho_{(-0)} \text{ and } \rho_{(i-)} = \rho_{(0-)}.$$

Hence

$$\log k_{ij}/k_{00} = \rho_{(-0)}\sigma_i + \rho_{(0-)}\sigma_j, \qquad (22.8)$$

where $\rho_{(-0)}$ and $\rho_{(0-)}$ are "sensitivity" constants for the following simple reaction series

$$X_i - Y_i + X_0 - Y_2 \rightarrow \text{reaction products};$$

$$X_0 - Y_1 + X_j - Y_2 \rightarrow \text{reaction products}.$$

The second possible solution can be written in the form

$$\frac{\rho_{(i-)} - \rho_{(0-)}}{\sigma_i} = \frac{\rho_{(-j)} - \rho_{(-0)}}{\sigma_j}, \qquad (22.9)$$

whence we obtain

$$\rho_{(i-)} = (\rho_{(-k)} - \rho_{(-0)})\sigma_i/\sigma_k + \rho_{(0-)} \qquad (22.10)$$

and

$$\rho_{(-j)} = (\rho_{(k-)} - \rho_{(0-)})\sigma_j/\sigma_k + \rho_{(-0)}, \qquad (22.11)$$

where k refers to some arbitrarily chosen substituent. Keeping k constant, we can calculate all the $\rho_{(i-)}$ or $\rho_{(-i)}$ values. On substituting (22.10) and (22.11) respectively in (22.7) we obtain

$$\log k_{ij}/k_{00} = \rho_{(-0)}\sigma_i + \rho_{(0-)}\sigma_j + \frac{\rho_{(-k)} - \rho_{(-0)}}{\sigma_k}\sigma_i\sigma_j \qquad (22.12)$$

and

$$\log k_{ij}/k_{00} = \rho_{(-0)}\sigma_i + \rho_{(0-)}\sigma_j + \frac{\rho_{(k-)} - \rho_{(0-)}}{\sigma_k}\sigma_i\sigma_j.$$

If the first solution is adopted, a reaction series having $m = 2$ is correlated by three specific parameters ($\rho_{(-0)}$, $\rho_{(0-)}$, and $\log k_0$) and $\varphi = n^2 : 3$. With the second solution a further specific parameter $\rho_{(k-)}$ (or $\rho_{(-k)}$) is added, and $\varphi = n^2 : 4$.

The physical meaning of the two solutions is as follows. If for some value of k, $\rho_{(-k)} \neq \rho_{(-0)}$ or $\rho_{(k-)} \neq \rho_{(0-)}$, this inequality must necessarily extend to all the remaining values of k, and Eqn. (22.12) must be used. If in the case of some one value of k, $\rho_{(-k)} = \rho_{(-0)}$ or $\rho_{(k-)} = \rho_{(0-)}$, such equality holds for all other values of k as well. In such a case (22.12) reduces to (22.8), and the first solution can be used.

When X_i and X_j are arranged symmetrically relative to the reactive centre, solution (22.8) reduces to the additivity rules considered in sections IV and IX. Jaffe[221] used (22.8) also in the case of two substituents in two benzene nuclei linked unsymmetrically to the reactive centre, and obtained a satisfactory result. The first solution proved to be applicable also in the case of the reaction series involving interaction of *meta*- and *para*-substituted diphenyldiazomethanes with *meta*- and *para*-substituted benzoic acids[212].

The problem of the choice between the first and the second solutions has been discussed by Exner[83]. He gives an actual example in which it is necessary to use a formula of the type (20.12) (see section XVII). He shows that the first solution cannot be applied universally.

The case in which $m = 3$ can be considered in an analogous manner to the above[210].

XXIII. CONCLUSION

Consideration of the information given above indicates that the LFE rule and the principle of the independence and the additivity of the individual terms of $\Delta\Delta F$ can be used for a quantitative investigation of the dependence of the reactivity of organic compounds on their structure, and also on the nature of the solvent, for a great variety of types of compounds and reactions. In several cases the Hammett and Taft equations (involving the polar and the steric components) can be used only when preparative data are available (percentage yield)[213].

Consequently we are dealing with quite general, although possibly approximate, laws of Nature, which can be regarded as the basis for a very general quantitative theory of the reactivity of organic compounds. An important point is that this theory utilises several well-known qualitative ideas about the structure and the reactivity of these compounds, so that in most cases the various constants in the correlation equations can be given a concrete physical meaning. Therefore the LFE rule and the additivity principle provide not only a means for practical calculations but also an extremely useful tool for investigating problems of the detailed structure of organic compounds and of the mechanisms of reactions.

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POLYMERIC CO-ORDINATION COMPOUNDS

I. Haiduc

CONTENTS

INTRODUCTION

The widespread practical application of polymeric compounds and theoretical aspects of polymer chemistry have governed the development of research in this field during recent years. At the present time a great deal of attention is being paid to inorganic and organo-elementary polymers.

Application of the concept of polymerism to inorganic chemistry is one of the factors which has recently determined progress in this branch of chemistry and influenced our ideas on the relation between organic and inorganic chemistry. Whereas in 1952 it was considered[1] that "organic chemistry is the science of a more highly organised form of matter than is inorganic chemistry" and "inorganic chemistry is mainly concerned with relatively simple molecules", this would not be correct today. Many structures known only in organic chemistry became known also in inorganic molecules, for example cyclic[2,3] and macromolecular[2,4-14] inorganic polymers, etc. Determination of the molecular weight and study of the structure of inorganic compounds, such as $PdCl_2$, $CuBr_2$, $Be(CH_3)_2$, has shown that they are often polymers. Many salts do not have a discrete structure (do not consist of independent ions or molecules), but are polymers having covalent or co-ordinate bonds more or less ionic in character.

The inorganic polymers to which we had been accustomed were mainly derivatives of non-metals, the macromolecular skeleton of which was formed by normal covalent bonds. Published reviews[2,4-8] with a few exceptions[4,10] consider only these inorganic polymers. However, the following considerations show that it is also possible to obtain polymers in which the molecular skeleton is formed by co-ordinate links.

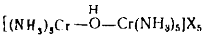
Since it is immaterial whether the two electrons of a covalent bond originate from the same atom or from two different atoms, a co-ordinate link does not differ fundamentally from a "normal covalent bond".[15,16] Because of the displacement of the electrons, the formation of a co-ordinate link involves the appearance of electric charges (whence the name "semipolar bond"). For example

covalent bond BN: $R_2B—NR_2$,

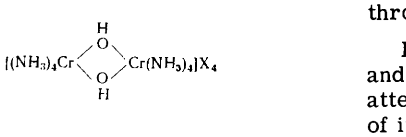
co-ordinate link BN: $R_3B \leftarrow NR_3$ or $R_3\overset{-}{B}—\overset{+}{N}R_3$.

Consequently, the existence of high polymers formed by normal covalent bonds leads to the conclusion that such polymers can be formed also by co-ordinate links[17].

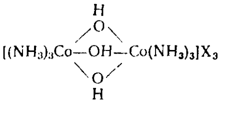
As early as the classical period of the chemistry of complex compounds, polynuclear complexes were synthesised in which the co-ordinate octahedra were joined by common corners, edges, or faces: *i.e.* in which one, two, or three bridging bonds are formed between the central atoms, for example



$[(NH_3)_5Cr—\overset{H}{O}—Cr(NH_3)_5]X_5$



$[(NH_3)_4Cr(OH)_2Cr(NH_3)_4]X_4$



$[(NH_3)_3Co(OH)_3Co(NH_3)_3]X_3$

It can be concluded that several co-ordination centres can be joined by such bridging bonds. For a long time the chemistry of complex compounds was unable to determine whether it is possible to obtain polymers of high molecular weight based on this principle.

Co-ordinate links increase the number of bonds between atoms by involving a larger number of electrons and unfilled orbitals[16]. Metal atoms form co-ordinate donor–acceptor links, the number of bonds formed exceeding the normal valency due to vacant orbitals. Non-metals utilise their lone pairs of electrons to form bridges. Such groups as $-\overline{\underline{O}}H$, $-\overline{N}H_2$, $-\overline{\underline{S}}H$, $-\overline{\underline{Cl}}|$, $-\overline{\underline{Br}}|$, etc., are able to form bridges, but the NH_3 molecule, which possesses only one lone pair of electrons, cannot form more than one bond, and can act only as a terminal group in a polymer.

X-Ray investigation has shown the polymeric nature of many "simple" and complex inorganic compounds[4,7,11-14], in which polymerisation is due to the formation of co-ordinate links.

Structures of both low and high molecular weight, such as palladium chloride $PdCl_2$, can be formed through co-ordinate links.

A more important concept than valency in the chemistry of co-ordination polymers is that of the "bondability" (*Bindigkeit, svyaznost'*) of an atom, *i.e.* the number of bonds which it forms with other atoms. In practice this is identical with the co-ordination number (C.N.).

Schmitz-Dumont[18,19] uses the term "high-polymer co-ordination compounds" (*hochpolymere Koordinationsverbindungen*) for these compounds, and Schwarzenbach[20] the term "high-polynuclear complexes" (*Hochpolynucleare*). In this review we will use the term "co-ordination polymers" for polymers of low and high molecular weight. We will count as *co-ordination polymers all polymeric compounds containing atoms forming a greater number of bonds than corresponds to the valency of given element.* This class includes both polymers formed by donor–acceptor bonds and electron-deficient polymers with many-centre bonds. In all cases polymerisation results from the tendency of elements to make maximum use of their valency electrons and vacant orbitals to form covalent, dative, co-ordinate, or many-centre bonds (for types of chemical bonds, see the review by Syrkin[16]). Polymers of this type can be formed by boron, transition metals, and elements of the main subgroups whose valency is less than their co-ordination number. All these elements tend to form bonds in excess of their valency: polymerisation provides one possible method of implementing this tendency.

Polymeric compounds of elements of co-ordination number equal to their valency, *e.g.* Mo, W, Te (C.N. = valency = = 6) cannot be regarded as co-ordination polymers. Condensed oxygen compounds of these elements constitute the class of isopoly compounds, which are ordinary covalent polymers.

Co-ordination polymers have formed the subject of two reviews[10,19]; a third[21] is known to the present writer only through *Chemical Abstracts*.

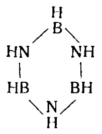
Here we will consider various aspects of the chemistry and the structure of co-ordination polymers, and will attempt to incorporate these compounds in a general scheme of inorganic polymers. The number of known co-ordination polymers is still small; many opportunities exist for preparing new types of co-ordination polymers. In the present work, therefore, we will examine, besides the work in the literature, some as yet unused methods, where existing knowledge indicates some promise of development in this field.

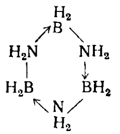
I. CLASSIFICATION OF INORGANIC POLYMERS

In order to assess the status of co-ordination polymers in the chemistry of macromolecular compounds we must consider the classification of inorganic polymers. Berlin and Parini[5,6] divide all polymers into (*a*) organic, (*b*) organo-elementary, and (*c*) inorganic, depending on the constitution of the main chain. Organo-elementary polymers contain other elements besides carbon (B, Si, Ge, P, As, Sb, etc., metals) in the chain; inorganic polymers contain no carbon in the main chain. Both organo-elementary co-ordination (chelate) polymers and purely inorganic co-ordination polymers are known.

Published reviews[5-8,10] make no distinction between polymers of low and of high molecular weight. The term "macromolecule" often refers to trimers and tetramers, most of which are cyclic compounds. Cyclic inorganic compounds possess definite peculiarities[3] and are therefore distinct from polymers of high molecular weight.

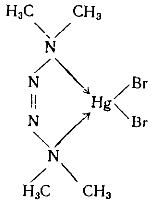
According to the present reviewer's classification[2,3], monocyclic compounds are divided into — (*a*) *homocyclic*, the ring of which is formed by atoms all of the same kind, *e.g.* S_8,[22] $(AsCH_3)_5$,[23] $(PCH_3)_5$,[24] etc.; (*b*) *pseudoheterocyclic* or *alternant*, in which the ring is formed by the alternation of two elements A and B, for example,


covalent ring


co-ordinate ring

(*c*) *true heterocyclic* compounds, such as S_7NH,[25] $R_6Si_3O_2NH$,[26] etc.

Cyclic co-ordination polymers consist almost exclusively of alternant rings, in which donor and acceptor atoms alternate. Very few examples are known of true heterocyclic compounds containing co-ordinate links, an example being the complex of tetramethyltetra-azen with mercuric bromide[27]:

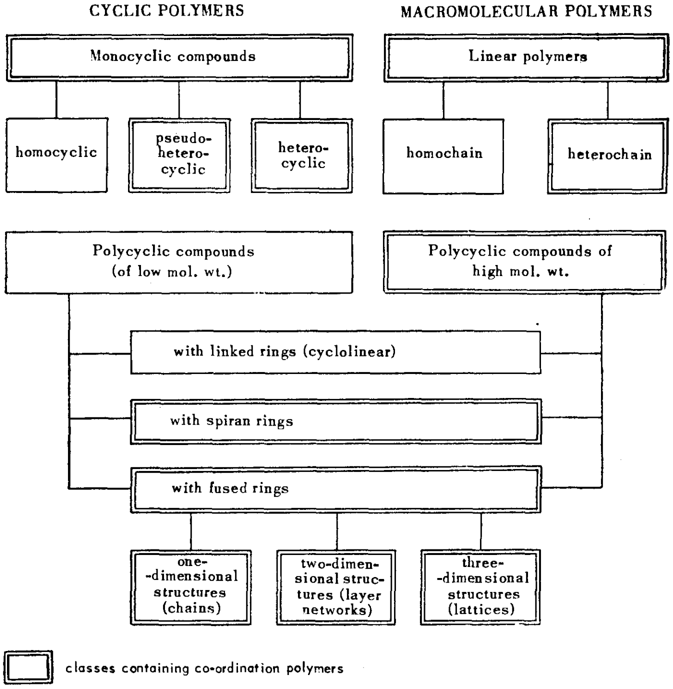


The following classification is suggested for inorganic polymers of high molecular weight — (*a*) homochain polymers and (*b*) heterochain polymers[2,4,28]. All co-ordination polymers, of course, are heterochain.

Table 1 gives a scheme for the classification of inorganic polymers.

Co-ordination polymers can be classified stereochemically according to the structural unit of the polymer —
(*a*) polymers having tetrahedral structural units (C.N. 4),
(*b*) polymers having square planar structural units (C.N. 4),
(*c*) polymers having octahedral structural units (C.N. 6),
(*d*) polymers having cubic structural units (C.N. 8), and
(*e*) polymers having different structural units (different co-ordination numbers in the structure).

TABLE 1. Classification of inorganic polymers.

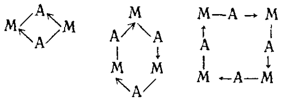


II. CO-ORDINATION POLYMERS OF LOW MOLECULAR WEIGHT

In this section we shall examine compounds having a low degree of polymerisation. This class includes cyclic co-ordination compounds (consisting of tetrahedral structural units) and several polymers containing heavy elements (their molecules being made up of octahedral structural units).

1. CYCLIC CO-ORDINATION POLYMERS WITH CO-ORDINATION NUMBER 4

When a compound contains both donor and acceptor elements in the molecule, polymerisation can occur by means of co-ordinate links, if other molecules which can take part in co-ordination are absent. The polymers of low degree of polymerisation (dimers, trimers, tetramers, hexamers) which are formed are usually cyclic compounds. If M is an acceptor, and A a donor, MA molecules can polymerise by means of co-ordinate links:



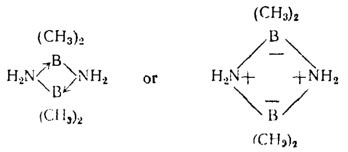
Cyclic compounds of this type are known in which M = B, Al, Ga, In, etc. If M has C.N. = 4, the cyclic polymers consist of tetrahedral structural units joined at the corners to form a ring.

The acceptor atom M is situated at the centre of the tetrahedron and is in a hybrid sp^3 state.

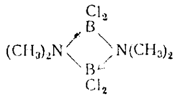
Compounds of boron. Trimethylboron forms with ammonia a compound $(CH_3)_3B.NH_3$, in which the free pair of electrons on the nitrogen and a vacant orbital in the boron form a co-ordinate (or semipolar) bond[29]:

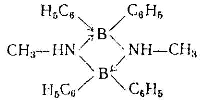
$$(CH_3)_3B \leftarrow NH_3 \quad \text{or} \quad (CH_3)_3\overset{-}{B}—\overset{+}{N}H_3.$$

Thermal decomposition of this compound involves the evolution of methane and the formation of $(CH_3)_2BNH_2$, which is a cyclic dimer[30]:

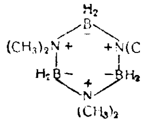


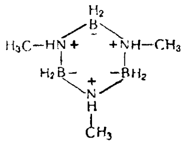
Its isomer[31] $[(CH_3)_2NBH_2]_2$ is also a dimer. The same cyclobutane type of structure occurs[32] in the compounds $[(CH_3)_2NBCl_2]_2$ and[33] $[CH_3NHB(C_6H_5)_2]_2$ as shown by molecular weight and infra-red spectral data:





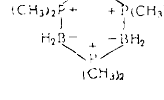
The compound $[(CH_3)_2NBH_2]_3$, obtained[34] by heating the corresponding dimer $[(CH_3)_2NBH_2]_2$, contains a six-membered ring. X-Ray examination of the trimer[35] showed that the B_3N_3 ring has the chair form, corresponding to its "saturated nature". A cyclic trimer is also known[36] having the composition $[NH(CH_3).BH_2]_3$:

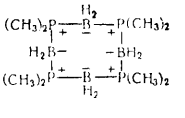




All these compounds evolve methane and are converted into borazole derivatives on being heated.

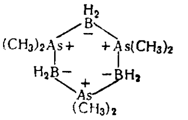
Burg and Wagner[37,38] prepared compounds in which phosphorus was the donor. They synthesised the cyclic compounds $[(CH_3)_2PBH_2]_3$ and $[(CH_3)_2PBH_2]_4$:

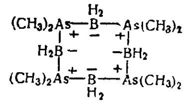




The cyclic structure of the trimer was confirmed by Hamilton[39] using X-rays. These compounds possess remarkable thermal stability: it has been established[40] by mass-spectroscopy that thermal decomposition of the trimer begins only at 360°, when hydrogen and methane are evolved. Very stable compounds having the composition $[(CF_3)_2PBH_2]_3$ and $[(CF_3)_2PBH_2]_4$ were synthesised[41] by reaction between $(CF_3)_2PF$ and B_2H_6. The compounds $[(C_6H_5)_2PBH_2]_3$, $[(C_5H_{10})_2PBH_2]_3$, $[(C_5H_{11})_2PBH_2]_3$, and $[(C_6H_{11})_2PBH_2]_3$ have been patented as dielectrics[42].

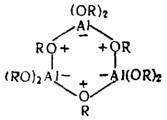
$(CH_3)_2AsH.BH_3$ yielded on heating cyclic trimers and tetramers[43]:

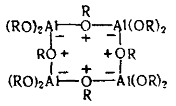




The stability of the co-ordinated boron rings decreases in the order N > P > As.

Compounds of elements of Group III (Al, In, Ga). In 1932 Ulich and Nespital[44] established that aluminium alkoxides $Al(OR)_3$ occurs as polymers in benzene solution. They showed that the solution contains co-ordinated cyclic trimers and tetramers:



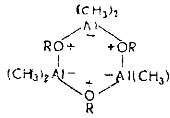


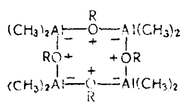
Later Mehrotra[45] studied a series of aluminium alkoxides, and showed that they were all polymeric (tetramers). Bradley, however, considers[46] that the degree of polymerisation of 4 is only apparent, and results from the presence of a dimer (C.N. 4) and an octamer (C.N. 6) in the solution.

In compounds of the type AlX_3 the aluminium atom is co-ordinatively unsaturated, having an unoccupied p orbital. In an oxygen-containing solvent, such as R_2O, the unshared electron pairs of the solvent molecule form a co-ordinate link with the aluminium atom, and the compound is monomeric owing to the formation of solvates. In benzene or other inert solvent such solvation is impossible, and co-ordination polymerisation provides the only opportunity for the aluminium to utilise all its valency orbitals.

The apparent co-ordination number of aluminium in the compounds $Al(OR)_3$ is 3; on polymerisation, the co-ordination number in the cyclic molecules is obviously 4. This is typical of co-ordination polymers: *the actual co-ordination number is greater than the apparent value.*

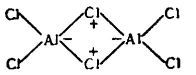
The polymers $[(CH_3)_2AlOCH_3]_x$ are similar cyclic compounds, forming six- and eight-membered rings[95,96].

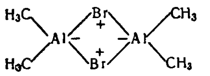




Ferric alkoxides $Fe(OR)_3$ are also trimeric[47,48] and probably have a cyclic structure.

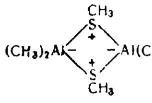
Not only oxygen acts as donor in co-ordination polymers of aluminium, but aluminium halides are known to be dimeric. The cyclic structure of these compounds has been established by electron diffraction[49,50] and X-ray diffraction in the case[51] of Al_2Br_6. $[(CH_3)_2AlBr]_2$ has a similar structure[52].



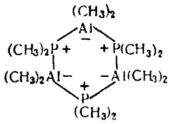


Jaffé[53] applied molecular orbital calculations to the Al_2Cl_6 molecule. The cyclic structure is retained in $Al_2Cl_4H_2$ and $Al_2Br_4H_2$, obtained[54] by the action of LiH on Al_2Cl_6 (or Al_2Br_6).

The compound $(CH_3)_2AlSCH_3$ is a cyclic dimer[55]

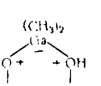


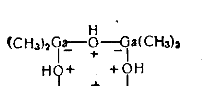
An interesting compound in which phosphorus is the donor is the trimer[55,56] of composition $[(CH_3)_2AlP(CH_3)_2]_3$.



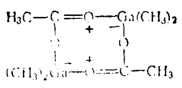
Attempts to obtain similar compounds containing Al and N in the ring were unsuccessful. Thermal decomposition of AlH_3NH_3 yielded[57-59] only acyclic polymers of high molecular weight.

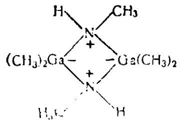
Gallium shows similar co-ordination polymerisation with formation of cyclic compounds. Gallium halides are dimeric: Ga_2Cl_6 [60-62] and Ga_2Br_6.[60,61] Kenney and Laubengayer[63] showed that $(CH_3)_2GaOH$ is trimeric in benzene solution. Smith and Hoard[64] used X-rays to study this compound, and demonstrated that it had an eight-membered cyclic structure

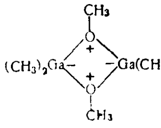




Dimethylgallium acetate $CH_3.COOGa(CH_3)_2$ is a cyclic dimer[65]. The compounds $(CH_3)_2GaNHCH_3$ and $(CH_3)_2GaOCH_3$ are also dimers, and contain four-membered rings[55].

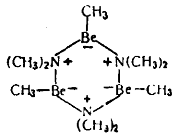


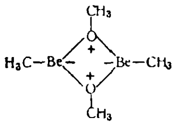




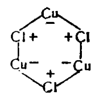
Indium and gallium form analogous compounds. Stone[55] showed that all compounds having the composition $(CH_3)_2M^{III}R$ [where M^{III} = Al, Ga, In, Tl; and R = H_2N-, $(CH_3)_2N-$, $(CH_3)_2P-$, CH_3O-, CH_3S-, CH_3Se-] are polymers having four-, six-, or eight-membered rings. Such polymerisation is the result of the tendency of elements of Group III to form four hybrid sp^3 bonds, one of which can be formed only if a pair of electrons is transferred from a donor (N, O, S, Se, P) (co-ordinate link).

Cyclic compounds are known in which the metal atom possesses sp^2 hybridisation (C.N. = 3). Beryllium forms such compounds[66]: the cyclic trimer $[CH_3BeN(CH_3)_2]_3$, and the dimer $[CH_3BeOCH_3]_2$

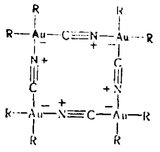




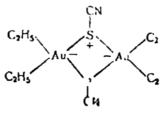
Other cyclic co-ordination polymers. Other cyclic co-ordination compounds have been described in the literature. It has been established[67,68] that cuprous chloride in the vapour state contains trimeric Cu_3Cl_3 molecules, which have been shown by electron diffraction[69] to have a cyclic structure. It is probable that the vapours of other metal halides (which are not decomposed at high temperatures) contain cyclic molecules. It is interesting that even the vapours of alkali-metal halides, as Akishin has shown[70,71] contain dimeric and trimeric molecules such as Na_2Cl_2 and Na_3Cl_3.

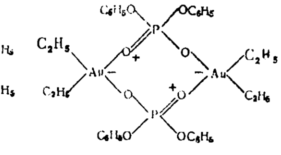


Among interesting cyclic co-ordination compounds are the dialkylgold cyanide[72,73] $[R_2AuCN]_4$ having a twelve-membered ring, $[(C_2H_5)_2AuSCN]_2$ having a four-membered ring[74], and the compound $[(C_2H_5)_2AuPO_2(OC_6H_5)_2]_2$, which has an eight-membered ring[75]:



R = C_2H_5-, iso-C_3H_7-





Cyclic dimers are known containing halogen bridges between gold atoms, such as Au_2Br_6,[76] and $(R_2AuBr)_2$,[77-79] which are made up of square planar units (Fig. 1*a*). The same structure is shown by the dimeric palladium derivatives $[(CH_3)_3AsPdCl_2]_2$ [80] and $[(CH_3)_3AsPdBr_2]_2$ [81] as well as by the $Pd_2Cl_6^{2-}$ ions present in an aqueous solution of palladium chloride[82].

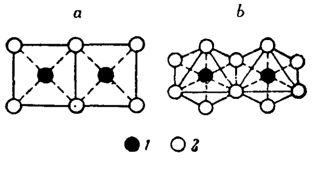
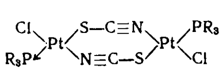
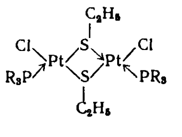


Fig. 1. *a*) Structure of planar cyclic dimer M_2A_6; *b*) structure of dimer $[MA_5]_2$, formed from octahedra.
1) Metal M; 2) ligand A; broken lines --- co-ordinate links.

Platinum also forms cyclic dimers, for example $[R_3P.PtClSCN]_2$ [83] and $[R_3P.PtSC_2H_5Cl]_2$:[84]





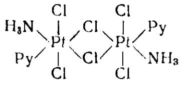
2. CO-ORDINATION POLYMERS WITH CO-ORDINATION NUMBERS 6 AND 8. ALKOXIDES

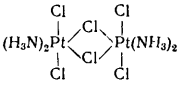
Most heavy metals form complex compounds having C.N. = 6 and an octahedral structure, and sometimes with C.N. = 8, which corresponds to a cubic structure.

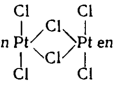
The simplest polymeric compounds containing octahedral structural units are the classical binuclear complexes described in all reviews on the chemistry of complex compounds [11,85-87]. The co-ordination octahedra in these dimers are joined at the corners, edges, or faces.

Several dimeric and trimeric compounds are made up of octahedral structural units. In organic solvents the compounds $NbCl_2(NHCH_3)_2$,[88] $VCl(NHCH_3)_2$,[89] $VCl_2(OR)_2.ROH$, and $MoCl_3(OR)_2$ [90] are dimeric, the metal atom having C.N. = 6 and octahedral co-ordination (Fig. 1*b*). It is interesting that tellurium halides TeX_4 have a trimeric structure[91] in benzene solution, owing to the fact that Te has C.N. = 6.

Platinum derivatives having bridging groups are also known[92-94], their structures being







Recently a large number of compounds having the composition $M(OR)_p$, so-called alkoxides (M = metal, R = aliphatic or aromatic radical, p = valency of metal), have been investigated. In very many cases these compounds are polymeric [44-48,95-121].

It has been found experimentally that the volatility and the degree of polymerisation of alkoxides depend on the atomic radius of the metal and on the degree of branching of the organic radical. The following rules have been established.

(a) The degree of polymerisation is greater the greater the atomic radius of the metal. Thus with a given radical R and metals of the same subgroup, *e.g.* in the series $[M(OR)_4]_x$, where M = Ti, Zr, Hf, Th, the degree of polymerisation in benzene (x) increases together with the atomic radius r_M from Ti to Th (see Table 2).

TABLE 2. Degree of polymerisation of some n-butoxides in solution.

	M in $[M(O.C_4H_9)_4]_x$			
	Ti	Zr	Ce	Th
x	3.0	3.4	4.2	6.3
r_M	1.36	1.48	1.65	1.65

(b) The degree of polymerisation depends on the degree of branching of the alkyl radical R. Compounds in which R is an n-alkyl radical are polymerised to a greater extent than those in which R is a branched radical. Table 3 shows the degree of polymerisation of several alkoxides determined cryoscopically in benzene.

When R is a branched radical, the compounds $M(OR)_p$ are often monomeric.

TABLE 3. Degrees of polymerisation of thorium alkoxides in benzene.[99, 100]

R_b $[Th(OR)_4]_x$	$-CH_3$	$-C_2H_5$	$-n\text{-}C_3H_7$	$-n\text{-}C_4H_9$	$-n\text{-}C_5H_{11}$	$-CH\begin{smallmatrix}C_2H_5\\C_2H_5\end{smallmatrix}$	$-CH\begin{smallmatrix}CH_3\\C_2H_5\end{smallmatrix}$	$-CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$
x	non-volatile, insol. polymer	non-volatile, insol. polymer	—	6.44	6.20	4.1	4.2	3.8

(c) The degree of polymerisation of alkoxides depends on the nature of the solvent. In inert solvents (benzene, toluene) polymerisation is possible. Solvents containing atoms having donor electrons either diminish (acetonitrile) or prevent (pyridine) polymerisation[103].

(d) The degree of polymerisation of alkoxides decreases with rise in temperature. Ebullioscopic determination of the molecular weight in toluene yields degrees of polymerisation which are lower than in benzene[99,100,102,104]. On the other hand, the energy of intermolecular bonding of alkoxides is low, 10 kcal $mole^{-1}$.[46]

Bradley[46] explained the structure of alkoxide polymers on the following premises: (*a*) the compound $M(OR)_p$ has that structure in which the co-ordination number of the metal atoms is a maximum; (*b*) the co-ordination number of oxygen does not exceed 4; (*c*) the metal assumes a steric configuration characteristic of a given valency state.

Table 4 gives Bradley's data[46] on the dependence of degree of polymerisation and structure on composition and the co-ordination number of the metal.

The derivatives of ter-, quadri-, and quinque-valent metals have been mainly studied hitherto. Table 5 gives literature references for the known classes of alkoxides.

Table 5 gives also the degree of polymerisation determined cryoscopically in benzene solution. In several cases this is only an apparent value, since the solution contains a mixture of products having different molecular weights. For example, thorium alkoxides $[Th(OR)_4]_x$ have an apparent degree of polymerisation of 6.4, the solution actually containing ~20% of the trimer and 80% of the octamer[99].

Most alkoxides are based on octahedral (C.N. = 6) and cubic (C.N. = 8) units. The octahedra can be combined in twos or threes, forming dimers or trimers (Figs. 1*b* and 2).

TABLE 4. Sterochemistry of alkoxides $[M(OR)_p]_x$.

Compound	C.N. of metal	Stereochemistry of metal (configuration of complex)	Degree of polymerisation (theoretical)	Examples	Refs.
MOR	2	OMO angle 120°	3	unknown	—
	3	pyramidal	3	$[Tl(OR)]_4$	105,106
$M(OR)_2$	4	tetrahedral	3	unknown	—
	4	square planar	4	unknown	—
	6	octahedral	three-dimensional polymer	$[Mn(OR)_2]_x$	107
$M(OR)_3$	4	tetrahedral	2	both in $[Al(OR)_3]_x$	46
	6	octahedral	8		
$M(OR)_4$	6	octahedral	3	$[Ti(OR)_4]_3$, $[Zr(OR)_4]_3$	108, 97
	8	cubic	8	$[Th(OR)_4]_x$ (partly depolymerised)	100
$M(OR)_5$	6	octahedral	2	$[Ta(OR)_5]_2$, $[Nb(OR)_5]_2$	109, 104
$M(OR)_6$	8	cubic	2	$[V(OR)_6]_2$	46

TABLE 5. Composition and degree of polymerisation of metal alkoxides.

Metal	Alkoxide	Degree of polymerisation (found)	Ref.
Tl^I	$Tl(OR)$	4	105, 106
Mn^{II}	$Mn(OR)_2$	insol.	107
Al^{III}	$Al(OR)_3$	2 . . .4	44—49, 110, 117
Fe^{III}	$Fe(OR)_3$	1.5 . . .3.0	47, 48
Ge^{IV}	$Ge(OR)_4$	1	120
Ti^{IV}	$Ti(OR)_4$	1 . . .3.0	97, 111, 114, 115
Sn^{IV}	$Sn(OR)_4$	1	111
Zr^{IV}	$Zr(OR)_4$	1 . . .3.0	97, 111, 121, 116
Th^{IV}	$Th(OR)_4$	1 . . .6.4	99, 100, 110, 111
Ce^{IV}	$Ce(OR)_5$	1 . . .4.3	99—102, 111
Nb^V	$Nb(OR)_5$	1 . . .2.0	101, 104
Ta^V	$Ta(OR)_5$	1 . . .2.0	98, 101, 103, 104, 109, 112
U^V	$U(OR)_5$	3.0	118
U^{VI}	$U(OR)_6$	2.2	46

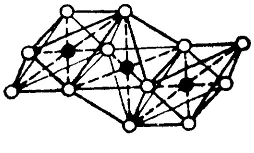


Fig. 2. Structure of octahedral trimer $[MA_4]_3$.

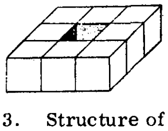


Fig. 3. Structure of octamer $[MA_4]_8$, made up of cubes having faces in common.

Zirconium, cerium, and thorium can also have a co-ordination number of 8, as in the acetylacetonates, in which the structural unit is cubic. The minimum degree of polymerisation of alkoxides having the composition $[M(OR)_4]_x$ with C.N. = 8 is 8, corresponding to a ring formed by eight cubes (Fig. 3). Thallium alkoxides $[Tl(OR)]_4$ (the benzyloxide[105] and the pentyloxide[106]) have a rather different structure (Fig. 4).

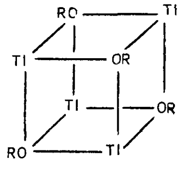


Fig. 4. Structure of tetramer $(TlOR)_4$.

The structure of alkoxides has not yet been investigated by means of X-ray or electron diffraction: the information quoted above is based only on theoretical considerations and on experimental molecular weights: the study of the structure of alkoxides by direct methods would be of great interest.

Non-volatile and insoluble alkoxides[110], such as $Mg(OCH_3)_2$, $La(OCH_3)_3$, and $Zr(OCH_3)_4$, are also known, these apparently being polymers of high molecular weight.

III. CO-ORDINATION POLYMERS OF HIGH MOLECULAR WEIGHT

In complex compounds the complex-forming metal M has a characteristic co-ordination number n. A given value of n can be achieved in two ways: (a) the central atom M may be surrounded by n "univalent" ligands A, mononuclear complexes with a discrete structure $[MA_n]$ being formed; (b) in compounds of the type $[MA_p]$, in which the apparent co-ordination number p is less than the real value (n), the central atom forms a configuration having C.N. = n by combining with ligands A which form bridges within a polynuclear complex. In the latter case co-ordination polymers $[MA_p]_x$ are produced.

Many "simple" compounds of the type MA_p, in which p is less than the characteristic co-ordination number of the metal, polymerise with the formation of co-ordination compounds of high molecular weight.

1. POLYMERIC COMPLEXES WITH CO-ORDINATION NUMBERS 2 AND 3

The simplest co-ordination polymers of high molecular weight are compounds having the composition MA, in which M is a complex-forming element with C.N. = 2, and A is a bifunctional ligand (capable of forming two links). Polymers of this type have a chain structure:

$$\ldots \rightarrow M{-}A \rightarrow M{-}A \rightarrow M{-}A \rightarrow \ldots$$

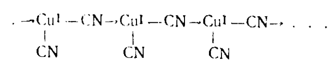
such as that of silver cyanide[122,123], silver thiocyanate[124]

$$\ldots \rightarrow Ag{-}C{\equiv}N \rightarrow Ag{-}C{\equiv}N \rightarrow Ag{-}C{\equiv}N \rightarrow \ldots \quad \ldots \rightarrow Ag{-}S{-}C{\equiv}N \rightarrow Ag{-}S{-}C{\equiv}N \rightarrow \ldots,$$

aurous cyanide[125], and mercuric cyanide[126,127]. Thallium fluoride has a similar linear structure[128].

$$\rightarrow Tl{-}F \rightarrow Tl{-}F \rightarrow$$

The complex compound $K[Cu^I(CN)_2]$, in which copper apparently has a co-ordination number of 2, is actually polymeric[129] and contains a spiral anion $[Cu(CN)_2^-]_\infty$ (C.N. = = 3 for copper). Only one of the CN groups is involved in forming the chain:



$$\ldots \rightarrow \underset{CN}{\overset{|}{Cu^I}}{-}CN \rightarrow \underset{CN}{\overset{|}{Cu^I}}{-}CN \rightarrow \underset{CN}{\overset{|}{Cu^I}}{-}CN \rightarrow \ldots$$

The anion $[Au(CN)_2]^-$ has a similar linear structure[130].

2. POLYMERIC COMPLEXES WITH CO-ORDINATION NUMBER 4

The co-ordination number 4, characteristic of Cu^I, Au^I, Pt^{II}, Pd^{II}, Cu^{II}, Ni^{II}, Zn^{II}, Be^{II}, Hg^{II}, Au^{III}, and other metals[85-87] is known in numerous compounds in the chemistry of complex compounds. Complex ions of these elements of the type $[MA_4]$ (where A is a unifunctional ligand) have either a square planar configuration (complexes of Pd^{II}, Pt^{II}, Cu^{II}) or a tetrahedral configuration (complexes of Zn^{II}, Hg^{II}, Cu^I, Au^I, Be^{II}). Classical complexes in solution and in the solid state contain individual $[MA_4]$ ions. Formation of polymeric structures involves the linking of $[MA_4]$ groups by means of common ligands A, leading to the formation of polymers $[MA_p]_x$ (p = 3, 2, 1) in which the metal has C.N. = 4.

A. Complexes Having Square Planar Units

(a) Polymers of type $[MA_3]_x$. The square planar units $[MA_4]$ can be combined at common corners in either the *cis* (Fig. 5) or *trans* (Fig. 6) positions, $[MA_3]_x$ chains being formed in both cases. The metal obviously retains a co-ordination number of 4 in the polymer chain.

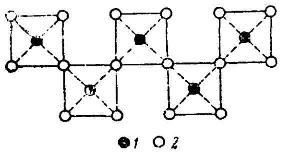


Fig. 5. Structure of *cis*-$[MA_{2+2/2}]_\infty K$ chain:
1) metal M; 2) ligand A; broken lines - - - co-ordinate links.

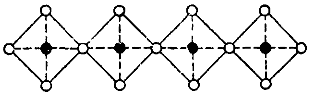
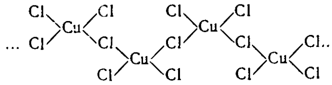


Fig. 6. Structure of *trans*-$[MA_{2+2/2}]_\infty K$ chain: key as in Fig. 5.

These structures can be represented by Niggli's stereochemical formulae[131]. Linear polymers of this type have the stereochemical formula $[MA_{2+2/2}]_\infty K$ (*K* = *Kettenstruktur*[131] = chain structure). The formula shows that two of the A groups are combined with only one M atom, and the other two are common to two M atoms (bridging groups).

The $[CuCl_3]_x^{x-}$ anion, which has been examined with X-rays[132], is a polymer of this type having the *cis* configuration. It consists of square planar $[CuCl_4]$ groups linked to form an infinite chain:

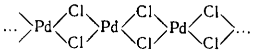


$[CuCl_{2+2/2}]_\infty K$

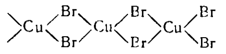
The polymeric structure is broken down by hydrolysis in water.

Polymer chains having the *trans*-configuration (Fig. 6) are not yet known.

(b) Polymers of type $[MA_2]_x$. Square planar groups can be joined at their edges, *i.e.* by two A groups (Fig. 7), forming $[MA_2]_x$ polymers having the stereochemical formula $[MA_{4/2}]_\infty K$. A typical example is palladium chloride[133]. This binary compound is really a high polymer having Pd atoms linked by two Cl atoms:



All the Pd–Cl bonds are the same (Pd–Cl = 2.31 Å). The compounds $CuBr_2$[134] and $CuCl_2$[135] have a similar structure.



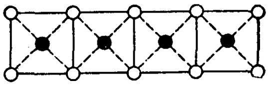


Fig. 7. Structure of $[MA_{4/2}]_\infty N$ chain (edges of squares in common).

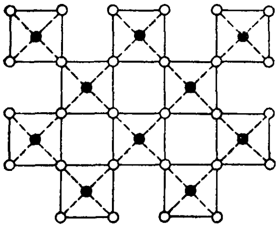


Fig. 8. Structure of planar network $[MA_{4/2}]_{\infty}N$.

The $[MA_2]_x$ structure is produced by joining square $[MA_4]$ groups at four corners to form a planar two-dimensional network (Fig. 8). Palladium cyanide $Pd(CN)_2$ possesses this type of structure[13].

B. Complexes Having Tetrahedral Units

Both planar and tetrahedral $[MA_4]$ units can be joined at their corners or edges to form one-dimensional chains, two-dimensional networks, or three-dimensional lattices.

(a) Polymers of type $(MA_3)_x$. The joining of tetrahedral units at their corners (as in the silicates) (Fig. 9) was described by Brink and Van Arkel[136] in the compounds $(NH_4)_2[Cu^ICl_3]$ and $(NH_4)_2[Cu^IBr_3]$, which consist of infinite-chain anions of the structure $[Cu^IX_3^{2-}]_{\infty}$ made up of tetrahedral $[CuX_4]$ units. The same structure was also found in $K_2[CuCl_3]$, $Cs_2[AgCl_3]$, $Cs_2[AgI_3]$,[137] $K_2[AgI_3]$, $Rb_2[AgI_3]$, and $(NH_4)_2[AgI_3]$.[138] Such polymeric chains, having the composition $[MA_{2+2/2}]_{\infty}K$, can also be expected in compounds of zinc, beryllium, etc. The fluoroberyllates $M^I[BeF_3]$ [139-141] apparently have a structure of this type, especially as $NaBeF_3$ is isomorphous with β-$CaSiO_3$.[142]

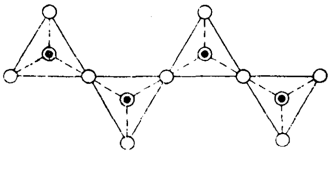


Fig. 9. Structure of chain of tetrahedra $[MA_{2+2/2}]_{\infty}K$ with common corners.

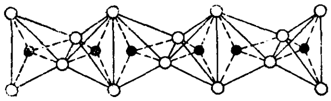
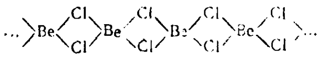


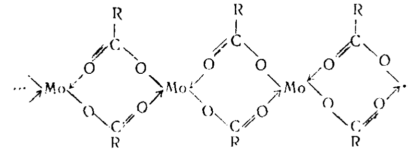
Fig. 10. Structure of chain of tetrahedra $[MA_{4/2}]_{\infty}K$ with edges in common.

(b) Polymers of type $[MA_2]_x$. If tetrahedra are joined at their edges, the structure $[MA_{4/2}]_{\infty}K$ results. Thus infinite chains of this type (Fig. 10) are formed in the structure of beryllium chloride $BeCl_2$:[143]

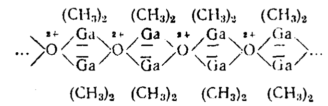


Double chains of tetrahedra are also known, in the structures of $Cs[Cu_2Cl_3]$ and $Cs[Ag_2I_3]$.[144]

The same structure (Fig. 10) has been ascribed to salts of bivalent molybdenum with organic acids[145]:



An interesting polymer, in which oxygen is situated at the centre of the tetrahedron, with metal atoms at the corners, is the compound $[(CH_3)_2Ga]_2O$, which has been assigned the structure[146]



Tetrahedral units combine less often to form two-dimensional networks (Fig. 11) $[MA_{4/2}]_{\infty}N$ (N = *Netzstruktur*[131] = network structure), as occurs in red mercuric iodide[147] and in γ-$ZnCl_2$.[148]

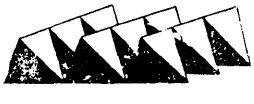


Fig. 11. Structure of red mercuric iodide HgI_2 (two-dimensional layer).

Tetrahedral $[MA_4]$ units can sometimes unite at four corners to form three-dimensional lattices having the structure $[MA_{4/2}]_\infty G$ (G = *Gitterstruktur*[131] = lattice structure). Thus, for example tetrahedral BeF_4^{2-} groups sometimes form three-dimensional lattices. Warren and Hill[149] showed that vitreous BeF_2 has a similar structure to vitreous silica. Brandenberger[150] and Wyckoff[151] prepared from $(NH_4)_2BeF_4$ beryllium fluoride having a β-cristobalite structure. Novoselova and her coworkers[152] also obtained a new form of beryllium fluoride with the β-cristobalite structure. Beryllium fluoride is a structural analogue of silicon dioxide[153,154]. The Be–F bond is not purely ionic but has some covalent character[139], making possible the formation of fluoroberyllates, which are similar to silicates in structure.

Recently Brehler[155] has shown that α-$ZnCl_2$ and β-$ZnCl_2$ possess a three-dimensional tetrahedral lattice in which the $ZnCl_4$ groups are joined at their corners. Beryllium hydroxide β-$Be(OH)_2$[156] and zinc hydroxide[157] have a structure in which a metal atom is surrounded tetrahedrally by four OH groups. Zinc cyanide[158] and cadmium cyanide[159] have three-dimensional polymeric structures of the anticuprite type (co-ordination number of metal = 4).

(c) Polymers of type $[MA]_x$. A three-dimensional lattice consisting of tetrahedral units, $[MA_{4/4}]_\infty G$, is formed by the two modifications of zinc sulphide — wurtzite[160] and zinc blende[161,162]. This type of structure is found in very many compounds[11,13,160-168]:

Sulphides:	ZnS, CdS, BeS, HgS, MnS
Oxides:	ZnO, BeO, CuO
Selenides:	ZnSe, CdSe, HgSe
Tellurides:	ZnTe, CdTe, HgTe
Antimonides:	InSb, GaSb, AlSb
Arsenides:	GaAs, AlAs, BAs
Phosphides:	GaP, AlP, BP
Iodides:	CuI, AgI
Bromides and chlorides:	CuBr, CuCl.

In other compounds — PbO, SnO, PdO, PtO,[169] and $Ag^{II}O$[170] — the metal has the same co-ordination number of 4, but the structure is different.

Co-ordination polymers in which the metals have a co-ordination number of 4 are very common. Table 6 gives possible co-ordination polymers made up of structural units having a co-ordination number of 4.

TABLE 6. Possible structures of co-ordination polymers of co-ordination number of 4.

Apparent C.N.	Composition of polymers	Stereochemical formula	Modes of formation of polymer	
			joining of square planar units	joining of tetrahedral units
3	MA_3	$[MA_{2+2/2}]_\infty K$	two corners in common: *cis* $[CuCl_3]Cs$ (Fig. 5); *trans* (Fig. 6)	two corners in common: $K_2[CuCl_3]$ (Fig. 9)
2	MA_2	$[MA_{4/2}]_\infty K$	two edges in common: $PdCl_2$ (Fig. 7)	two edges in common: $BeCl_2$ (Fig. 10)
		$[MA_{4/2}]_\infty N$	four corners in common: $Pd(CN)_2$ (Fig. 8)	four corners in common: HgI_2 (two-dimensional network) (Fig. 11)
		$[MA_{4/2}]_\infty G$		four corners in common: BeF_2 (three-dimensional lattice)
1	MA	$[MA_{4/4}]_\infty G$		four corners in common: ZnS (three-dimensional lattice)

3. POLYMERIC COMPLEXES WITH CO-ORDINATION NUMBER 6

The number of complex compounds in which the central atom has a co-ordination number of 6 is very large. This value is characteristic of Cd^{II}, Cr^{III}, Co^{III}, Al^{III}, Fe^{III}, Ir^{III}, Rh^{III}, Sc^{III}, Sn^{IV}, Pb^{IV}, Pt^{IV}, Ru^{IV}, Ti^{IV}, Sb^{V}, etc.[85-87] Complex ions $[MA_6]$ of these elements have an octahedral configuration: the metal atom M is surrounded by six ligands situated at the corners of an octahedron.

A co-ordination number of 6 is achieved in polymeric compounds in which the structural units are joined at the corners, edges, or faces. This is possible when A is a bi- or ter-functional ligand able to form two or three bonds.

(a) Polymers of type $[MA_5]_x$. If the octahedral $[MA_6]$ units are joined by having a corner in common, forming an infinite chain (Fig. 12), the resulting polymers $[MA_5]_x$ have the stereochemical formula $[MA_{4+2/2}]_\infty K$.

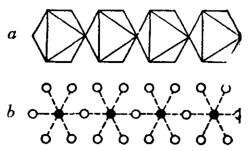
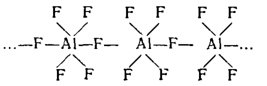


Fig. 12. Structure of chain of octahedra $[MA_{4+2/2}]_\infty K$ having common corners: a) stereochemical view; b) co-ordinate links (chemical structure).

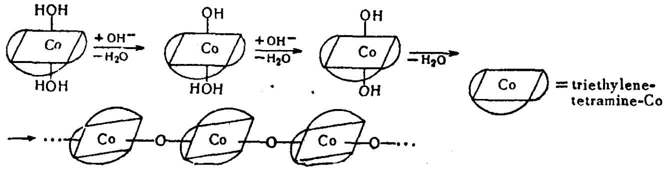
Aluminium is known to have a co-ordination number of 6 with respect to fluorine, e.g. in cryolite $Na_3[AlF_6]$. In the insoluble compound $Tl_2[AlF_5]$ the co-ordination number of the aluminium is not 5, as might appear, for this compound contains a polymeric anion $[AlF_5^-]_\infty$, which has a linear structure[171].



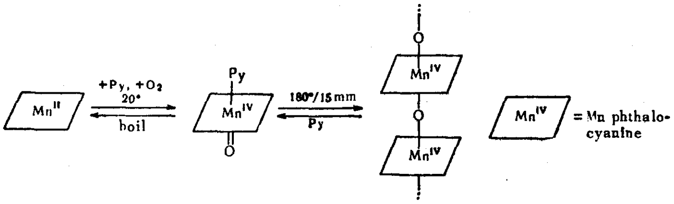
The thallium ions are distributed around the macromolecular chain.

The compound SbF_5 contains linear molecules[172] made up of octahedral units, $-SbF_4-F-SbF_4-F-$. The complex polymers $[IrPy_2Cl_3]_x$ and $[RhPy_2Cl_3]_x$ (Py = pyridine), obtained by Delépine[173], probably have a similar structure.

When a solution of the triethylenetetramine complex of tervalent cobalt is made alkaline, a linear polymer[174] $[CotnO]_x$ (tn - triethylenetetramine) is formed in which the octahedral complexes have oxygen atoms in common (in the axial positions):

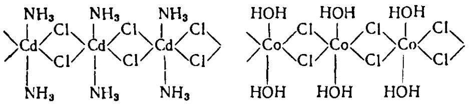


A similar polymer is obtained also from manganese phthalocyanine[175]:



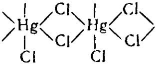
(b) **Polymers of type $[MA_4]_x$.** If the octahedra are joined edge to edge in the chain, complex polymers having the stereochemical formula $[MA_{2+4/2}]_\infty K$ are formed. This mode of union can be effected in two ways, with the formation of straight (Fig. 13) or kinked (Fig. 14) chains.

In the complex compound $[CdCl_2(NH_3)_2]$ the central cadmium atom has a co-ordination number of 6, since the complex is made up of octahedral units (Fig. 13). The chlorine atoms form bridging groups between the cadmium atoms, and the ammonia molecules occupy the free co-ordination positions. This structure corresponds to the formula $[Cd(NH_3)_2Cl_{4/2}]_\infty K$, and was established by means of X-rays[176]; another example is $CoCl_2.2H_2O$:[177]



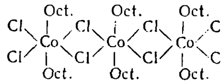
Of course, not all $[M(NH_3)_2Cl_2]$ complexes have a polymeric structure of this type: $[Zn(NH_3)_2Cl_2]$ is a mononuclear tetrahedral complex[178], and the compound $[Pt(NH_3)_2Cl_2]$ has a square planar structure (co-ordination number of 4 for zinc and platinum).

This structure is found in the compounds $K_2[SnCl_4].2H_2O$[179] and $K_2[HgCl_4].H_2O$,[180] in which chlorine atoms form bridging groups and the K^+ ions and water molecules surround the polymeric chain.

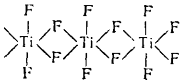


$[HgCl_{2+4/2}]_\infty K$

Complex polymers of this type have also been detected in solution. In octanol[181], for example, nickel and cobalt chlorides form polymers of the following type:



The fluorides TiF_4 and SnF_4 are assigned a linear polymeric structure[11]



Hoppe[182] considers that SnF_4 has a two-dimensional layer structure (see below). The mode of combination of octahedra shown in Fig. 14 has not been observed in any complex compound. Brookite TiO_2 contains chains of octahedra of this type, but the chains are linked by common oxygen atoms to form a three-dimensional lattice.

Another possibility in $[MA_4]_x$ compounds is the linking of the octahedral groups at four corners to form a planar two-dimensional network (layer structure) (Fig. 15). This structure has been observed in the following compounds: $K_2[NiF_4]$,[183] $K_2[CuF_4]$,[184] $Tl[AlF_4]$,[185] $K[AlF_4]$,[186] SnF_4,[182] $K_2[MgF_4]$,[187] $La_2[NiO_4]$,[188] $Ba_2[SnO_4]$ and $Ba_2[PbO_4]$,[189] and others[190–193]. It was established that β-$UO_2(OH)_2$ has a structure of the same type[194], the OH groups in the plane forming "equatorial bonds", and the oxygen atoms "uranyl bonds".[195]

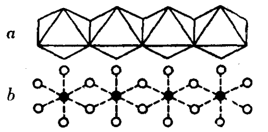


Fig. 13. Structure of chain of octahedra $[MA_{2+4/2}]_\infty K$ having common edges (linear chain). For key see Fig. 12.

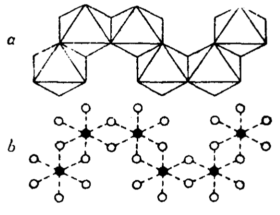


Fig. 14. Structure of chain of octahedra $[MA_{2+4/2}]_\infty K$ having common edges (wavy chain). For key see Fig. 12.

(c) **Polymers of type $[MA_3]_x$.** In many compounds having the composition MA_3 the actual co-ordination number of the central atom is 6. The simplest way in which this composition can be achieved is for the octahedra to be joined along three edges (Fig. 16) to form a planar two-dimensional network of the type $[MA_{6/2}]_\infty N$. This structure is shown by several anhydrous halides of ter-

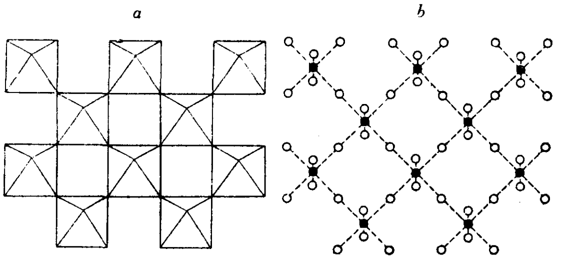


Fig. 15. Structure of octahedral layer $[MA_{2+4/2}]_\infty K$ (octahedra with common corners). For key see Fig. 12.

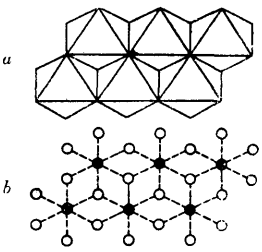


Fig. 17. Structure of double octahedral chain $[MA_{1+2/2+3/3}]_\infty K$ (NH_4CdCl_3 structure). For key see Fig. 12.

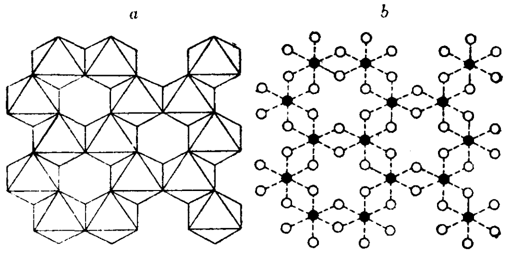


Fig. 16. Structure of octahedral layer $[MA_{6/2}]_\infty N$ (octahedra with common edges). For key see Fig. 12.

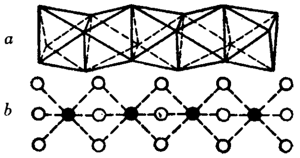


Fig. 18. Structure of octahedral chain $[MA_{6/2}]_\infty K$ (octahedra with faces in common). For key see Fig. 12.

valent metals: $CrCl_3$,[196] $RuCl_3$,[197] $AlCl_3$,[198] $FeCl_3$,[199] AlF_3,[200,201] BiI_3,[13] etc.; also by hydroxides of tervalent metals such as $Al(OH)_3$ (hydrargillite)[202], and some complex compounds having macromolecular anions, such as $NH_4[HgCl_3]$.[203]

In the lattice of these compounds the metal atom is surrounded by six halogen atoms (or OH groups), which form bridging groups with other nuclei. Every halogen atom is combined with two metal atoms.

Another way in which octahedra can be combined to form a polymer of type $[MA_3]_x$ is shown in Fig. 17, corresponding to the stereochemical formula $[MA_{1+2/2+3/3}]_\infty K$. This type of structure is found in $NH_4[CdCl_3]$.[204,205]

Combination of octahedra at their opposite faces yields a chain having the composition $[MA_3]_x$ and of type $[MA_{6/2}]_\infty K$ (Fig. 18). This occurs, for example, in $Cs[NiCl_3]$,[206] which contains the $[NiCl_3]_x^{x-}$ chain.

When the octahedral structural units are joined at six corners, a three-dimensional lattice of the rhenium trioxide ReO_3 type[207], having the formula $[MA_{6/2}]_\infty G$, is formed (Fig. 19). The ReO_3 structure is found also in the compounds WO_3, MoO_3, and CrO_3, which are not co-ordination but ordinary polymers, since the co-ordination number is then equal to the valency of the metal.

The ferricyanides of iron are based on the rhenium trioxide type of structure. X-Ray diffraction has established that ferric and ferrous ferricyanides,[208], like other ferrocyanides of the transition metals[209-213], have similar structures. In $Fe^{III}[Fe^{III}(CN)_6]$ the iron atoms form a cubic lattice, the CN groups being situated on the edges of the cube and being combined with the iron by the nitrogen atom (N → Fe co-ordinate links) and by the carbon atoms. This results in the three-dimensional lattice $[Fe(CN)_{6/2}]_\infty G$ (Fig. 19). Since not all the Fe atoms are tervalent in ferrous ferricyanides, the lattice is negatively charged, and is neutralised by alkali-metal ions situated interstitially in the lattice, as represented by the formula $K[Fe^{II}Fe^{III}(CN)_6]$. In copper ferrocyanide some of the iron atoms have been replaced by copper atoms, the correct formula of this compound being $K_2[CuFe^{II}(CN)_6]$. It is noteworthy that the

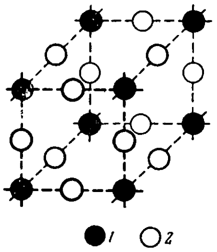


Fig. 19. Rhenium trioxide type of structure $[MA_{6/2}]_{\infty}G$: 1) Fe, Re, or other metal (C.N. = = 6); 2) CN, O, or other ligand.

ferrocyanides and ferricyanides of the alkali and alkaline-earth metals are not polymeric, their lattice containing separate $[Fe(CN)_6]^{4-}$ or $[Fe(CN)_6]^{3-}$ ions and metal ions. Macromolecular structures are formed only when transition metals such as copper, iron, etc., themselves capable of forming complexes with CN groups, are present in the outer sphere of the complex ions. Such compounds may be termed "supercomplexes". It may be supposed that, when the outer-sphere cation can itself form co-ordinate links with ligands, and a multifunctional (multidentate) ligand is present, the ligands form bridging groups between the metal atoms in the lattice, resulting in a co-ordinated macromolecular structure. Hence most salts formed by complex $[MA_n]^{p-}$ anions (where A is a bi- or tri-dentate ligand) with transition metals are co-ordination high polymers. X-Ray investigation of such compounds is of great interest from the point of view of polymer chemistry.

Another polymer having the rhenium trioxide structure is the compound InF(OH).[214]

The structure of perovskite $CaTiO_3$ is related to the ReO_3 structure[168,215,216]. The anion of the original acid is polymeric, forming a $(TiO_3)_x^{2x-}$ lattice with a rhenium trioxide type of structure; the Ca cations are arranged interstitially in the cubic lattice. This structure exists in a large number of compounds:

1) in double oxides[217-221]:

$CaTiO_3$ $NaNbO_3$ $NaTaO_3$ $LaGaO_3$ KIO_3 $SrSnO_3$ $CaZrO_3$
$SrTiO_3$ $KNbO_3$ $KTaO_2$ $LaAlO_3$ $RbIO_3$ $CaSnO_3$ $BaZrO_3$
$BaTiO_3$ $LaFeO_3$

2) in complex compounds:

$K[MnF_3]$[218], $K[NiF_3]$[192], $Cs[HgCl_3]$[223], $Cs[CdCl_3]$[224], $CsAgCl_3 \cdot CsAuCl_3$[226], $Rb[MnF_3]$[218],
$K[MgF_3]$[222], $Cs[HgBr_3]$[225], $Cs[CdBr_3]$[224], $Cs[AuCl_3]$[226].

An interesting $[MA_3]_x$ polymer is represented by the compound $[SAg_3]NO_3$, in which sulphur acts as the central atom[227], surrounded by six silver atoms. The $[SAg_6]$ groups are joined to form a macromolecular $[SAg_3]_x$ lattice.

(d) Polymers of type $[MA_2]_x$. It may be imagined from the above that a co-ordination number of 6 can also be achieved in the structures of some compounds having an apparent co-ordination number of 2, the co-ordinate octahedra being joined at six edges to form a two-dimensional layer lattice $[AB_{6/3}]_{\infty}N$ (Fig. 20). The structure of lead iodide has been investigated quite thoroughly[228-232]. Each lead atom is surrounded by six iodine atoms, and every iodine atom forms co-ordinate links with three lead atoms†. Layer structures are also encountered in other *halides*, such as CdI_2,[232-244] $CdBr_2$,[229-232,245] CdIBr,[246] CaI_2,[247] $MgBr_2$,[248] $MnCl_2$, $MnBr_2$,[248] MnI_2,[249] FeI_2,[249] $FeBr_2$,[248] $FeCl_2$,[250] CoI_2,[249] $CoCl_2$,[251] $NiCl_2$,[252] NiI_2,[252] VCl_2,[253,254] $HgBr_2$,[255] and yellow HgI_2;[255] in *sulphides*, *selenides*, and *tellurides* $TiSe_2$, $TiTe_2$, SrS_2, $ZrSe_2$,[256] and Tl_2S;[257] *hydroxides* $Cd(OH)_2$,[249,258] $Mg(OH)_2$,[259] α-$Zn(OH)_2$,[260,261] β-$Zn(OH)_2$,[262] $Ni(OH)_2$,[263] and $Co(OH)_2$;[264] *mixed hydroxides*, Ni–Zn and Co–Zn;[265] and in *basic salts*,[266-271] for example Zn(OH)Cl [272] and Cd(OH)Cl.[274]

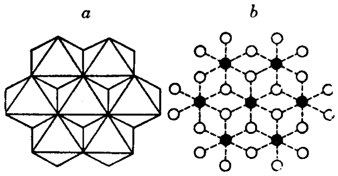


Fig. 20. Structure of octahedral layer $[MA_{6/3}]_{\infty}N$. For key see Fig. 12.

Krebs showed[273] that covalent character is superimposed on the ionic state of the bond in typical salts and in layer structures, confirming the polymeric structure of these compounds.

Other types of structure having the co-ordination number of 6 are found in AlO.OH,[275,276] AlOCl,[277] ReO_2,[278] $HCrO_2$,[279] etc. The rutile TiO_2 structure is based on straight chains of octahedra (Fig. 13) linked to form a three-dimensional lattice[11], while the structure of brookite, TiO_2, is based on wavy chains of octahedra (Fig. 14) linked three-dimensionally.

These ways of forming macromolecular structures based on octahedral units are set out in Table 7.

4. OTHER POLYMERS

The examples quoted here do not, of course, exhaust all the possible ways in which co-ordinated macromolecular structures may be formed. Co-ordinated polymeric structures may be produced by combining different structural units.

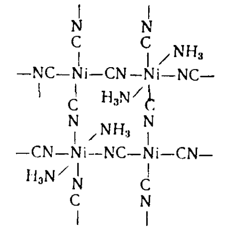
---

† Iodine can also act as the central atom with C.N. = 3, for example in the complex compound $[IAg_3](NO_3)_2$.[233]

TABLE 7. Possible structures of co-ordination polymers C. N. = 6.

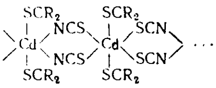
Apparent C.N.	Composition of polymer	Stereochemical formula	Mode of combination of octahedra
5	MA_5	$[MA_{4+2/2}]_{\infty}K$	chain of octahedra with two corners in common (Fig. 12)
4	MA_4	$[MA_{2+4/2}]_{\infty}K$	chain of octahedra with two edges in common (Figs. 13 and 14)
		$[MA_{2+4/2}]_{\infty}N$	two-dimensional layer of octahedra with four corners in common (Fig. 15)
3	MA_3	$[MA_{1+2/2+3/3}]_{\infty}K$	double chain of octahedra with four edges in common (Fig. 17)
		$[MA_{6/2}]_{\infty}K$	chain of octahedra with faces in common (Fig. 18)
		$[MA_{6/2}]_{\infty}N$	two-dimensional layer of octahedra with three edges in common (Fig. 16)
		$[MA_{6/2}]_{\infty}G$	three-dimensional lattice of octahedra with six corners in common (Fig. 19)
2	MA_2	$[MA_{6/3}]_{\infty}N$	two-dimensional layer of octahedra with six edges in common (Fig. 20)

The compound KCr_3O_8, for example, contains[280] CrO_4 tetrahedra and CrO_6 octahedra. In the compounds $Ni(CN)_2.NH_3$ [281] half the nickel atoms have a co-ordination number of 6, and the other half a co-ordination number of 4.

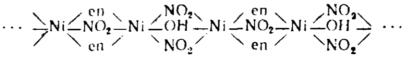


In the compound V_3O_5 the VO_6 octahedra are joined in a complicated manner — at the corners, edges, and faces simultaneously[282]. Many examples of such structures can be found in the literature on structural chemistry.

An interesting co-ordination polymer is di-(2-thioimidazolidine)cadmium thiocyanate, described by Cavalca *et al.*[283] It is made up of octahedra linked by SCN groups to form an infinite chain



The compound $Ni_2en_2(NO_2)_3OH$ has the structure[284]

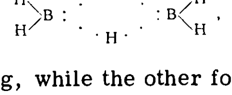


Thus many compounds which we have been accustomed to regard as "simple" are actually polymeric. The somewhat paradoxical conclusion can be drawn that binary compounds (having a polymeric co-ordinate structure), which are regarded as "simple compounds", have more complicated structures than the "complex" compounds (which have a discrete, non-polymeric structure). Hence it follows that the concept of "complex compound" is quite arbitrary: the chemistry of complex compounds must include also those binary compounds whose structures bring them into the class of co-ordination polymers. We must, of course, distinguish the polymeric $CuCl_2$ from the mononuclear hydrate $CuCl_2.2H_2O$, which has a discrete structure. Among the compounds $[CdCl_2(NH_3)_2]$, $[ZnCl_2(NH_3)_2]$, and $[PtCl_2.(NH_3)_2]$, only the first is polymeric. It is therefore necessary, in the chemistry of complex compounds, to use a classification based on the structure of the complexes and not solely on the empirical formula.

IV. ELECTRON-DEFICIENT POLYMERS

We have already mentioned the tendency of elements to form as many bonds as possible by drawing unpaired electrons into vacant orbitals, with formation of a larger number of bonds than would correspond to the classical valency. Sometimes the tendency of elements to increase the number of bonds by utilising unoccupied valency orbitals is so strong that polymerisation takes place even in compounds in which the electrons are sufficient only to form the bonds corresponding to the valency of the element. In the compounds BH_3, $Be(CH_3)_2$, $Al(CH_3)_3$, $Pt(CH_3)_4$ all the electrons are involved in normal covalent bonds, which elementary classical valency theory describes as two-centre electron-pair bonds. Nevertheless, these compounds do form polymers because of the tendency of B, Be, Al, and Pt atoms to make full use of their valency orbitals. The resulting polymers contain a larger number of chemical bonds than of electron pairs necessary for this purpose. Such compounds are therefore said to be "electron-deficient". The polymerisation of these compounds is made possible by the formation of three-centre and many-centre bonds, *i.e.* bonds in which the electron pair is situated in the field of three or more nuclei[16,285,286].

The simplest polymer of this type is diborane B_2H_6. It has been established that this compound has a structure in which two hydrogen atoms act as bridging groups between the two boron atoms[287-291]



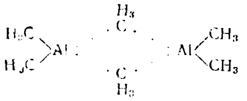
forming a B_2H_2 ring, while the other four hydrogen atoms remain outside this ring. Several hypotheses have been put forward to explain the nature of the B...H...B bonds[292].

The diborane molecule contains eight atoms, so that it should have seven covalent bonds, *i.e.* fourteen electrons, whereas it actually has only twelve electrons, eight of which are used in the four outer B-H bonds. Only four electrons remain for the B...H...B bonds. The mechanism whereby four electrons can link four atoms has been clarified by the theory of molecular orbitals. It was found that the hybrid-orbitals of the two boron atoms can overlap the 1*s* orbital of the hydrogen atom and the formation of the B_2H_2 ring is based on that of two three-centre B...H...B bonds.

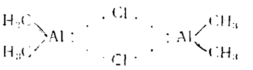
The idea of many-centre orbitals was extended to explain the structure of other boron hydrides:[293] B_5H_9,[294,295] B_5H_{11},[296] B_4H_{10},[297,298] B_6H_{10},[299] $B_{10}H_{14}$,[300] etc.[301-305], and was used to interpret the structures of other electron-deficient molecules.

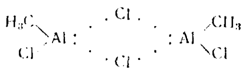
An interesting polymeric boron compound having many-centre bonds is B_4Cl_4, obtained by Urry *et al.*[306] This compound might have been homocyclic, but electron diffraction[307,308] showed that the boron atoms were arranged at the corners of a regular tetrahedron and were held together by many-centre bonds involving the $3p\pi$ electrons of the chlorine.

Trimethylaluminium is a dimer[309]. Its structure was determined by means of electron diffraction[310,311] and involves methyl bridges



The Al...CH_3...Al bonds are three-centred, and are produced by the overlapping of the vacant orbitals of the aluminium atoms and the *p* orbitals of the CH_3 group. In $(CH_3)_2AlCl$ and CH_3AlCl_2, which also are dimeric, chlorine atoms act as bridging groups:

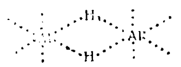




These molecules are not electron-deficient, but it is probable that the Al...Cl...Al bonds are also three-centred.

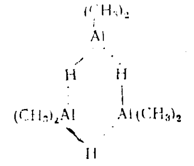
It is interesting that $Ga_2(CH_3)_6$ is less stable, probably because the large size of the gallium atom prevents sufficient overlapping of the three orbitals.

Formation of many-centre bonds may explain the structure of aluminium hydride $(AlH_3)_x$, in which every aluminium atom is surrounded by six hydrogen atoms[312].



The polymeric nature of gallium hydride $(GaH_3)_x$[313-315] and indium hydride $(InH_3)_y$ [316] can also be explained in this way.

Dimethylaluminium hydride $HAl(CH_3)_2$ is a cyclic trimer[317,318]. Other similar compounds, for example $[HAl.(C_2H_5)_2]_3$ and $[HAl(iso\text{-}C_4H_9)_2]_3$, are also electron-deficient polymers containing many-centre bonds



Indium has a higher co-ordination number than aluminium, and therefore trimethylindium is a tetramer $[In(CH_3)_3]_4$. This compound has a cubic structure[319], a proportion of the methyl groups, situated at the corners of the cube, serving as bridges. The tetrameric molecule is formed by means of many-centre orbitals. The external In–CH_3 bonds are ordinary covalent bonds.

X-Ray analysis has shown that tetramethylplatinum $[Pt(CH_3)_4]_4$ has a similar composition[320] and structure[321] (Fig. 21). The compound $[(CH_3)_3PtCl]_4$ has an analogous structure, the chlorine and platinum atoms being arranged at the corners of a cube[321]. In these compounds the platinum has a co-ordination number of 6 owing to the utilisation of d^2sp^3 orbitals, the tendency to complete utilisation of which[16] leads to polymerisation. Tetramethyl-lead $Pb(CH_3)_4$ is not polymeric, since lead has only four sp^3 orbitals.

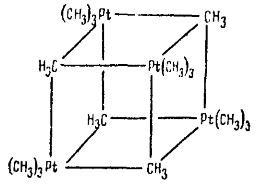


Fig. 21. Structure of $[Pt(CH_3)_4]_4$.

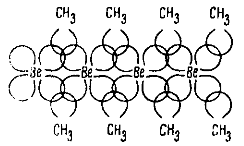
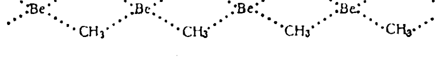


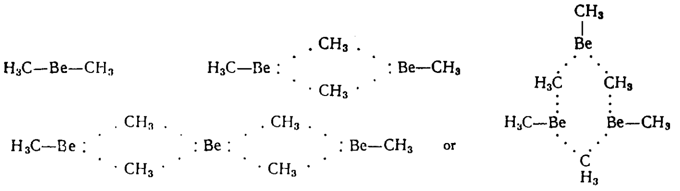
Fig. 22. Formation of three-centre bonds in $[Be(CH_3)_2]_x$ chain.

Many-electron many-centre bonds can also govern the formation of electron-deficient polymers of high molecular weight. X-Ray diffraction patterns have shown[311] that $Be(CH_3)_2$ consists of endless linear chains, the beryllium atoms being linked by methyl bridges (Fig. 22).



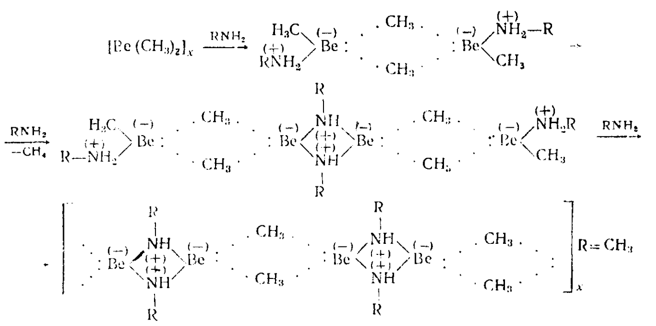
The beryllium atoms are surrounded tetrahedrally by four CH_3 bonds. The Be...CH_3...Be bonds are weaker than simple covalent bonds, and can be regarded as "half-bonds"; this depends also on the bond length[322] Be...CH_3 = 1.92 Å (normal covalent Be–C bonds have a length of 1.73 Å).

Monomeric, dimeric, and trimeric molecules are formed in $Be(CH_3)_2$ vapour



Electron-deficient compounds behave chemically as Lewis-acids: *i.e.* they react with electron-donors. This is because a two-centre electron-pair bond is more stable than a pair of unshared electrons and than a three-centre electron-pair bond[285]. It is therefore clear why boron hydrides react readily with amines and other electron-donors[305,324,325].

The interesting reactions of $[Be(CH_3)_2]_x$ with amines[326], ethers, and phosphines[327] can be explained in a similar manner. On reaction with primary amines the polymer is broken down with the formation of Be–$\overset{R}{N}$H–Be co-ordinate bridges and a polymer containing both two-centre co-ordinate links and three-centre bonds:



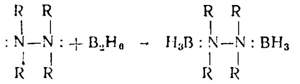
In this way groups of compounds are obtained having the general composition

$$[(CH_3)_2Be]_x\,[(CH_3)_3P]_y \quad x = 1\ldots5;\; y = 1\ldots3^{327}$$

$$[(CH_3)_2Be]_x\,[(CH_3)_2O]_y \quad x = 1, 2, 6;\; y = 1\ldots3^{327}$$

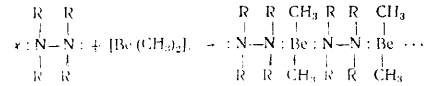
$$[(CH_3)_2Be]_x\,[(CH_3)_3N]_y{}^{326}$$

Recently an interesting derivative of tetramethylhydrazine and diborane has been prepared[328]



$$:\underset{R}{\overset{R}{N}}-\underset{R}{\overset{R}{N}}: + B_2H_6 \rightarrow H_3B:\underset{R}{\overset{R}{N}}-\underset{R}{\overset{R}{N}}:BH_3$$

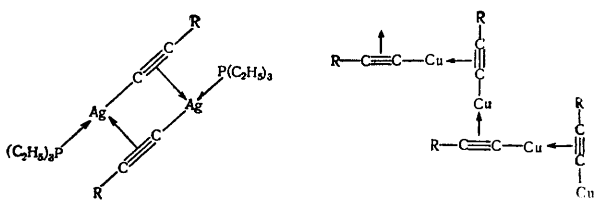
Dimethylberyllium, which has two vacant orbitals, is able to form a linear polymer of high molecular weight



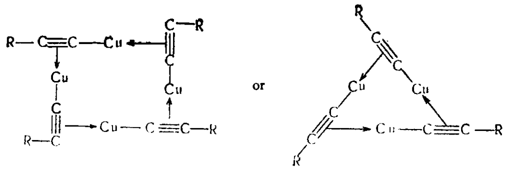
$$x:\underset{R}{\overset{R}{N}}-\underset{R}{\overset{R}{N}}: + [Be(CH_3)_2] \rightarrow :\underset{R}{\overset{R}{N}}-\underset{R}{\overset{R}{N}}:\underset{CH_3}{\overset{CH_3}{Be}}:\underset{R}{\overset{R}{N}}-\underset{R}{\overset{R}{N}}:\underset{CH_3}{\overset{CH_3}{Be}}\cdots$$

Although electron-deficient compounds are unstable, which would hinder their practical application, they may be of interest for the synthesis of other chain polymers.

The recently prepared acetylenic polymers of univalent copper and silver[329] can probably be included in the same group: $(C_2H_5)_3PAgC\,\vdots\,CR$ is dimeric in nitrobenzene, while the corresponding copper compound is trimeric or tetrameric. The following structures are assumed for these compounds



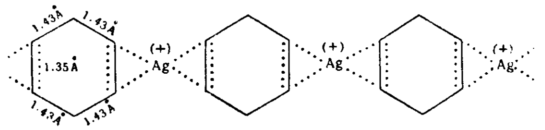
The present reviewer suggests a cyclic structure for the copper compound



The bond between the metal atom and the C ⋮ C group is probably three-centred. The same type of bond is probably present also in the compound $C_6H_6.AgClO_4$, which can be represented as a polymeric chain[330]

$$\cdots C_6H_6\cdots Ag\cdots C_6H_6\cdots Ag\cdots$$

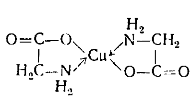
in which the benzene rings are strongly distorted (four C–C bonds of 1.43 Å, and two C–C bonds of 1.35 Å).



Such polymers very probably exist. The study of electron-deficient compounds is only in its initial stages, and the results of investigations in this field are of great scientific value.

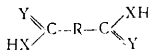
V. POLYMERIC CHELATE COMPOUNDS

Chelate compounds[85-87,331] are of great importance in the chemistry of complex compounds; they are complexes in which the metal atom forms part of a ring (usually five- or six-membered), for example

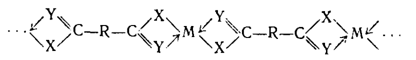


Berlin and Matveeva[332] have recently suggested the term "chelatophor" for groups which are able to form chelate rings.

Organic compounds of the type



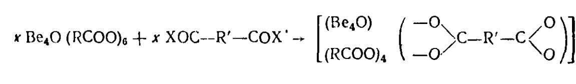
(X = O, S, NH, etc.; Y = O, S, NH) can react with metal ions to form chelate polymers having the general structure



Since the chemistry of chelate polymers has been discussed in detail by Berlin and Matveeva[332], we shall consider only examples of compounds in which metal atoms alternate with organic groups to form the main chain. Several classes of compounds of this type are known.

Elliot[333] obtained polymers of cobalt with bis-α-amino acids. It would be useful to study thioamine acids, amides, and other acid derivatives of similar structure with a view to obtaining new chelate polymers.

Sometimes merely the presence of a carboxyl group at the ends of a hydrocarbon chain is sufficient for the formation of co-ordination polymers. Thus basic beryllium acetate $(CH_3.COO)_6Be_4O$ forms polymers with dibasic organic acids



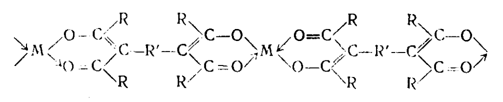
$$x\,Be_4O(RCOO)_6 + x\,XOC{-}R'{-}COX' \rightarrow \left[\begin{matrix}(Be_4O)\\(RCOO)_4\end{matrix}\left(\begin{matrix}-O\\-O\end{matrix}{>}C{-}R'{-}C{<}\begin{matrix}O\\O\end{matrix}\right)\right]_x$$

where X = OH, OR.

Polymers containing beryllium can be prepared from succinic[334,335], adipic, sebacic, isophthalic, and terephthalic acids[336].

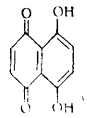
Even copper salts of α,ω-dicarboxylic acids have a two-dimensional macromolecular structure[337]. Compounds of univalent copper with α, ω-dinitriles $[Cu(NC.R.CN)_2]NO_3$ are also polymeric, as is shown by an X-ray investigation of the complexes of succinonitrile[338], glutaronitrile[339], and adiponitrile[340].

A large number of co-ordination polymers have been obtained by the reaction of tetraketones with Be, Cu, Ni, Zn, Co, Fe, Pd, Mn, Sr, Cd, etc.[341-344]



Chelate polymers of aluminium have a similar structure[345].

Hydroxynaphthaquinones are also able to form polymers. Linear polymers of beryllium with naphthazarin and alkannin have been obtained[346]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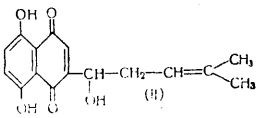
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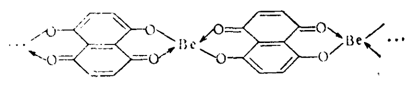
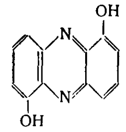


Polymers are known containing various metal ions and 1,6-dihydroxyphenazine (III),[347] 2,5-dihydroxybenzoquinone (IV),[347] rubeanic acid (V),[348,349] 5-formylsalicylaldehyde,[350] quinizarin (VI),[351] bis-8-hydroxyquinolinylmethane (VII),[352] and other ligands[353-359]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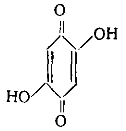
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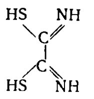
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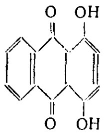
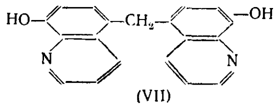
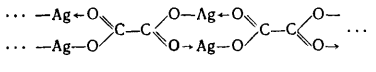
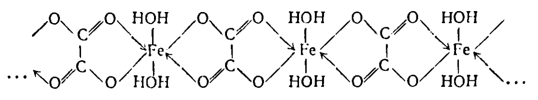

(VI)


(VII)

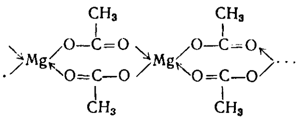
Among interesting polymers are those in which the chelate ring contains two metal atoms, *e.g.* silver oxalate[330]:



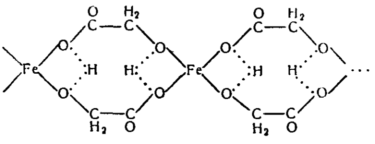
Ferrous oxalate also is a linear polymer[361]:



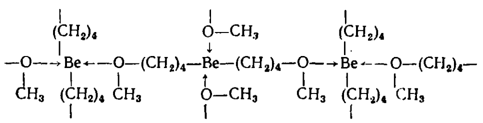
The high viscosity of concentrated solutions of magnesium acetate is explained by the formation of polymers[362,363]



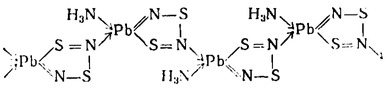
Infra-red spectra have shown that ferrous glycollates are polymers of similar type[364]



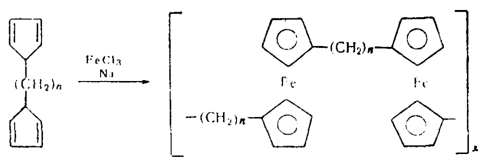
Interesting polymers are encountered among organic derivatives of beryllium[365]



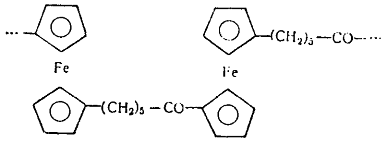
The existence of purely inorganic chelate polymers is possible, for example $Pb(NS)_2NH_3$:[366]



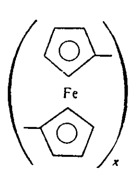
Progress in metallocene chemistry has made it possible to obtain new types of polymers containing such groups in the main chain. The following reaction was carried out[367,368]



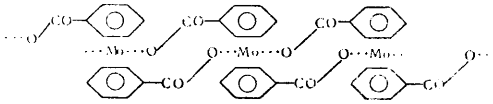
Other workers[368] have prepared polymers with the structure



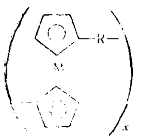
Recently Korshak *et al.*[369] have synthesised a polyferrocene with a molecular weight of ~ 2500

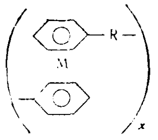


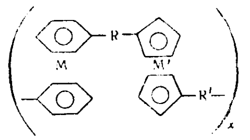
An interesting metallocene polymer is molybdenum(II) dibenzoate[370], which has been given the structure



There are many as yet unused methods which could be applied to the synthesis of new types of polymers. It would be interesting to obtain polymers of the following types

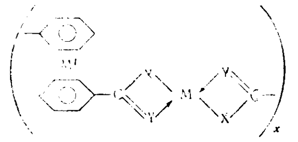




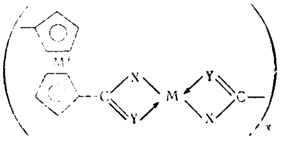


where R = alkyl or aryl group, O, S, NH, $R_2Si.O$, $R_2P:N$, etc.

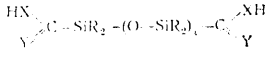
Another method would be addition of a chelatophoric group to a metallocene skeleton to obtain the corresponding chelate polymers



or

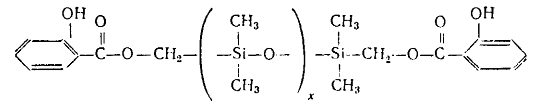


It would also be interesting to obtain chelate polymers in which the chelatophor was combined with a siloxane or other organo-elementary radical



$$\overset{HX}{\underset{Y}{}}\!>C-SiR_2-(O-SiR_2)_x-C\!<\overset{XH}{\underset{Y}{}}$$

The compound[371]



is of interest from this point of view.

Since chelate polymers combine the properties of organic and of inorganic polymers, and possess great thermal and chemical stability, it can be assumed that in the future they will play a special part in the production of new synthetic materials with special properties.

VI. FORMATION OF CO-ORDINATION POLYMERS IN SOLUTION

1. FORMATION IN WATER

It has long been known that ions in aqueous solutions are hydrated but a detailed study of aqueous solutions of metal salts has shown that the phenomena occurring in solution are very varied and complicated. Aqueous solutions of salts are often acidic or alkaline indicating that chemical interaction between metal ions and water molecules (hydrolysis) takes place in solution. Since modern research has shown that such reactions not infrequently involve the formation of polynuclear complexes which are co-ordination polymers, we will examine these phenomena below.

The first reaction which takes place when a salt is dissolved in water is hydration of the ions. In the case of a salt of a cation M^{p+}, having a co-ordination number of *n* with respect to water, and an anion A (A is assumed to be univalent in order to simplify the chemical equations), hydration can be represented by the equation

$$\underset{\text{crystalline salt}}{MA_p\cdot x\,H_2O} + n\,H_2O \rightleftarrows [M(H_2O)_n]^{p+}\,aq + p\,A^-\cdot aq \quad (1)$$

This simple hydration reaction is followed by a number of secondary reactions, which to a large extent determine the macroscopic properties of the solution (pH, electrical conductivity, etc.). The water molecules co-ordinated with the central ion can lose hydrogen ions or can be replaced by OH^- ions from the solution:

$$[M(H_2O)_n]^{p+} + H_2O \rightleftarrows [M(H_2O)_{n-1}(OH)]^{(p-1)+} + H_3O^+ \quad (2)$$

$$[M(H_2O)_n]^{p+} + OH^- \rightleftarrows [M(H_2O)_{n-1}(OH)]^{(p-1)+} + H_2O \quad (3)$$

This reaction is favoured by a decrease in the hydrogen ion concentration. Complexes can be formed having one, two, or more hydroxyl groups co-ordinated to the central ion

$$[M(H_2O)_{n-1}(OH)]^{(p-1)} + H_2O \rightleftarrows [M(H_2O)_{n-2}(OH)_2]^{(p-2)+} + H_3O^+. \quad (4)$$

When their number is equal to the valency *p* of the metal, the hydroxide is precipitated.

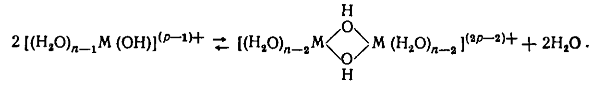
These reactions are accompanied by an increase in the concentration of H^+ (or H_3O^+) ions in the solution, and can therefore be studied by the usual methods for determining hydrogen ion concentrations in solution.

We are especially interested in the formation of hydroxo complexes in solution, since they can be condensed to form polynuclear complexes[85-87], *i.e.* co-ordination polymers.

We shall therefore ignore, with Pokras[372,373], other possible reactions in aqueous solution and confine ourselves to the formation of these complexes, in which the OH groups act as bridges (reviewed by Basset[374]).

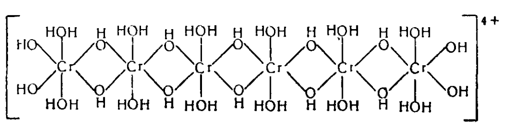
Hydrolytic co-ordination polymerisation. Reactions of this type can be represented by the following equations

$$[M(H_2O)_n]^{p+} + [M(H_2O)_{n-1}(OH)]^{(p-1)+} \rightleftarrows \qquad (5)$$
$$\rightleftarrows [(H_2O)_{n-1}M{-}OH{-}M(H_2O)_{n-1}]^{(2p-1)+} + H_2O.$$



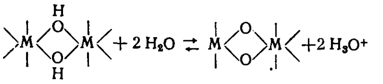
$$2\,[(H_2O)_{n-1}M(OH)]^{(p-1)+} \rightleftarrows [(H_2O)_{n-2}M\genfrac{}{}{0pt}{}{\overset{H}{O}}{\underset{H}{O}}M(H_2O)_{n-2}]^{(2p-2)+} + 2H_2O. \qquad (6)$$

These reactions can continue with the formation of co-ordination polymers of increased molecular weight containing 3, 4, 6, or more metal nuclei. Formation of complex polymers of the following type is possible[87]



We have seen that an increase in the concentration of OH^- ions in the solution favours reactions (2)–(4), which form the initial stages of the polymerisation process in solution. When a salt solution is made alkaline until the metal hydroxide separates, co-ordination polymers are present in the solution. Polymerisation develops as the solution is made alkaline, and is terminated by precipitation of the hydroxide, which is a high polymer (see section IV).

When a solution is allowed to stand, other reactions take place, which change the nature of the polymers, for example



$$\rangle M\genfrac{}{}{0pt}{}{\overset{H}{O}}{\underset{H}{O}}M\langle + 2H_2O \rightleftarrows M\genfrac{}{}{0pt}{}{O}{O}M\langle + 2H_3O^+$$

This reaction is favoured by a decrease in the hydrogen ion concentration of the solution and by an increase in temperature.

These facts make it possible to understand the formation of hydroxides, oxides, and basic salts in aqueous solution and the polymeric structure of these compounds. These views on hydrolysis reactions (which are better termed hydrolytic co-ordination polymerisation reactions) have been expounded in papers by Stiasny[375,376], Thomas[377–380], Jander and Jahr[381–384], and later in the investigations of Hall and Eyring[385], Pokras[372,373], Kraus[386,387], Faucherre[388–391], Souchay[392,393], and Sillén and his collaborators[394–422]. The work carried out at Kungl. Tekniska Högskolan in Stockholm during the past ten years[387,394–419] has made a particularly great contribution towards elucidating the reactions occurring during the process of hydrolysis.

Sillén obtained general equations representing the process of hydrolysis, and worked out a mathematical method for calculating the composition and the degree of polymerisation of co-ordination polymers in solution. The method has been described in several reviews[387,394] and in the original papers[395–398].

Let us examine further some hydrolysis reactions. In order to simplify the reaction

$$M(H_2O)_6^{3+} + H_2O \rightleftarrows M(H_2O)_5(OH)^{2+} + H_3O^+,$$

we shall represent it as follows

$$M^{3+} + H_2O \rightleftarrows MOH^{2+} + H^+.$$

Study of a large number of metal ions has enabled metals to be classified as follows with respect to their behaviour on hydrolysis.

(a) Metals which form only mononuclear complexes on hydrolysis: Hg(I),[399] Hg(II),[400] Fe(II),[401] Tl(III),[402,403] Cd(II),[404] and Ag(I).[405,406] Thus, for example, Hg^{2+} forms $[HOHgOH_2]^+$ and [HOHgOH]. In Fe^{2+} solutions, $[FeOH]^+$ ions are formed, etc.

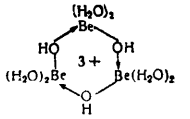
(b) Ions which on hydrolysis form dinuclear complexes or a limited number of complexes of definite degree of polymerisation: Be(II),[407] Cu(II),[408] Sn(II),[409] Fe(III),[403,410] Bi(III),[411,412] and Al(III).[403,413]

(c) Ions which on hydrolysis form continuous series of polynuclear complexes, of general formula

$$\{M[(OH)_pM]_x\}^{[(n-p)x+n]+},$$

where p is the number of OH groups, n the charge on the metal ion M^{n+}, and x the degree of polymerisation. This group includes the ions UO_2^{2+},[414] In(III),[403,415] Sc(III),[403,416] Th(IV),[417,418] and U(IV),[418,419]

Ions which form definite polynuclear complexes. Hydrolysis of the beryllium ion Be^{2+} has been studied potentiometrically using the quinhydrone and the calomel electrodes[394,407]. The main product of hydrolysis is the $Be_3(OH)_3^{3+}$ ion, accompanied by small amounts of the Be_2OH^{3+} ion and of $Be(OH)_2$.



It is supposed that beryllium has tetrahedral co-ordination, as in $Be(OH)_2$, involving water molecules: the $Be_3(OH)_3^{3+}$ cation has a cyclic structure. The main reaction in the hydrolysis of beryllium is

$$3Be^{2+} + 3H_2O \rightleftarrows Be_3(OH)_3^{3+} + 3H^+;\ \log K = -8.66 \pm 0.03$$

These workers assume that the compounds $BeOH(H_2O)_2 \cdot [HgCl_3]$, $Be(OH)(H_2O)_2[HgBr_3]$, and $Be_3(OH)_3(H_2O)_6[Hg_2I_7]$, described by Slavvo[423–425] contain polymeric cyclic cations similar structure.

The hydrolysis of the beryllium ion was also studied by Faucherre[388–390] and by Souchay[392,393] who assumed the existence of the $Be_4(OH)_4^{4+}$ ion in solution. Scandinavian workers[407] did not support this view. The $Be_2(OH)_2^{2+}$ ion, which was assumed by other workers[426,427] is also absent from solution.

In aqueous solution the Cu^{2+} ion forms only dinuclear complexes $Cu_2(OH)_2^{2+}$ on hydrolysis[408].

Hydrolysis of the Sn^{2+} ion yields mono-, di-, and trimeric complexes — $SnOH^+$, $Sn_2(OH)_2^{2+}$, and $Sn_3(OH)_4^{2+}$ — by the reactions[409]

$$3Sn^{2+} + 4H_2O \rightleftarrows Sn_3(OH)_4^{2+} + 4H^+;\ \log K = -6.77$$
$$2Sn^{2+} + 2H_2O \rightleftarrows Sn_2(OH)_2^{2+} + 2H^+;\ \log K = -4.45$$
$$Sn^{2+} + H_2O \rightleftarrows SnOH^+ + H^+;\ \log K = -3.9.$$

The following equilibria occur in the hydrolysis of the bismuth ion, Bi^{3+},[411,412]

$$Bi^{3+} + H_2O \rightleftarrows BiOH^{2+} + H^+;\ \log K = -1.58 \pm 0.02$$

$$6Bi^{3+} + 12H_2O \rightleftarrows Bi_6(OH)_{12}^{6+} + 12H^+;\ \log K = 0.330 \pm 0.005.$$

The main reaction product is the $Bi_6(OH)_{12}^{6+}$ (or $Bi_6O_6^{6+}$) ion. A continuous series of complexes $\{Bi[(OH)_2Bi]_n\}^{3+n}$, as seemed possible earlier, is not formed[420].

These polycations having six bismuth atoms are hydrolysed with the formation of a nonanuclear cation[412]:

$$1.5\,Bi_6(OH)_{12}^{6+} + 2H_2O \rightleftarrows Bi_9(OH)_{20}^{7+} + 2H^+;\ \log K = -3.5 \pm 0.1$$

$$Bi_9(OH)_{20}^{7+} + H_2O \rightleftarrows Bi_9(OH)_{21}^{6+} + H^+;\ \log K = -3.2 \pm 0.2.$$

The structure of these complexes is unknown

The presence of polynuclear bismuth complexes in solution has been demonstrated by various methods. The ions $Bi_4O_4^{4+}$, $Bi_5O_5^{5+}$, and $Bi_6O_6^{6+}$ have been detected photometrically[428]. It was not possible with the ultracentrifuge to establish whether the complexes contain five or six bismuth atoms[429].

Tobias[430] considers that hydrolysis of Bi^{3+} proceeds according to the equations

$$6Bi^{3+} + 6H_2O \rightleftarrows Bi_6O_6^{6+} : 12H^+;\ Bi_6O_6^{6+} + 3H_2O \rightleftarrows Bi_6O_6(OH)_3^{3+} + 3H^+.$$

Hydrolysis of ferric iron yields only mono- and di-nuclear complexes[403,410]

$$Fe^{2+} + H_2O \rightleftarrows FeOH^{2+} + H^+;\ \log K = -3.05$$

$$FeOH^{2+} + H_2O \rightleftarrows Fe(OH)_2^+ + H^+;\ \log K = -3.26$$

$$2Fe^{3+} + 2H_2O \rightleftarrows Fe_2(OH)_2^{4+} + 2H^+;\ \log K = -2.91$$

When hydrolysis is continued, the hydroxide is formed.

Hydrolysis of the Pb^{2+} ion gives the following products[421]

$$Pb^{2+} + H_2O \rightleftarrows PbOH^+ + H^+$$

$$4Pb^{2+} + 4H_2O \rightleftarrows Pb_4(OH)_4^{4+} + 4H^+$$

$$3Pb^{2+} + 4H_2O \rightleftarrows Pb_3(OH)_4^{2+} + 4H^+$$

$$6Pb^{2+} + 8H_2O \rightleftarrows Pb_6(OH)_8^{4+} + 8H^+$$

Pedersen[431] proved that the ions Pb_2OH^{3+} and $Pb_4(OH)_4^{4+}$ are formed, and Faucherre[432] considers that hydrolysis of Pb^{2+} gives $Pb_4(OH)_4^{4+}$, $Pb_9(OH)_{12}^{6+}$, and $PbOH^+$.

The hydrolysis of the Al^{3+} ion has been investigated by various workers, who have emphasised the presence of polynuclear complexes in the solution. Brosset, Biedermann, and Sillén[403,413] were unable to determine exactly whether complexes having definite degrees of polymerisation or continuous series of polymers were formed in solution. In acid medium ions having the composition $Al[(OH)_5Al_2]^{(3+x)+}$ are formed, and in alkaline medium $[Al(OH)_3]_x(OH)^-$ ions; it cannot be said whether x assumes a series of values or only certain values. Formation of the complex $Al_6(OH)_{15}^{3+}$, for which a cyclic structure (Fig. 23) is suggested, is most probable in acid medium. This agrees with results obtained by Kohlschütter and Hantelman[433], who found cryoscopically that the size of the molecule in a solution containing Al : OH = 1 : 1.5 corresponds to six Al atoms, *i.e.* to the $Al_6(OH)_{15}^{3+}$ ion.

The complex ions $Al_2(OH)_2^{4+}$ and $Al_3(OH)_6^{3+}$ are not the chief products of hydrolysis, even if they are formed in solution. The presence in solution of complexes having higher degrees of polymerisation is not excluded.

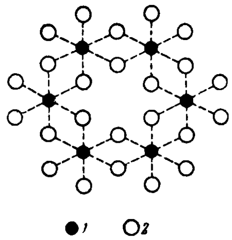


Fig. 23. Structure of hexanuclear complex $Al_6(OH)_{15}^{3+}$ aq complex: 1) Al; 2) OH or H_2O.

Ions which form continuous series of polymers. Ions of several metals form polynuclear complexes of indefinite degree of polymerisation on hydrolysis. Continuous series of polymers are formed, with the general formula $M[(HO)_pM]_x$, where x = 1, 2, 3, 4, 5, 6, ...

Hydrolysis of the In^{3+} ion involves the equilibria[403,415]

$$In^{3+} + 2H_2O + In^{3+} \rightleftarrows In(OH)_2In^{4+} + 2H^+;\ \log K = -5.21$$

$$In[(HO)_2In]_x^{(3+x)+} + 2H_2O + In^{3+} \rightleftarrows In[(OH)_2In]_{x+1}^{(x+4)+} + 2H^+;\ \log K = -4.69$$

the general equation being

$$(x+1)In^{3+} + 2xH_2O \rightleftarrows In[(OH)_2In]_x^{(3+x)+} + 2xH^+.$$

These polymers probably have a linear structure, since X-ray analysis has shown[214,434] that basic salts of indium contain linear polymeric ions $In(OIn)_x^{(x+3)+}$.

Hydrolysis of the Sc^{3+} ion[403,416] is represented by the general equation

$$(x+1)\,Sc^{3+} + 2xH_2O \rightleftarrows Sc[(OH)_2Sc]_x^{(x+3)+} + 2xH^+;\ \log K = 0.70 - 6.87x$$

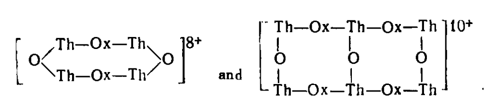
The solution contains species having x = 1, 2, 3, such as, for example, $Sc(OH)^{2+}$, $Sc(OH)_2^+$, $Sc_2(OH)_2^{4+}$, and $Sc_3(OH)_4^{5+}$, as well as higher polymers. The degree of polymerisation increases step by step, according to the equation

$$Sc[(OH)_2Sc]_x^{(x+3)+} + 2H_2O + Sc^{3+} \rightleftarrows Sc[(OH)_2Sc]_{x+1}^{(x+4)+} + 2H^+$$

New data[417,418] on the hydrolysis of thorium Th^{4+} indicate the formation of a series of complexes $Th[(OH)_3Th]_x$, where x = 1, 2, 3, ..., 6, and above. Early work showed that formation of $Th_4O_4^{8+}$ ions takes place, but other workers[435] point to the formation of the ions $Th(OH)_2^{2+}$, $Th_2(OH)_2^{6+}$, and $Th_5(OH)_{12}^{8+}$. The $Th_2(OH)_2^{6+}$ ion was detected by Hietanen and Sillen[436]. A linear structure is suggested for the polycations formed on hydrolysis: $Th\substack{O\\OH}Th\substack{O\\OH}Th\substack{O\\OH}\ldots Th\substack{O\\OH}Th$ or $Th(\substack{O\\OH}Th)_x$. This hypothesis is based on X-ray analysis[422], which showed the presence of $Th[\substack{O\\OH}Th]_x^{(4+x)+}$ chains in the structures of the basic sulphate and the basic chromate of thorium (SO_4ThOH and CrO_4ThOH), as well as on an electron-diffraction study[437,438] of thorium hydroxide.

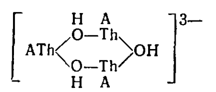
It is interesting that polynuclear thorium complexes containing Th–O–Th bridges are also formed with oxalic acid[439].

The ions $[Th_4O_2(Ox)_2]^{8+}$ and $[Th_6O_3(Ox)_4]^{10+}$, where Ox = $= (COO)_2^{2-}$, were detected, having the possible structure



Water molecules, of course, are co-ordinated to the thorium atoms.

Chelates of thorium with ethylenediaminetetra-acetic acid (EDTA) hydrolyse with the formation of a cyclic trimer[440]



A = EDTA

Hydrolysis of the U^{4+} ion[418,419] is similar to that of the Th^{4+} ion. A mononuclear complex is formed first

$$U^{4+} + H_2O \rightleftarrows UOH^{3+} + H^+,$$

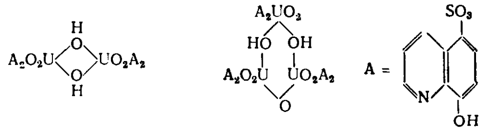
and then the polymers

$$(x+1)\,U^{4+} + 3xH_2O \rightleftarrows U[(OH)_3U]_x^{(4+x)+} + 3xH^+.$$

These polymers apparently have a linear structure $U[{}^{O}_{OH}U]_x^{(4+x)+}$, similar to the compound $U(OH)_2SO_4$, studied by X-ray diffraction[441], which contains $[U(OH)_2]_x^{2x+}$ infinite chains. In the compound $U_6O_4(OH)_4(SO_4)_6$ X-ray analysis has detected[442] the presence of discrete $U_6O_4(OH)_4^{12+}$ ions.

Hydrolysis of the UO_2^{2+} ion results in the formation of a series of polymers having the composition $UO_2[(OH)_2UO_2]_x^{(2+x)+}$ (or $UO_2[OUO_2]_x^{(2+x)+}$).[414] It is suggested that the structure of these complexes is based on layers of the given composition in which the UO_2 group forms four U–O co-ordinate links, as in the structure of $BaUO_2O_2$ [443] and $CaUO_2O_2$.[444] Recent work has shown[445] the formation of cations having the composition $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_4^{2+}$.

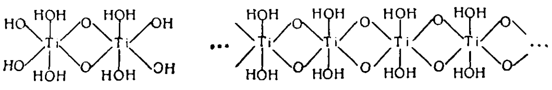
Co-ordination polymers are formed by an analogous mechanism in solutions of several uranyl chelates[446]. Thus dimers and trimers of the following structure are formed[446]



The precise structure of such trimers is still unknown.

The literature contains data on the hydrolysis of other ions, but the results are not yet sufficiently convincing, and the precise composition of the hydrolysis products is unknown. Polymerisation phenomena have been observed in solutions of cerium salts[447,448], in which dimers, trimers, and polymers are present. X-Ray patterns have shown[449] that the basic salt $CeOSO_4.H_2O$ contains macromolecular Ce–O chains, while the salt $Ce_6O_4(OH)_4(SO_4)_6$ is made up of $Ce_6O_4(OH)_4^{12+}$ ions.

Other workers have shown the presence of polymeric complexes in solutions of titanium salts. Thus the Ti^{4+} ion in solution forms polymeric complexes of the type[450]



It has been shown spectrophotometrically[451] that solutions of peroxotitanic acid are also polymeric. The presence of macromolecular Ti–O chains in the structure of $TiOSO_4.H_2O$ has been established by means of X-rays[452].

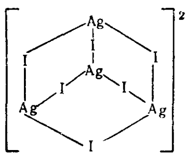
The zirconium ion Zr^{4+} is also able to form polymers[453]. The ions $Zr_3(OH)_4^{8+}$ and $Zr_4(OH)_8^{8+}$ exist, and higher polymers are probable. This agrees with Lundgren's X-ray results[454] showing that basic zirconium chromate contains $[Zr_4(OH)_6.CrO_4]_x^{8x+}$ endless chains containing Zr–OH–Zr co-ordinate links. The ions $Zr_4(OH)_8(H_2O)_{16}^{8+}$ have been detected[455] in both $ZrOCl_2.8H_2O$ and $ZrOBr_2.8H_2O$. Oxalate polymers $Zr_{nx}.[(COO)_2]_x$ ($n = 2, 3, 4, \ldots$) have been discovered[456]. Some chelate compounds of zirconium are also polymeric[457,458].

The hydrolytic polymerisation of the chromic ion, Cr^{3+}, has been widely studied[375,376,459-464] and formation of polynuclear complexes of high molecular weight is possible. The Cr^{3+} ion can probably form a continuous series of polymers on hydrolysis.

Polycations of high molecular weight are also formed in the hydrolysis of salts of magnesium Mg(II),[383] zinc,[384] and plutonium[456].

In all these cases it is unknown whether continuous series of complexes or complexes having a definite degree of polymerisation are formed and it would be very useful to apply Sillén's method to an investigation of the hydrolysis of these ions.

Other ligands besides the OH ion are able to form polymeric, polynuclear complexes in solution. Interesting work by Nilssen[466] has shown that the complexes $Ag_2(S_2O_3)_4^{6-}$, $Ag_3(S_2O_3)_5^{7-}$, and $Ag_6(S_2O_3)_8^{10-}$ are formed having co-ordinate links between the silver ions and the thiosulphate groups. In the $Ag_4I_6^{2-}$ ion the Ag and I atoms occupy positions corresponding to a urotropine type of structure[467]



Sillén's method can probably be used also with multivalent ligands: it would be useful to study systems containing metal ions together with these ligands both in aqueous solution and in organic solvents. Most precipitation reactions are probably preceded by the formation in solution of polymeric (polynuclear) complex ions. The formation of sparingly soluble sulphides and other precipitation reactions employed in analytical chemistry would merit careful study from this angle.

We see from this section that the formation of polymeric complexes in solution is associated with the formation of basic salts. Study of the latter is therefore of great interest in connection with the chemistry of co-ordination polymers; existing results may give an impetus to such investigations. In addition to work cited, note must be taken also of that of Feitknecht[266-271, 468], who studied a number of basic salts, which X-ray studies showed to be macromolecular co-ordination compounds[468]:

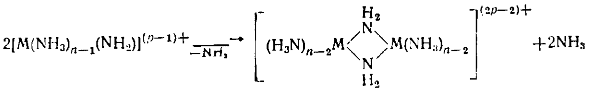
$[Cu_2(OH)_3NO_3]_\infty N$ — two-dimensional lattice of single layers
$[Zn_3(OH)_4Zn_2Cl_2H_2O]\,N$ — two-dimensional lattice of double layers
$[Mg_2(OH)_3(H_2O)_3ClH_2O]_\infty K$ — linear macromolecular structure
$[Cu_2(OH)_3Cl]_\infty G$ — three-dimensional macromolecular structure

2. Formation in Liquid Ammonia

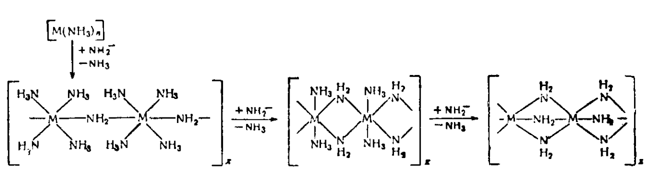
We have seen that in aquo systems the OH^- ions can replace water molecules in the solvated complex $[M(H_2O)_n]$ with the formation of polynuclear complexes. Several contemporary investigations showed that reactions of complex ammines $[M(NH_3)_6]^{p+}$ with alkali metal amides MNH_2 in liquid ammonia involve reactions analogous to those occurring in aqueous solutions

$$[M(NH_3)_n]X_p + nNH_2^- \rightleftarrows [M(NH_3)_n](NH_2)_p + pX^-$$
$$\downarrow\uparrow$$
$$[M(NH_3)_{n-p}(NH_2)_p] + pNH_3$$

Formation of amido complexes may be accompanied by the formation of polymers with elimination of NH_3 groups from the complex, co-ordination unsaturation being met by a bifunctional group, NH_2, acting as a bridge

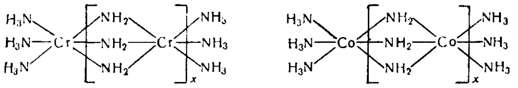


If the concentration of NH_2^- ions increases, macromolecular complexes are formed in the solution

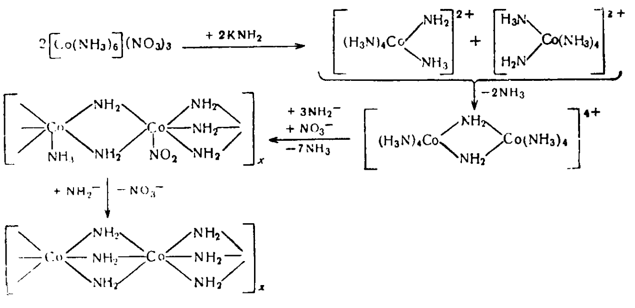


Schmitz-Dumont and his coworkers [19,469-471] obtained co-ordination polymers from metal amides, hydroxoamides, μ-oxoamides, and alkoxoamides using such reactions.

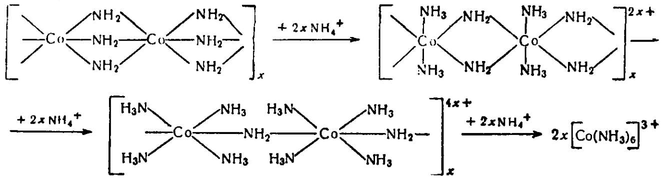
Treatment of $[Cr(NH_3)_6](NO_3)_3$ and $[Co(NH_3)_6](NO_3)_3$ with potassamide KNH_2 yielded the corresponding amides $Cr(NH_2)_3$ and $Co(NH_2)_3$, in which Cr and Co retain a co-ordination number of 6.[472] Schmitz-Dumont ascribed a linear polymeric structure to these compounds



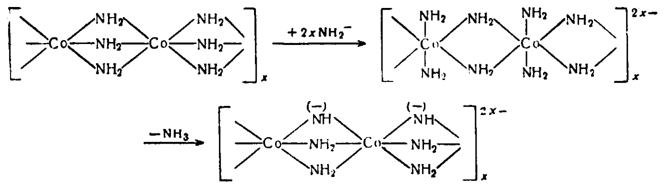
In the reviewer's opinion a two-dimensional structure, similar to that of the hydroxides of tervalent metals (Fig. 21), is more probable. These complexes are formed by the following mechanism[473]



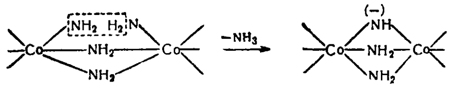
Like the corresponding hydroxides, the amides of chromium and cobalt have amphoteric properties. Ammonium salts NH_4X, which in liquid ammonia are acids, react with amides, rupturing some of the amide bridges ($-NH_2-$) with the formation of *macromolecular cations*, and finally mononuclear complexes



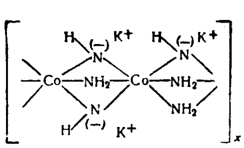
Potassamide is a base in liquid ammonia; it reacts with amides, rupturing NH_2 bridges with the formation of *macromolecular anions*



The latter reaction involves elimination of ammonia from two neighbouring NH_2 groups



In this way a compound of the following structure is formed[474]



Thermal decomposition of this compound leads to the polymer $(Co_2N_3K_3)_x$. The reactions with chromium amide are similar.

Polymeric amides have also been obtained of titanium[475], vanadium[476], and thorium[477]

$$x[Ti(SCN)_6]K_2 \xrightarrow[-KSCN]{+KNH_2} [Ti(NH_2)_4K]_x \xrightarrow[-NH_3]{} [Ti(NH)_2K]_x$$

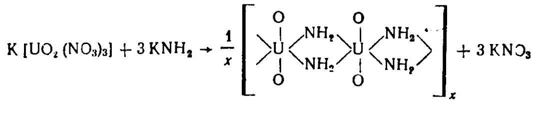
$$x[V(SCN)_6]K_3 \xrightarrow[-KSCN]{+KNH_2} [V(NH_2)_4K]_x \xrightarrow[-NH_3]{} [V(NH)_2K]_x$$

$$x[Th(NO_3)_6]K_2 \xrightarrow[-KNO_3,\ -NH_3]{+KNH_2} [Th(NH_2)_2NH_2K]_x$$

$$x[Th(NO_3)_6]K_2 \rightarrow [Th(NH_2)_2NH]_x \xrightarrow[-NH_3]{50^\circ} [Th_2(NH)_3(NH_2)_2]_x \rightarrow$$
$$\xrightarrow[-NH_3]{100^\circ} [Th(NH)_2]_x \xrightarrow{130^\circ} Th_3N_4$$

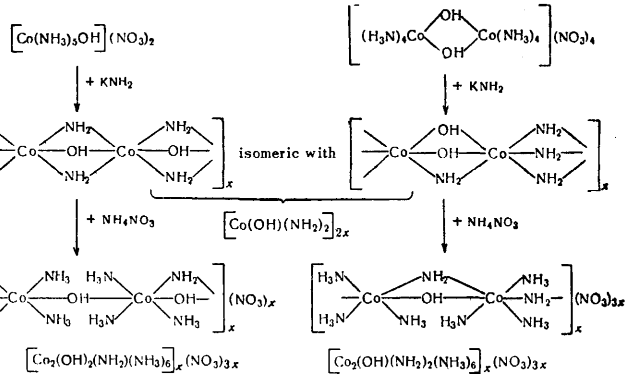
All these compounds are polymers in which the metal atoms are linked by NH_2, NH, or N groups. Polymerisation of these compounds is caused by the tendency of the metal to maintain a co-ordination number of 6.

A linear uranyl amide has also been obtained[478]

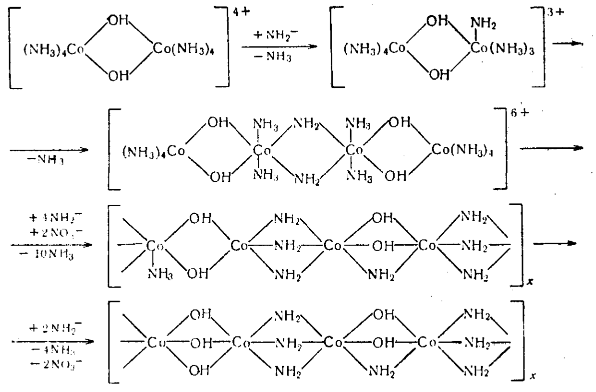


This compound possesses amphoteric properties, forming $UO_2(NH_3)_2I_2$ with ammonium iodide, and $[UO_2(NH_2)_2K_2]$ with potassamide. Thermal decomposition yields the polymer $[(UO_2)_3N_4K_6]_x$. A number of complexes containing both OH and NH_2 bridges have been prepared.

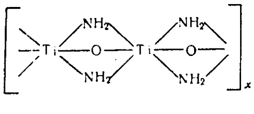
The action of potassamide on $[Co(NH_3)_5OH](NO_3)_2$ and $[(NH_3)_4Co(OH)_2.Co(NH_3)_4](NO_3)_4$ in liquid ammonia yields[473] two isomers having the formula $[Co(NH_2)_2(OH)]_x$. This is probably the first case of isomerism in the chemistry of co-ordination polymers. Both isomers are amphoteric. A scheme for the formation of these isomers, their structure, and their reaction with NH_4NO_3 are given below



The mechanism of the reaction was elucidated by identifying intermediate products.

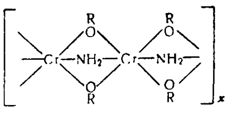


Among oxoamides only titanylamide is known[479], having the structure



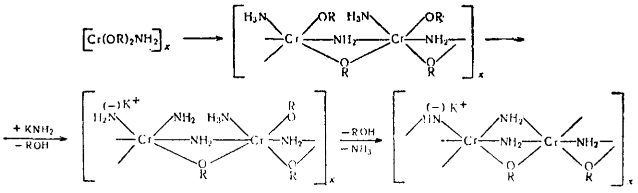
The hydrogen atom of the OH bridges can be replaced by organic radicals, yielding amidoalkoxides or alkoxoamides[480] $[M(OR)(NH_2)_2]_x$ and $[M(OR)_2NH_2]_x$, where M = Co, Cr.

Reaction among $[Cr(NH_3)_6](NO_3)_3$, alcohols, and potassamide in liquid ammonia yields[481,482] amphoteric compounds $[Cr(OR)_2NH_2]_x$

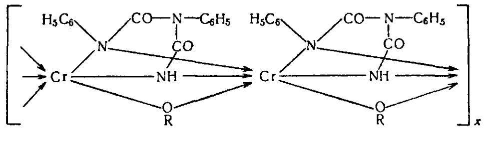


where R = $CH_2.C_6H_5$ [481] or C_6H_5.[482]

With ammonium iodide these compounds are converted into $[Cr(NH_3)_6]I_3$, and with potassamide several bridges are ruptured with the formation of a new polymer



Treatment of $[Cr(OR)_2NH_2]_x$ compounds with phenylisocyanate yields polymers of the structure



A study has been made[480] of cobalt amidoalkoxides $[Co(NH_2)_2OR]_x$, where R = CH_3, C_2H_5.

In liquid ammonia the compound KPH_2 reacts similarly to potassamide, forming polymers. The compounds $[Co(PH_2)_3]_x$ and $[Ni(PH_2)_2]_x$ have been obtained[483], as well as other compounds containing $-NH_2-$ and $-PH_2-$ groups.

VII. PROSPECTS AND OUTSTANDING PROBLEMS

This review of co-ordination polymers has shown the special role of co-ordinate bonds in macromolecular chemistry. The chemistry of co-ordination polymers is an interesting branch of modern inorganic chemistry and of the chemistry of complex compounds, offering new methods of synthesis of macromolecular compounds.

It is evident from the present survey that research in this field is only in its initial stage of development. It is necessary to continue and extend investigations into the following problems in the chemistry of co-ordination polymers:

(a) A study of the structure of inorganic compounds which are potentially polymeric, in particular derivatives of transition metals such a cyanides, sulphides, halides thiocyanates, complex compounds having an abnormal co-ordination number, basic salts, metal amides, chelate compounds, etc. For this purpose wide use must be made of X-ray and electron diffraction, spectroscopic, and other physical methods.

(b) Determination of the molecular weight of inorganic compounds and their organic derivatives under various conditions, mainly in inert solvents, in which the phenomena of co-ordinate association (*i.e.* polymerisation) take place, or in the vapour phase (when possible).

(c) Synthesis of new co-ordination polymers, metallocene polymers are of great interest in this connection.

(d) Physicochemical study of co-ordination polymers — mechanism and kinetics of formation and decomposition, equilibrium in solution, determination of thermodynamic constants, etc.

(e) Theoretical study of co-ordination polymers. It would be interesting to study the nature of the chemical bond in these polymers, many-centre many-electron bonds probably playing a great part here. The stereochemistry of these polymers is especially interesting.

(f) The discovery of new opportunities for their practical application. These compounds are of interest from the point of view of producing new materials having special properties, for example, increased thermal stability, and semiconducting, dielectric, catalytic, and other properties.

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SYNTHETIC ANALOGUES OF THE ALKALOID RESERPINE

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CONTENTS

I. INTRODUCTION

Most of the therapeutically valuable alkaloids have synthetic substitutes containing the same structural elements. They are simpler in structure and are manufactured on an industrial scale. At present the synthetic antimalarials (atebrin, bigumal), anaesthetics (promedol), local anaesthetics (novocaine), and other synthetic drugs are often superior in their properties to the natural ones and are favoured in medical practice.

In 1952, from the plant *Rauwolfia serpentina*, Müller, Schlittler, and Bein[1] isolated reserpine (I), an alkaloid of the indole group, with a sedative and hypotensive action.

The remarkable activity of reserpine and its wide applicability in medicine[2,3] for the treatment of hypertonia and mental diseases has attracted considerable interest. Its structure was established[4] in 1954, and in 1956 Woodward and his collaborators[5] carried out its complete synthesis.

Studies of the correlation between the structure of reserpine and its pharmacological activity were started in 1954. Yakhontov[6] discussed this subject in his review of the alkaloids from *Rauwolfia*.

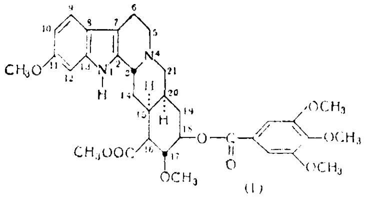
A good deal of work is being done at present in an attempt to find simple analogues of reserpine. All efforts to synthesise a reserpine substitute are directed towards the preparation of various fragments of the reserpine molecule, *viz.* the derivatives of yohimbine, β-carboline, indole, isoquinoline, cyclohexanol, and trimethoxybenzoic acid.

This review discusses all the attempts made so far to synthesise simple analogues of reserpine.

II. EFFECT OF STRUCTURAL CHANGES IN THE RESERPINE MOLECULE ON ITS BIOLOGICAL ACTIVITY

The pharmacological study of the alkaloids from *Rauwolfia* led to the discovery of an interesting type of action on the central nervous system, the so-called reserpine-like action, which is at once sedative and hypotensive.

Reserpine is an alkaloid of very complex structure, which has 6 asymmetric carbon atoms. Its complex stereochemical formula, established by conformational analysis, is as follows (I):



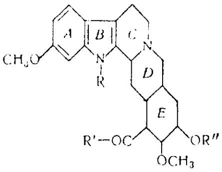
(I)

The biological properties of reserpine depend on steric factors, since its stereoisomer, 3-isoreserpine, is inactive[7]. The characteristic action of reserpine can be changed by small structural changes in its molecule. For example, its hypotensive properties are lost after hydrolysis into methyl reserpate (II) and trimethoxybenzoic acid[8].

Chatterjee and Talapatra[9,10] assumed that the biological activity of reserpine is due to the combined effect of all substituents in the rings. The same was observed by Huebner, Lucas, and their collaborators[11]. In order to establish the effect of changes in the reserpine structure on its properties, Huebner[12] alkylated the indole nitrogen in reserpine, and also prepared the reserpamide (V).

Methyl reserpate (II), in the form of its *N*-potassium derivative, was caused to react with methyl iodide and allyl bromide in liquid ammonia. The resulting *N*-alkylmethyl reserpates were then esterified with 3, 4, 5-trimethoxybenzoyl chloride giving (III)–(IV).

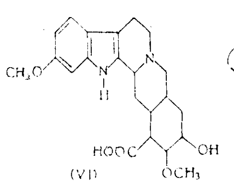
The action of an excess of sodamide upon reserpine in liquid ammonia results in the ammonolysis of both its ester linkages. Re-esterification of reserpamide with 3, 4, 5-trimethoxybenzoyl chloride yields the amide corresponding to reserpine (V):



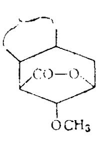
where for (II) $R = H$, $R' = OCH_3$, $R'' = H$; (III) $R = CH_3$, $R' = OCH_3$, $R'' = COC_6H_2(OCH_3)_3$-3, 4, 5; (IV) $R = CH_2-CH=CH_2$, $R' = OCH_3$, $R'' = COC_6H_2(OCH_3)_3$-3, 4, 5; (V) $R = H$, $R' = NH_2$, $R'' = COC_6H_2(OCH_3)_3$-3, 4, 5.

The pharmacological investigation of these reserpine derivatives showed that they lack tranquillising and hypotensive properties. In fact, (II) acts as a reserpine antagonist.

Without any activity whatsoever are the quaternary salt[13] and the products of degradation of reserpine: reserpinic acid and its lactone (VII):



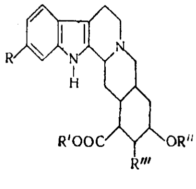
(VI)



(VII)

Certain functional groups of reserpine are of no importance for the biological activity of this alkaloid. The naturally occurring alkaloids deserpidine (VIII), [14,15] which is 11-desmethoxyreserpine, and *DL*-17-desmethoxydeserpidine (IX) also have the characteristic reserpine-like activity[16]. In fact the difference in the biological activity of deserpidine and reserpine is quantitative rather than qualitative[17]. Reserpine *N*-oxide also exhibits reserpine-like activity[18].

The reserpine homologue containing an ethyl instead of methyl radical (X) is comparable to reserpine in its activity[19]. Unfortunately, the homologue esters of reserpinic acid are relatively difficult to prepare. Esterification under acid conditions is complicated by the epimerisation at C_3 into corresponding inactive iso-compounds. The preparation of esters from lactones gives unsatisfactory yields. The only promising method for the preparation of esters is from diazoalkanes.



(VIII) $R = H$, $R' = CH_3$, $R''' = OCH_3$
(IX) $R = OCH_3$, $R' = CH_3$, $R''' = H$
(X) $R = OCH_3$, $R' = C_2H_5$, $R'' = OCH_3$
(XI) $R = OCH_3$, $R' = CH_3$, $R''' = OCH_3$
$R'' = COC_6H_2(OCH_3)_3$-3, 4, 5
$R'' = COCH = CHC_6H_2(OCH_3)_3$-3, 4, 5

Substitution of the trimethoxybenzoyl radical by a trimethoxycinnamoyl radical in the alkaloid rescinnamine[21,22] (XI) does not alter the pharmacological activity. Other acids could therefore probably be used for the acylation of methyl reserpate to give preparations with reserpine-like activity.

A series of pharmacologically active derivatives of similar type were patented in the United States[23-25]. Methylreserpate *O*-(β-cyclopentylpropionate)[23], methylreserpate *O*-acetoacetate[24], and methylreserpate-*O*-cathylate[25] are all strong hypotensive and sedative agents.

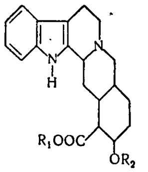
Lukas and his collaborators[19] prepared more than a hundred esters of methyl reserpate. These exhibited three types of activity: reserpine-like activity, hypotensive activity with a small sedative effect, and a predominantly sedative activity. For instance, 3, 5-dimethoxy-4-ethoxycarbonylbenzoic acid is almost equivalent to reserpine in its hypotensive activity, while showing only one-quarter of its sedative activity, 3-Dimethylaminobenzoic ester exhibits approximately one-quarter of the sedative activity of reserpine, with a more rapid onset, and only one-fortieth of its hypotensive activity.

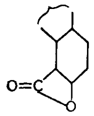
The example of these two compounds shows that the characteristic activity of reserpine, consisting in the combination of hypotensive and sedative activity, can be effectively resolved into its main components. This is of interest because, by making some definite changes in the structure of reserpine, compounds with selective activity should result. Hypotensive preparations free of sedative properties are very important in clinical practice.

Investigations of the structure of reserpine showed that certain functions which have no effect on the characteristic activity of the starting alkaloid could be omitted in the synthesis of reserpine-like preparations, as for instance the methoxy groups at C_{11} and C_{17}, and that the trimethoxybenzoyl radical, acylating the hydroxyl group at C_{18}, could be changed.

III. DERIVATIVES OF YOHIMBINE

Reserpine is a 3, 4, 5-trimethoxybenzoyl ester of methyl reserpate (II). Methyl reserpate has the pentacyclic structure of yohimban, contained in the alkaloids from *Yohimba.* It is remarkable that in the transition from reserpine to yohimbine (XII) the pharmacological action undergoes a sharp change. Various stereochemical changes in the molecule of yohimbine considerably affect the biological activity of these substances[26-31]. Yohimbic acid (XIII), its amide, hydrazide, and lactone[32] (XIV) display no reserpine-like activity. The lactone shows a combination of adrenolytic and hypotensive activity, typical of yohimbine.





(XIV)

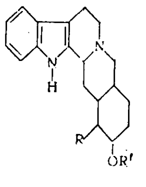
where for (XII) $R_1 = CH_3$, $R_2 = H$, and for (XIII) $R_1 = H$, $R_2 = H$.

Yohimbine was nevertheless used as starting material for the synthesis of reserpine substitutes, since the largest part of the reserpine molecule resembles yohimbine.

Huebner *et al.*[11] carried out the synthesis of a number of esters of yohimbine (XII) and its two stereoisomers corynanthine and α-yohimbine, with a view to obtaining reserpine substitutes. The esterification of these hydroxyl-containing alkaloids was carried out in pyridine at room temperature by reaction with acid chlorides. These authors obtained *O*-benzoyl-, *O*-anisoyl-, and *O*-veratroyl-3, 4, 5-trimethoxybenzoylyohimbines, as well as *O*-(3, 4, 5-trimethyloxybenzoyl)-α-yohimbine, *O*-(3, 4, 5-trimethoxybenzoyl)-corynanthine and *O*-acetylyohimbine. These esters were found not to exhibit any of the reserpine-like properties. Like other yohimbine derivatives, they had adrenolytic and hypotensive properties. Certain amongst them were relatively less toxic than reserpine.

Chatterjee and Talapatra obtained trimethoxybenzoyl and trimethoxycinnamoyl esters of α-yohimbine[33]. Both esters, which are the analogues of reserpine and rescinnamine, lower the blood pressure without having a sedative effect.

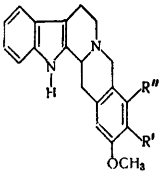
Esters (XVII) and (XVIII) were obtained[34] by the action of 3, 4, 5-trimethoxybenzoyl chloride upon yohimbol (XV) and 16-methylyohimbol (XVI):



where for (XV) $R = H$, $R' = H$; (XVI) $R = CH_3$, $R' = H$; (XVII) $R = H$, $R' = COC_6H_2(OCH_3)_3$-3, 4, 5; (XVIII) $R = CH_3$, $R' = COC_6H_2(OCH_3)_3$-3, 4, 5.

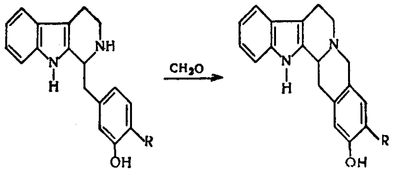
There are unfortunately no data as yet regarding the pharmacological activity of these compounds.

Logemann *et al.*[35] synthesised the yohimbine derivatives of the following general formula:

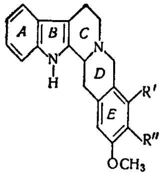


$$\begin{array}{lll} (XIX) & R' = OH & \\ (XX) & R' = OCOCH_3 & \\ (XXI) & R' = OCOCH_2CH_3 & \left.\right\} R'' = H \\ (XXII) & R' = OCOCH_2CH_2CH_3 & \\ (XXIII) & R' = OCOCH_2C_6H_5 & \\ (XXIV) & R' = OCOCH_2C_6H_5 & R'' = OCH_3 \end{array}$$

These compounds were prepared using the Hahn method[36-37] for the preparation of the derivatives of 15, 16, 17, 18, 19, 20-hexadehydroyohimban:



Compound (XIX) causes a sharp fall of the arterial blood pressure in anaesthetised dogs and rabbits. Compound (XXI) has a similar effect. The activity of compounds (XXIII) and (XXIV) is very low. The same authors[38] further studied the effect of introducing oxygen-containing groups into nucleus *E* on the pharmacological properties of the resulting compounds. They obtained 17, 19-dimethoxy-18-hydroxy-15, 16, 17, 18, 19, 20-hexadehydroyohimban (XXV), which contains an additional methoxy group in ring *E*:

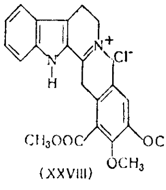


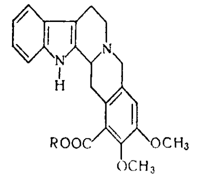
(XXV) $R' = OCH_3$, $R'' = OH$
(XXVI) $R' = OCH_3$, $R'' = OCOCH_2CH_3$
(XXVII) $R' = OCH_3$, $R'' = OCOC_6H_2(OCH_3)_3$-3,4,5

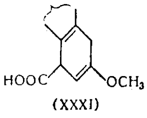
This compound was obtained by the condensation of tryptamine with 3, 5-dimethoxy-4-hydroxyphenylpyruvic acid followed by the cyclisation of 1-(3, 5-dimethoxy-4-hydroxybenzyl)-1, 2, 3, 4-tetrahydro-β-carboline with formaldehyde. Its esters with propionic (XXVI) and trimethoxybenzoic acid (XXVII) were also prepared.

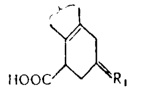
Pharmacological investigations showed that the introduction of an additional methoxy group changes the properties of the starting compounds; the resulting preparations are considerably less active than their desmethoxy analogues, trimethoxybenzoic ester being also less active than propionic ester.

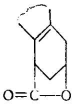
Compounds containing substituents at the 16- and 18-positions of the yohimban skeleton, were also prepared as reserpine substitutes[39]. The condensation of a 2-methoxycarbonyl-3, 4-dimethoxy-6-chloromethylphenylacetate ester with tryptamine gave *N*-[2-(3-indolylethyl)]-3-oxo-5-methoxycarbonyl-6, 7-dimethoxy-1, 2, 3, 4-tetrahydroisoquinoline. This was cyclised in the presence of phosphorus oxychloride into the unsaturated base (XXVIII), which was then reduced by platinum in methanol giving the saturated base (XXIX). The hydrolysis of (XXIX) by aqueous-alcoholic KOH yields the acid (XXX), which on reduction with sodium in liquid ammonia in the presence of isopropanol loses its methoxy group at position 17, and is further reduced to the enolic ester (XXXI). On hydrolysis (XXXI) yields the ketonic acid (XXXII), which, reduced in the presence of sodium borohydride, forms the hydroxy acid (XXXIII). Its lactone, (XXXIV), after treatment with sodium methoxide in methanol, formed 18-hydroxy-16-methoxycarbonyl-$\Delta^{15(20)}$-yohimbene (XXXV). There are no data on the biological properties of these compounds.

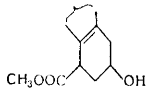

(XXVIII)


(XXIX) R = CH_3; (XXX) R = H;


(XXXI)


(XXXII) R_1 = O; (XXXIII) R_1 = H, OH

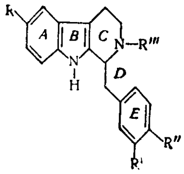

(XXXIV)


(XXXV)

IV. DERIVATIVES OF β-CARBOLINE

The synthesis of yohimbine derivatives is a laborious multistage process. Somewhat simpler is the preparation of the derivatives of yohimbine with the *D* ring open, and an aromatic or a cyclohexane ring *E*, as in reserpine. These compounds are the derivatives substituted in position 1 of 1, 2, 3, 4-tetrahydro-β-carboline, which can be obtained using the Bischler–Napieralski or Pictet–Spengler reactions.

Logemann *et al.*[35] obtained the derivatives of β-carboline (XXXVI–XLII) using the general method put forward by Hahn and his collaborators:

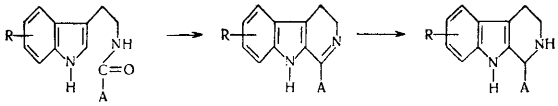


where for (XXXVI) R = R'' = R''' = H, R' = OH; (XXXVII) R = R'' = H, R' = $OCOC_6H_2(OCH_3)_3$-3, 4, 5, R''' = $COC_6H_2(OCH_3)_3$-3, 4, 5; (XXXVIII) R = R''' = H, R' = OCH_3, R'' = OH; (XXXIX) R = H, R' = OCH_3, R'' = $OCOCH_3$, R''' = $COCH_3$; (XL) R = H, R' = OCH_3, R'' = $OCOC_6H_2(OCH_3)_3$-3, 4, 5, R''' = $COC_6H_2(OCH_3)_3$-3, 4, 5; (XLI) R = R' = OCH_3, R'' = OH, R''' = H; (XLII) R = R'' = OCH_3, R' = $OCOC_6H_2.(OCH_3)_3$-3, 4, 5, R''' = $COC_6H_2(OCH_3)_3$-3, 4, 5.

Only the compounds (XXXVI), (XXXVII), (XL), and (XLII) have any pharmacological interest, but in anaesthetised rabbits they only cause a temporary lowering of blood pressure in doses of 10–20 mg kg^{-1}.

A group of Czech chemists working under Protiva[40] are now making a systematic search for simple analogues of reserpine.

By acylation of tryptamine, 4-methoxytryptamine, and 7-methoxytryptamine the appropriate tryptamides (XLIII) were obtained, which upon the action of phosphorus oxychloride are cyclised forming 1-aralkyl-3, 4-dihydronorharmanes (XLIV); on reduction with sodium in ethanol (XLIV) yielded 1-aralkyl-1, 2, 3, 4-tetrahydronorharmanes (XLV).

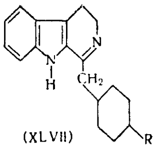


(XLIII) (XLIV) (XLV)

A = $CH_2C_6H_5$ (XLVI)
A = $CH_2C_6H_4(OCH_3)$-4
A = $CH_2C_6H_3(OCH_3)_2$-3,4
A = $CH_2CH_2C_6H_5$
A = $CH_2CH_2CH_2C_6H_5$
A = $C(CH_3)_2C_6H_5$
A-α-$C_{10}H_{11}$(5, 6, 7, 8-tetrahydronaphthyl)
} R = H
A = $CH_2C_6H_5$, R = 6-OCH_3
A = $CH_2C_6H_5$, R = 8-OCH_3

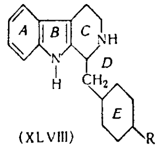
Methane sulphonates of these compounds, which are more soluble than hydrochlorides, were used in their pharmacological assay. In doses of 1–5 mg kg^{-1} these methane sulphonates, introduced intravenously, lower the blood pressure by 10–70%. Compared with reserpine, their action is very rapid, but transient. As with reserpine, the lowering of the blood pressure is not based on adrenolytic action. Owing to its favourable hypotensive activity and low toxicity, preparation (XLVI), named "Phenoharmane" has been selected for clinical studies[41].

Protiva and his collaborators[42] also synthesised the simple reserpine analogues, containing a cyclohexane ring *E*. In their structure these compounds are more similar to reserpine than those obtained earlier, containing an open ring *D* and an aromatic ring *E*. For their preparation, cyclohexylacetic and 4-methoxycyclohexylacetic tryptamides were cyclised in the presence of phosphorus oxychloride and the resulting dihydrobases (XLVII) subsequently reduced with sodium in ethanol to form 1-cyclohexylmethyl-1, 2, 3, 4-tetrahydronorharmane (XLVIII) and 1-(4-methoxycyclohexylmethyl)-1, 2, 3, 4-tetrahydronorharmane (XLIX), respectively. Their hydrochlorides and methanesulphonates had hypotensive activity.



(XLVII)

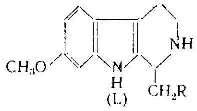
(XLVII) R = H or OCH_3



(XLVIII)

(XLVIII) R = H
(XLIX) R = OCH_3

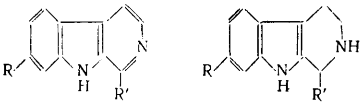
An American patent[43] claims the synthesis of the compounds of general formula (L), which have sedative properties:



(L)

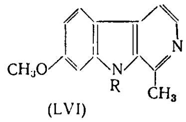
where R = 1-hydroxycyclohexyl; 1-hydroxy-2-methylcyclohexyl; 1-hydroxy-2, 6-dimethylcyclohexyl, and 1-hydroxycyclopentyl. These compounds were prepared by the condensation of the lithium compound of harmine with cyclohexanone, 2-methylcyclohexanone, 2, 6-dimethylcyclohexanone, and cyclopentanone. The reaction of the Li-derivative of 9-benzylharmine with 2-methylcyclohexanone gave 9-benzyl-1-(1'-hydroxy-2'-methylcyclohexylmethyl)-harmine. The reserpine analogue was in this case obtained by starting from the more accessible alkaloid harmine (LI), which has practically the same structure as reserpine.

In addition to harmine (LI) and tetrahydroharmine (LII) as starting material in the synthesis of the β-carboline derivatives, a number of research workers[44-51] used synthetic harmane (LIII), tetrahydroharmane (LIV), and norharmane (LV). All these compounds contain the same *A*, *B*, and *C* rings as reserpine, and harmine and tetrahydroharmine also contain a methoxy group corresponding to the methoxy group in position 11 in reserpine.



(LI) R = CCH$_3$, R′ = CH$_3$; (LII) R = OCH$_3$, R′ = CH$_3$;
(LIII) R = H, R′ = CH$_3$; (LIV) R = H, R′ = CH$_3$;
(LV) R = H, R′ = H

Zhelyazkov and his collaborators[44,45] obtained indole-*N*-alkyl derivatives (LVI) of harmine by reacting harmine-sodium with the appropriate chlorine derivatives:



(LVI)

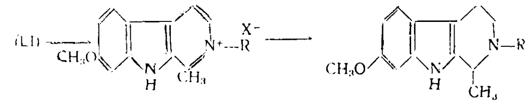
where R = CH$_2$C$_6$H$_5$; CH$_2$CH$_2$N(CH$_3$)$_2$; CH$_2$CH$_2$N(C$_2$H$_5$)$_2$; CH$_3$; n-C$_4$H$_9$; CH$_2$C$_6$H$_4$(OCH$_3$)-4.

Koretskaya, Danilova, and Utkin[46] obtained several indole-*N*-alkyl- and pyridine-*N*-substituted-derivatives of harmine (LVII)–(LIX) and tetrahydroharmine (LX)–(LXI):

(LVII) R′ = H; R″ = CH$_2$CH$_2$N (C$_2$H$_5$); X = Cl$^-$;
(LVIII) R′ = CH$_2$C$_6$H$_5$; R″ = CH$_3$; X = I
(LIX) R′ = CH$_2$C$_6$H$_5$; R″ = CH$_3$.
(LX) R′ = CH$_2$CH$_2$N (C$_2$H$_5$)$_2$; R″ = H;
(LXI) R′ = H, R″ = COOH;

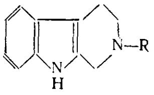
Pyridine-*N*-substituted tetrahydroharmines are closer in structure to reserpine than indole-*N*-derivatives of harmine.

Rubtsov and Yakhontov[47] developed a method for the reduction of the pyridine ring in harmine quaternary salts (LXII) using sodium borohydride which they applied to the synthesis of the pyridine-*N*-derivatives of tetrahydroharmine. In collaboration with Krasnokutskaya[48] they carried out the synthesis of pyridine-*N*-alkyltetrahydroharmines (LXIII) according to the following scheme:



(LXII) (LXIII)

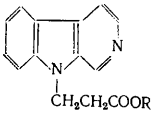
Pyridine-*N*-alkyl derivatives of β-carboline can be obtained by the reaction of tetrahydro-β-carbolines with appropriate chlorine compounds. For instance, by the reaction of tetrahydroharmane with 2-dimethylaminoethyl, benzyl, or 3-methoxybenzyl chlorides, the pyridine-*N*-substituted derivatives of 1,2,3,4-tetrahydronorharmane (XIV) were obtained[49]. They all had hypotensive properties.



(LXIV)

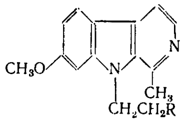
where R = CH$_2$CH$_2$N(CH$_3$)$_2$; CH$_2$C$_6$H$_5$; CH$_2$C$_6$H$_4$(OCH$_3$)-m.

A U.S. patent[50] described the preparation of the hydrochloride of indole-*N*-norharmanpropionic acid (LXV) and its ethyl ester (LXVI), and indicated their hypotensive properties.



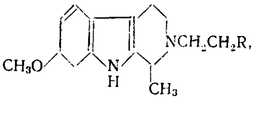
where for (LXV) R = H; (LXVI) R = C$_2$H$_5$.

Mndzhoyan and Agbalyan[51] prepared simple reserpine analogues by the reaction of harmine with acrylonitrile in the presence of trimethylbenzylammonium hydroxide, yielding indole-*N*-β-cyanoethylharmine (LXVII), and its hydrolysis product, the corresponding acid (LXVIII)



where for (LXVII) R = CN; (LXVIII) R = COOH.

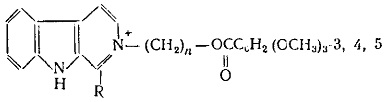
Pyridine-*N*-(β-cyanoethyl)tetrahydroharmine (LXIX) was obtained by the condensation of tetrahydroharmine with acrylonitrile without a catalyst, and was saponified to pyridine-*N*-(β-carboxyethyl) tetrahydroharmine (LXX)



where for (LXIX) R = CN; (LXX) R = COOH.

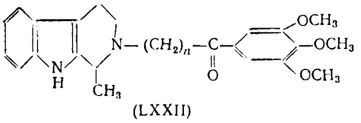
In addition to containing the *A*, *B*, and *C* rings of reserpine, the last two compounds contain the nitrile and carboxyl group at a distance from the salt-forming nitrogen, similar to that of the trimethoxybenzoyl radical in reserpine.

A U.S. patent[52] described certain pharmacologically active compounds which contained the *A*, *B*, and *C* rings of reserpine and the trimethoxybenzoyl radical. They were prepared by the reaction of harmane and norharmane with the bromoethyl and bromopropyl esters of trimethoxybenzoic acid, yielding quaternary salts (LXXI):



(LXXI)

The reaction of 1,2,3,4-tetrahydroharmane with the bromoethyl or bromopropyl esters of the same acid gave the corresponding esters of tetrahydroharmylethanol and tetrahydroharmylpropanol (LXXII):

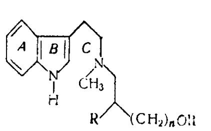


(LXXII)

V. DERIVATIVES OF TRYPTAMINE

The tryptamine derivatives synthesised as reserpine substitutes contain the indolyl fragment of reserpine, *i.e.* the rings *A*, *B*, with ring *C* opened.

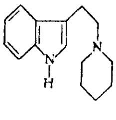
Protiva *et al.*[49] synthesised several tryptamine derivatives containing the 3,4,5-trimethoxybenzoyl radical (LXXIII–LXXVII):



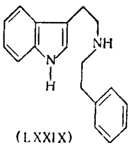
(LXXIII)	R = H,	$n = 0$	$R' = COC_6H_2(OCH_3)_3$-3, 4, 5
(LXXIV)	R = CH_3	$n = 0$	
(LXXV)	R = H	$n = 1$	
(LXXVI)	R = H	$n = 2$	
(LXXVII)	R = H,	$n = 4$	

By the addition of ethylene and propylene oxides to *N*-methyltryptamine, and the subsequent reduction of the resulting *N*-methyltryptamido-esters of malonic, succinic and adipic acids with lithium aluminium hydride, *N*-methyltryptamino-alcohols were prepared, and were further converted to esters by reaction with 3,4,5-trimethoxybenzoyl chloride.

The reaction of 3-indolylacetic acid or its chloride with piperidine and the subsequent reduction of the piperidide of 3-indolylacetic acid with lithium aluminium hydride gave 3-(2-piperidinoethyl)indole (LXXVIII). Similarly, *N*-(2-phenylethyl)tryptamine (LXXIX) was obtained from the tryptamide of phenylacetic acid[49].



(LXXVIII)

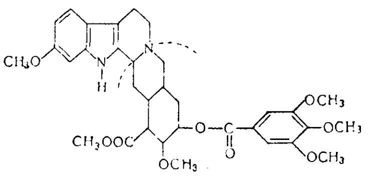


(LXXIX)

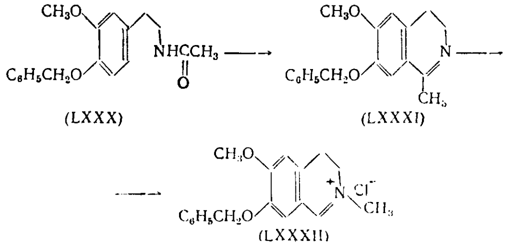
Nogradi[53] synthesised compound (LXXVIII) alongside other amino derivatives of the indole series. To judge from his results, (LXXVIII), as well as 3-(β-diethylaminoethyl)indole, display only one-thirtieth–one-fortieth of the activity of reserpine.

VI. DERIVATIVES OF ISOQUINOLINE

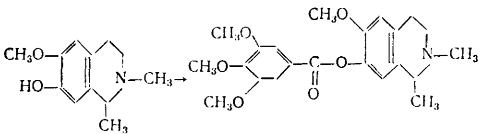
Considering that the reserpine molecule is a condensed ring system consisting of β-carboline and decahydroisoquinoline with functional groups in the appropriate positions, certain authors have synthesised simple reserpine analogues based on isoquinoline.



Strukov and Kolganova[54] synthesised and investigated pharmacologically derivatives of "salsoline". Acetylation of 3-methoxy-4-benzyloxyphenylethylamine gave the acetyl derivative (LXXX), which was converted to 1-methyl-6-methoxy-7-benzyloxy-3,4-dihydroisoquinoline (LXXXI). 1,2-Dimethyl-6-methoxy-7-hydroxy-1,2,3,4-tetrahydroisoquinoline (LXXXIII) and its 3,4,5-trimethoxybenzoate (LXXXIV), were obtained from the iodo- or chloro-methylates derived from LXXXI (LXXXII).

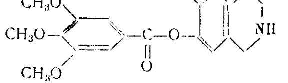


(LXXX) (LXXXI) (LXXXII)



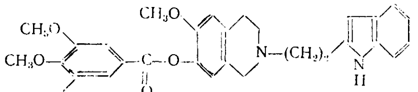
(LXXXIII) (LXXXIV)

The Japanese chemists Onda, Kawanishi, and Sasamoto[55] had earlier synthesised several isoquinoline derivatives as a route to the synthetic reserpine analogues. The condensation of 6-methoxy-7-hydroxy-1,2,3,4-tetrahydroisoquinoline with trimethoxybenzoic acid in the presence of phosphorus pentoxide and 88% phosphoric acid yielded 6-methoxy-7-(3,4,5-trimethoxybenzoyloxy)-1,2,3,4-tetrahydroisoquinoline (LXXXV):



(LXXXV)

The reaction of the same starting material with trimethoxybenzoyl chloride gave 2-(3,4,5-trimethoxybenzoyl)-6-methoxy-7-hydroxy-1,2,3,4-tetrahydroisoquinoline. 2-[β-(3-Indolyl)ethyl]-6-methoxy-7-(3,4,5-trimethoxybenzoyloxy)-1,2,3,4-tetrahydroisoquinoline (LXXXVI) was also prepared.

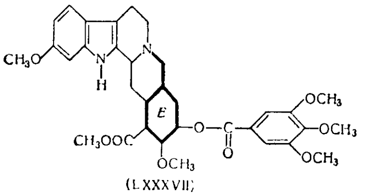


(LXXXVI)

This compound consists of three fragments of the reserpine structure: the indole ring, the *D* and *E* rings, and the trimethoxybenzoyl group.

VII. DERIVATIVES OF CYCLOHEXANOL

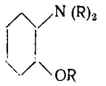
Reserpine contains in its molecule a cyclohexane ring *E*, which is acylated by trimethoxybenzoic acid and bound to the basic nitrogen by means of a CH_2 group (LXXXVII):

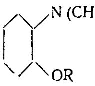


(LXXXVII)

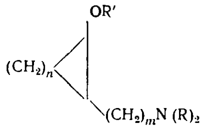
Esters of dialkylaminocyclohexanols (LXXXVIII) were prepared by a number of research workers[56–60]. In their effort to obtain reserpine substitutes, Dubravkova *et al.*[61]

prepared, and assayed the pharmacological activity of, the esters of dimethylaminocyclohexanol (LXXXIX) with aliphatic and aromatic acids (acetic, propionic, isobutyric, anisic, veratric, and trimethoxybenzoic).


(LXXXVIII)


(LXXXIX)

The preparation of esters of trimethoxybenzoic acid with 2-aminocycloalkanols (XC) has also been described[62]:

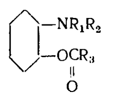


where R′ = $COC_6H_2(OCH_3)_3$-3, 4, 5.

R	n	m	R	n	m
CH_3	3	1	Piperidyl	4	1
C_2H_5	3	1	Morpholyl	4	1
Piperidyl	3	1	C_2H_5	4	2
CH_3	5	1	CH_3	4	1
			C_2H_5	4	1

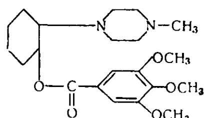
The condensation of cyclic ketones with formaldehyde and secondary amines gave 2-aminomethylcycloalkanones, which on reduction with lithium aluminium hydride yielded the corresponding 2-aminocycloalkanols; these amino alcohols were subsequently esterified with trimethoxybenzoyl chloride.

Shapiro *et al.*[63] prepared a series of the *trans*-2-amino-substituted cyclohexyl esters (XCI).


(XCI)

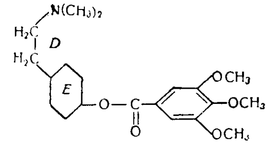
They prepared altogether 46 compounds containing various substituents in the amino group and various acyl groups. The final products were obtained by the reaction of the secondary amines with cyclohexene oxide forming substituted aminocyclohexanols, which were then esterified with various acid chlorides.

Hypotensive activity was displaced mainly by the derivatives of methylpiperazine. A relatively small number of compounds caused significant depression of the activity of the central nervous system; the only compound which exhibited this effect as well as the hypotensive effect was the ester of 3, 4, 5-trimethoxybenzoic acid (XCII):


(XCII)

The fact, however, that these compounds do not lengthen the period of sleep caused by evipan (hexenal) means that they are not completely reserpine-like in their action.

Hexahydrohordenine, obtained by hydrogenation of hordenine, was esterified with trimethoxybenzoic acid (XCIII):



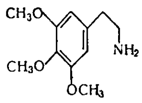
(XCIII)

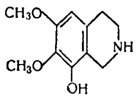
This ester resembles the ring *E* of the reserpine molecule, with the trimethoxybenzoyl radical in the same position as in reserpine. The aminoethyl radical is reminiscent of the ring *D*. The hydrochloride derived from this ester had no hypotensive activity.

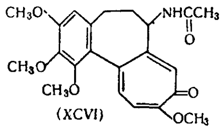
VIII. DERIVATIVES OF TRIMETHOXYBENZOIC ACID

Investigations of the derivatives of trimethoxybenzoic acid are among the most important in the search for reserpine substitutes. The great number of papers on this subject is probably due to the fact that the derivatives of trimethoxybenzoic acid are easier to obtain than the types of compounds discussed so far.

Of all the *Rauwolfia* alkaloids only reserpine contains the trimethoxybenzoyl radical. Cases are known, however, of the accumulation of methoxy groups in other physiologically active substances, *e.g.* the anhalonine alkaloids mescaline (XCIV) and anhalamine (XCV), as well as colchicine (XCVI) and other alkaloids.


(XCIV)


(XCV)

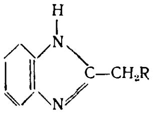

(XCVI)

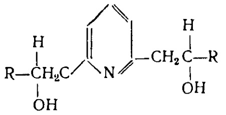
Mescaline, the alkaloid from *Kaktee anhalonium L.*, is known to act on the central nervous system causing hallucinations, but in doses from 0.006 – 0.008 mg kg^{-1} it displays a hypotensive activity[64].

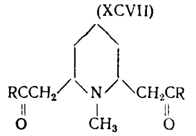
The methoxy groups obviously play an important part in the action upon the central nervous system; the trimethoxybenzoyl radical is therefore considered by several authors to be one of the most vital components in the manifestation of reserpine activity.

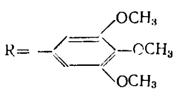
Of all the imidazoline derivatives which cause an increase in blood pressure, 3, 4, 5-trimethoxybenzylimidazoline (Phedrasin) has the strongest effect. This may be accounted for by the accumulation of methoxy groups[65].

For a comparative study of the effect of methoxy groups on the well-known pharmacological preparations containing a phenyl radical, compounds of similar structure, but containing the 3, 4, 5-trimethoxyphenyl radical, were synthesised: for example the trimethoxy analogues of 2-benzylbenzimidazole[66] (XCVII), lobeline[67] (XCVIII) and lobelanidine[67] (XCIX)


(XCVII)


(XCVIII)


(XCIX)

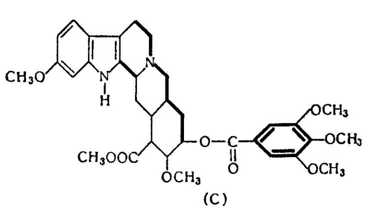


Miller and Weinberg[68] came to the conclusion that the trimethoxybenzoyl radical, though important, is not alone sufficient to account for the pharmacological effect of reserpine. On the basis of existing information regarding the pharmacological activity of nitrogen-containing compounds, these authors synthesised various esters of trimethoxybenzoic acid containing a nitrogen atom in positions 2 or 3 with respect to the oxygen atom in the carboxylic group. Of all the esters they synthesised, only the tertiary diethylaminopropyl ester had reserpine-like activity (one-third). The corresponding primary aminopropyl ester and the tertiary aminoethyl ester were inactive. On the basis of their results they concluded that oxygen and nitrogen must be separated by three carbon atoms, and that the nitrogen must be tertiary.

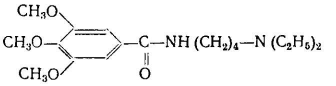
This communication was followed by numerous preparations of various amino-esters, as well as the amino-amides of trimethoxybenzoic acid. It is known that the pharmacological effect can sometimes be made to last longer by replacing the ester linkage by an amide linkage.

Dialkylaminoethyl esters of 3, 4, 5-trimethoxybenzoic acid, synthesised by Rabjohn and Mendel[69] had only local anaesthetic activity, but no activity characteristic of reserpine.

Sastry and Lasslo[70], starting from the premise that the diethylaminobutyl ester of trimethoxybenzoic acid has a structure closer to that of reserpine than the diethylaminopropyl ester, synthesised the former ester in the hope of obtaining a compound with biological properties similar to those of reserpine.


(C)

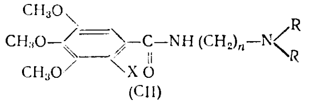
By substituting the ester by the amide linkage they also obtained *N*-[4-(*N'N'*-diethylaminobutyl)]-3, 4, 5-trimethoxybenzamide (CI).


(CI)

The ester- and amino-amide were prepared by the reaction of trimethoxybenzoyl chloride with 4-*N*,*N*-diethylaminobutanol and *N*-(4-*N'*,*N'*-diethylamino) butylamine, respectively.

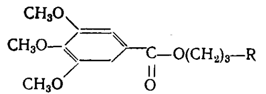
Lunsford, Murphey, and Rose[71] also prepared 4-dialkylaminobutyl esters of 3, 4, 5-trimethoxybenzoic acid and found them devoid of any reserpine-like activity.

Shiemenz and Engelhard[72] synthesised the amino-amides of 3, 4, 5-trimethoxybenzoic and 2-bromo-3, 4, 5-trimethoxybenzoic acids because their structure was similar to those of the dialkylaminoalkyl esters obtained earlier by others. Amino-amides were obtained by the reaction of the appropriate primary–tertiary diamines with the mixed anhydride of monoethylcarbonate and trimethoxybenzoic acid. This anhydride reacts readily with dialkylaminoalkyl amines forming compounds of the general formula (CII).


(CII)

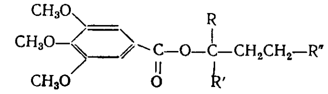
where X = H, Br; n = 2, 3; R = CH_3, C_2H_5.

In addition to esters with aliphatic amino alcohols, trimethoxybenzoates containing nitrogen in a ring were also prepared (CIII):


(CIII)

where R = *N*-pyrrolidyl, *N*-morpholinyl, and *N*-piperidyl[73,74]. The condensation of acid chlorides with the appropriate diamines gave amino-amides containing the same heterocyclic radicals[73].

The synthesis has also been described of the esters of the following general formula (CIV):

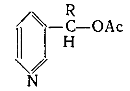


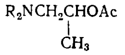
R	R'	R"
H	H	1-methylpiperazyl
C_6H_5	C_6H_5	pyrrolidyl
C_6H_5	C_6H_{11}	pyrrolidyl
C_6H_{11}	C_6H_{11}	pyrrolidyl

In the paper by Vejdělek and Trčka[75], the reserpine-like activity of the esters of 3, 4, 5-trimethoxybenzoic acid was discussed in some detail. The authors noted that the activity of the 3-diethylaminopropyl ester of 3, 4, 5-trimethoxybenzoic acid bears some resemblance to that of the alkaloid reserpine. They therefore synthesised the esters of this acid with amino-alcohols in which the tertiary atom is separated by 2, 3, or 4 carbon atoms from the oxygen atom. Using the normal method for the preparation of amino-esters, *viz.* the reaction of trimethoxybenzoyl chloride with various amino-alcohols, they obtained 11 esters, which were simple reserpine analogues. They were all assayed for hypotensive activity.

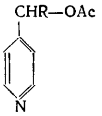
$R_2NCH_2CH_2CH_2OAc$

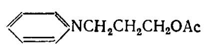
(CV)R= CH_3; (CVI)R= C_2H_5

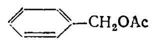

(CXI)R= H; (CXII)R= CH_3

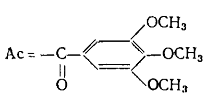

$R_2NCH_2\underset{CH_3}{\underset{|}{C}}HOAc$

(CVII)R= CH_3; (CVIII)R= C_2H_5


(CXIII)R= H; (CXIV)R= CH_3

(CIX)


(CX)




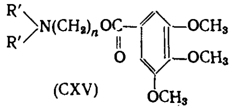
The piperidine ring in these compounds may be considered as ring *C* of the reserpine molecule. In many cases the distance between the nitrogen and oxygen atoms is shorter than in reserpine, *viz.* two carbon atoms instead of three. The authors point out, however, that the *cis*-condensation of rings *D* and *E* in reserpine is more important for the linear distance between tertiary nitrogen and oxygen and shortens it.

As a result of the pharmacological investigations, the active compounds were found to be the dialkylaminopropyl and dialkylaminoisopropyl esters of 3, 4, 5-trimethoxybenzoic acid (CV – CVIII).

The most active preparations contain a normal propyl radical. Diethylamino derivatives act longer and more deeply than their dimethyl analogues; the most active preparation was the diethylaminopropyl ester (CVI). The increased length and branching of the chain between N and O atoms, as well as the increased size of the substituent bound to tertiary nitrogen, result in a shortening of the time of action and an increase of toxicity. All the enumerated compounds have a sedative effect.

On the basis of their results the authors concluded that none of these esters approaches reserpine in hypotensive activity or length of action. The finding that the diethylaminopropyl ester had one-third of the reserpine activity the authors regard with some doubt.

Solov'ev, Arendaruk, and Sklodinov[76] prepared a series of esters of trimethoxybenzoic acid (CXV):

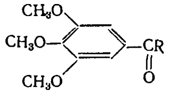


(CXV)

R'R"N	n	R'R"N	n
$(CH_3)_2N$	2	$(C_2H_5)_2N$	3
$(C_2H_5)_2N$	2	$(C_2H_5)_2N$	4
$C_5H_{10}N$	2	$C_5H_{10}N$	4
$O[(CH_2)_2]_2N$	2	$(CH_2)_6N$	4
$(CH_2)_6N$	2	$O[(CH_2)_2]_2N$	4

including the diethylaminopropyl ester. On pharmacological investigation this last ester made only one-quarter of the reserpine sedative activity (it was one-third according to Miller and Weinberg). None of the amino-esters had hypotensive activity, and only a few had a sedative effect.

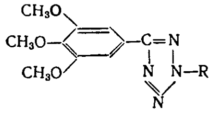
With a view to preparing reserpine-like compounds, various amides, amino-amides, and ureides of trimethoxybenzoic acid were prepared (CXVI) by the reaction of the acid chloride with various amines and substituted ureas. The authors were prompted by the data on the sedative, hypotensive, and narcotic activity of innumerable acylamides and ureides:



R = NHC_4H_9; NHC_6H_5; NHC_6H_5; $NHCH_2COOC_2H_5$;
$NHCH_2CONH_2$; $NHCH_2CH_2N(C_2H_5)_2$; $NHCONHCH_3$;
$NHCONHC_4H_9$; $NHCOC_6H_{11}$; $NHCONHC_6H_5$.

2-Substituted 5-(3, 4, 5-trimethoxyphenyl)tetrazoles (CXVII)[77], in which the nucleus is alkylated by dialkylaminoalkyl groups, have also been prepared as reserpine analogues. The authors were encouraged by the fact that disubstituted tetrazoles might be pharmacologically similar to the corresponding amino-esters.

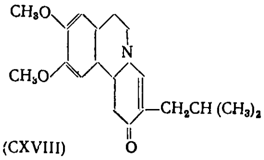
To prepare the tetrazoles, trimethoxybenzonitrile was reacted with sodium azide and acetic acid in boiling butanol. Alkylation was carried out with the chlorides derived from amino-alcohols in aqueous acetone in the presence of caustic soda:



(CXVII)

where R = H; $CH_2CH_2N(C_2H_5)_2$; $(CH_2)_3N(CH_3)_2$; $(CH_2)_3N.$ $.(C_2H_5)_2$.

Owing to the inadequacy of the data at present available on the pharmacological activity of simple reserpine analogues it cannot be said with certainty which of the types of compounds examined are likely to be the most promising as regards reserpine-like activity. It is not inconceivable that compounds most similar in activity to reserpine may be structurally very dissimilar to it. Compound (CXVIII)[78] is very interesting in this respect.



(CXVIII)

The pharmacological investigations showed that, like reserpine, various synthetic derivatives of 1,2,3,4,6,7-hexahydrobenzo-(a)-quinolizine cause the liberation of serotonine in the organism, and have a sedative effect free of any hypnotic effect, which recalls the action of the alkaloids from *Rauwolfia*.

One thing is certain, and that is that the development of the current investigations on the synthetic substitutes of reserpine[80-90] may – and indeed should – result in the discovery of compounds highly effective in their reserpine-like activity, as well as their sedative and hypotensive action.

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METHODS FOR CONVERTING CARBOHYDRATES TO CARBOCYCLIC COMPOUNDS

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CONTENTS

INTRODUCTION

Among the various reactions undergone by carbohydrates an important place is occupied by processes in which the carbon framework of the monosaccharide is rearranged. The changes produced in the carbohydrate-carbon chain differ in character and may be reduced to three basic reaction types.

Reactions in which isomerisation and rearrangement of the carbon chain lead to the formation of branched-chain compounds, for example, saccharinic, isosaccharinic, and parasaccharinic acids, belong to the first type. Reactions of the second type include various processes that lead to a change in the number of carbon atoms in the carbohydrate molecule. To this type belong well-known methods of lengthening the carbon chain of sugars by addition of a molecule through the aldehyde group, organo-metallic, catalytic and condensation methods of synthesis of carbon-substituted carbohydrates with aliphatic, aromatic, and some heterocyclic aglycones [1,2], and also numerous methods in which the carbon chain is cleaved into smaller fragments.

Reactions of the third type, the literature on which is scanty, are of great theoretical and practical interest; in these the carbon framework of the monosaccharide or its derivatives cyclises to form various carbocyclic and heterocyclic compounds.

Because of a marked tendency to form cyclic compounds under the action of chemical agents or enzyme systems of living organisms, natural hexoses and pentoses and their derivatives are easily converted to mono- and poly-hydric phenols and to compounds containing furan, pyran, pyrrole, imidazole, and other ring systems.

The tendency of carbohydrates to cyclise and form carbocyclic compounds is of exceptional importance in elucidating the part played by sugars in the biosynthesis of various carbocyclic (particularly aromatic) compounds in plants and animal organisms. The concept developed in recent years that carbohydrates are the probable precursors in the biosynthesis of the aromatic nucleus in compounds of exceptional importance for the normal biological functioning of plants and animals, such as phenols, phenylglycosides, hydroxyacids, tannins, catechins, and amino-acids, has received fresh experimental confirmation.

The results of recent research work have shown that it is possible in principle to convert carbohydrates to aromatic and hydroaromatic compounds by chemical methods.

Cyclisation reactions are used in the preparation of many heterocyclic compounds. The conversion of carbohydrates to furfural by dilute acids [3] is well known. In the laboratory, carbohydrates and their derivatives are used for the preparation of many furan [4,5], pyran [6,7], pyrrole [8,9], and imidazole [10,11] compounds. Data are available on possible syntheses from carbohydrates of thiophene [12], pyridine [13], and pyrazine [14] derivatives. The preparation of heterocyclic compounds from monosaccharides and their derivatives is dealt with, although not completely covered, in several reviews [3-9], but information on methods of preparing carbocyclic compounds from carbohydrates is widely scattered. Micheel's monograph [15] contains isolated data on conversions of this type, and there is a more detailed, but less readily accessible, discussion by Dansi and Brocca [16].

In this review an attempt is made to generalise and systematise the information in the literature on the cyclisation of the carbohydrate-carbon chain, in the belief that this is of undoubted interest for synthetic organic chemistry, the chemistry of natural compounds, and biochemistry.

1. THERMAL CARBOCYCLISATION OF CARBOHYDRATES

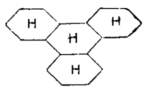
The thermal decomposition of carbohydrates, especially cellulose, has received detailed treatment in the chemical literature, because of the industrial applications of this process [17-20].

It is known that on dry distillation cellulose forms a complex mixture consisting of gaseous, liquid, and solid (carbon) products. The liquid decomposition products consist of an aqueous distillate and a resin, formic acid, acetic acid, and acetone being present in small amounts; formaldehyde, methylglyoxal, furfural, 5-hydroxymethylfurfural, di-, tri-, and tetra-methylfuran, maltol, γ-valerolactone, phenol, traces of toluene, and many other compounds have also been found. The separation of aromatic compounds (toluene, phenol [21], cresol [22], and others) from the distillate is of particular interest; cellulose tar contains as much as 2–4% of these.

Smith and Howard [23] oxidised and decarboxylated the liquid fraction from the thermal decomposition of cellulose and obtained benzene and diphenyl. Their results indicate that various alkyl homologues of benzene and diphenyl are present in the pyrolysis products.

When cellulose is reduced at high temperature, cyclisation of the carbon chain also occurs and aromatic and alicyclic compounds are formed. When cellulose is hydrogenated in the presence of a nickel catalyst at 400°–440°, gaseous and liquid products are formed. A tar is obtained in 23% yield, the main constituent of which is an oxygen-containing compound of unknown composition; phenol is formed in 2% yield [24].

Willstätter and Kalb have shown [25] that, when xylose, glucose, and cellulose are reduced by phosphorus and hydriodic acid in sealed tubes at 250°, a mixture of hydrocarbons is formed with the mean composition $CH_{1.6}$ and molecular weights from 167 to 842. Schrauth [26], who made a detailed examination of Willstätter's hydrocarbon fraction, showed it to be identical with perhydro-9,10-benzophenanthrene, $C_{18}H_{30}$:



It is very significant that compounds with the perhydrophenanthrene skeleton, for example, abietic acid, fichtelite, etc., are constituents of brown-coal, peat, and resin acids. These compounds may be products of extensive chemical transformations of carbohydrates of various plant remains from remote geological epochs.

The literature contains many other reports on the isolation of aromatic compounds from the products of the pyrolysis of carbohydrates. All this evidence undoubtedly indicates that acyclic carbohydrate compounds form carbocyclic compounds during pyrolysis.

It has been suggested that the formation of aromatic compounds in the pyrolysis of carbohydrates is due to the catalytic action of incandescent carbon, ash, or the walls of the retort on the glucose residues of cellulose or their cleavage products [19].

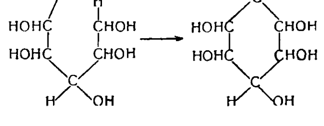
2. BIOSYNTHESIS OF ALICYCLIC AND AROMATIC COMPOUNDS FROM CARBOHYDRATES

According to Shorygin and Shorygina [27], in living animal organisms and plants there is a continual conversion of carbohydrates, the primary products of assimilation of atmospheric carbon dioxide, into various cyclic compounds widely distributed in the plant world, such as resins, terpenes, essential oils, tannins, dyes, sterols, etc. These workers consider that the genetic relation of these cyclic compounds to carbohydrates is evident — they are all formed in the plant organism by the biochemical conversion of carbohydrates, probably through a series of intermediate processes.

Recently two fundamental ideas on the biosynthesis of the aromatic nucleus have become widely current in biochemistry. According to the first, the main precursors of cyclic compounds in plants and living organisms are acyclic compounds with six carbon atoms in the molecule (most probably glucose or other carbohydrate compounds), which are converted by ring closure to cyclohexane derivatives (inositol, quercitol, etc.); these are then dehydrated to polyphenols and phenols. According to the second hypothesis, other initial compounds (possibly sedoheptuloses and other higher sugars) with longer carbon chains are present, and these cyclise to form various aromatic compounds with side chains of different lengths.

It may be that both these hypotheses correctly reflect the biosynthesis of the aromatic nucleus and are not contradictory. This is confirmed by the immense variety of aromatic compounds isolated from natural materials, which are probably formed from several types of alicyclic precursors. Both hypotheses have received experimental confirmation and are beginning to form the subject of modern monographs [28-32] and reviews [33,34].

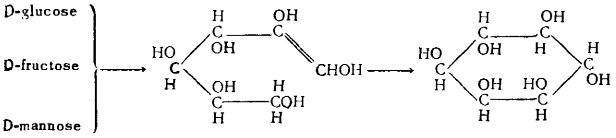
Thanks to the Soviet workers Bach, Oparin, Kursanov, and others, the essential features of many biochemical processes occurring in the tea plant have been elucidated, and the problem of the conversion of carbohydrates to aromatic compounds and tannins is being successfully solved. Kursanov and his coworkers have recently developed a theory, supported by convincing experimental evidence, according to which the first conversion product of carbohydrates in the tea leaf is *meso*-inositol, formed from hexoses by ring closure of the aldol condensation type [31,36,37]:



meso-Inositol, both free and combined, is widely distributed in the plant and animal world, being encountered in all tissues of plant and animal organisms. In animals *meso*-inositol has been found in muscle, kidney, liver, brain (as cephalin), and other organs.

In plants *meso*-inositol occurs free and as the hexaphosphate (phytin), first discovered by Palladin [35] in cereal grains. The high content of inositol in bran, oranges, peaches, strawberries, cabbage, tomatoes, carrots, and tea leaves is noteworthy. It has been shown that *meso*-inositol is a growth factor for some cultivated species of yeast; it acts as a vitamin in mice and it stimulates the microbiological synthesis of many vitamins, for example, biotin.

Kursanov and his coworkers found[36,37] that inositol can be synthesised experimentally in tea leaves by introducing glucose, sucrose, or some glucosides into the tissue. The amount of *meso*-inositol in tea leaves increases by 10 to 12% an hour after glucose has been injected. *meso*-Inositol is formed at the same rate from fructose and mannose, which are related to glucose in their spatial configuration and have an enolic form in common with it. Sugars of different configuration (galactose, rhamnose, arabinose), hydroxyacids (glycollic and glyceric), and pyruvic acid are not converted to *meso* or other forms of inositol in tea leaves. From this, it can be concluded that the process is specific; it depends on the stereochemical configuration of the sugar and proceeds through a stage in which the enol form, common to D-glucose, D-fructose, and D-mannose, reacts



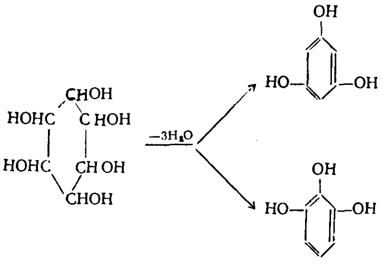
It has been shown experimentally[36,37] that the rate of *meso*-inositol synthesis increases several times when some α- and β-glucosides are injected instead of glucose. Compounds which are rapidly converted to inositol in tea leaves include sucrose, glucose 1-phosphate, and the plant glucosides arbutin and saligenin. From these facts, the hypothesis may be put forward that cyclisation of carbohydrates to inositol is preceded by activation of the hexose by the formation of a glucoside linkage, which facilitates ring closure[31].

The carbocyclisation of carbohydrates in plants is an enzymic process; up to the present it has not been possible to synthesise *meso*-inositol in one step by chemical means. In 1944, the enzyme cyclase, which converts glucose into inositol[38], was isolated from *Lactica virosa* L. When a 2% aqueous solution of glucose was maintained at 37° (pH 5.8) in the presence of cyclase, small quantities of *meso*-inositol were formed.

Further detailed studies of the biochemical conversion of sugars in tea leaves showed that the accumulation of polyphenols and tannins is closely connected with the synthesis of *meso*-inositol. The more active the biosynthesis of *meso*-inositol, from whatever precursor, the greater the amount of polyphenols (phloroglucinol and pyrogallol) that are produced in the tea plant[39,40].

As would be expected, the synthesis of phloroglucinol in the tea leaf proceeds most readily when *meso*-inositol is injected; the introduction of compounds which do not promote the synthesis of inositol does not lead to the formation of polyphenols[40].

Kursanov concludes from these experiments that polyphenols are formed in the tea plant from inositol, which in turn is produced from carbohydrates by cyclisation of the carbon chain by an aldol condensation. When inositol is dehydrated, three molecules of water are split off and the trihydric phenols pyrogallol and phloroglucinol are formed[31,40]:



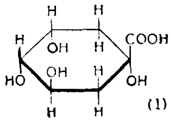
Nick[41] has obtained interesting results that confirm Kursanov's theory: he found that immersion of half-leaves of snakeweed in glucose or sucrose solution leads to the active production of tannins.

The first report on the biosynthesis of inositol in the living organism was made by Needham[42] in 1924. New proofs of the direct conversion of glucose to inositol in the living organism have been obtained quite recently by the tracer method. Glucose labelled with ^{14}C was introduced into the abdominal cavity of mice[43]. After some time, the experimental animals were killed and *meso*-inositol labelled with ^{14}C was isolated from the livers and other organs; it was purified by recrystallisation and paper chromatography. The amount of inositol in the tissues of mice varied between 0.08 and 1.8 mg per gramme of live weight. Similar results were obtained when glucose labelled with ^{14}C was introduced into the chick embryo shell, radioactive inositol being found 64 h after the injection.

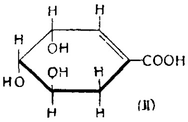
The reversibility of the inositol biosynthesis has been demonstrated in a number of investigations[44,45]. Thus, when *meso*-inositol deuterated in position 2 was administered to mice, the glucose separated from the urine was found to be labelled mainly in the 6-position[44]. When deuterium-labelled inositol was injected into mice, 7% was converted to glucose after 24 h.[45]

The isolation from mouse kidney of an enzyme system that converts inositol to D,L-glucuronic acid has recently been reported[46,47].

Recent work has shown that an exceptionally important part in the biosynthesis of aromatic compounds from carbohydrates is played by quinic acid(I) and shikimic acid(II), which occupy an intermediate position in the biochemical conversion of carbohydrates and cyclitols to aromatic compounds. Both acids are widely distributed in the plant world and have been found in microbes and other living organisms[33,34].



(I)



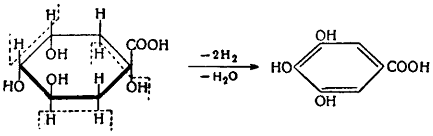
(II)

Like *meso*-inositol, quinic and shikimic acids have spatial configurations related to that of D-glucose.

Over 30 years ago Butkevich[48] and Kizel'[49,50] showed that quinic acid is genetically related to glucose in natural materials. In plants quinic acid is readily formed by the biochemical conversion of inositol, which, as shown above, is obtained from carbohydrates[31].

Quinic acid has recently been prepared by a multi-stage chemical synthesis from 4-chlorocyclohexanone[51]. A complete synthesis of shikimic acid was not achieved until in 1960, when it was prepared from 2-acetylfuran and maleic anhydride *via* a number of intermediate reactions[52]. Quinic and shikimic acids are readily interconvertible (by the action of chemical agents) both *in vivo* and *in vitro*.[53,55]

In 1935 Blagoveshchenskii put forward the hypothesis that quinic acid is a precursor of gallic acid, one of the most widely distributed constituents of tea tannins[56]. It is not difficult to suppose that the conversion of quinic acid to gallic acid occurs by dehydration and oxidative dehydrogenation in the following way:

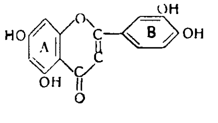


Kursanov showed[31] that, when quinic acid is introduced into the tea leaf, it is readily converted to polyphenols with vicinal hydroxyl groups.

Recently the attention of many workers has been drawn to shikimic acid as the probable precursor of aromatic compounds in living tissue. Thanks to the studies of Davis and his coworkers[57,58], it has been established that radioactive shikimic acid can be produced by a culture of *Escherichia coli* growing in glucose labelled with ^{14}C. Similarly, shikimic acid is obtained in 90% yield from sedoheptulose 1,7-diphosphate or mixtures containing erythrose 4-phosphate and phosphoenolpyruvate[59,60]. The mechanism of these interesting conversions, which was elucidated by Davis's school, comprises a preliminary cleavage of sedoheptulose 1,7-diphosphate into erythrose phosphate and dihydroxyacetone phosphate. The latter is oxidised to phosphoenolpyruvate, which condenses with erythrose 4-phosphate to form shikimic acid. Shikimic acid plays an important part in the formation of aromatic lignin components in various plants.

Brown and Neish[61,62] introduced [^{14}C]shikimic acid into wheat stems and maple twigs, and they isolated radioactive vanillin and syringic aldehyde from the lignin of these plants. Eberhardt and Schubert[63] introduced [^{14}C]shikimic acid into sugar-cane leaves over a period of six days. After oxidative degradation of lignin isolated from the plant, radioactive vanillin containing ^{14}C in the same positions as the initial shikimic acid was obtained. It has been shown by the tracer method that shikimic acid is converted in the metabolic process by specific enzymes to aromatic acids[64] and other cyclic compounds.

Neish and coworkers[65], who studied the mechanism of the biosynthesis of the flavonol quercitin in buckwheat, suggested that shikimic acid is probably the precursor of the aromatic B-ring in the quercitin molecule.

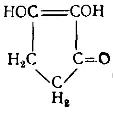


In recent years new and convincing evidence has been obtained, showing that the enzyme systems of microorganisms (lower fungi, bacteria) can synthesise from carbohydrates aromatic and heterocyclic amino-acids[34,66] necessary for their biological activity. Gilvarg and Bloch[67], who grew the yeast *Saccharomyces* on a culture medium containing [1-^{14}C]glucose, isolated from the solution phenylalanine and tyrosine labelled in positions 2 and 6. In the same way, microorganisms supported on a carbohydrate nutrient produce *p*-aminobenzoic acid, tryptophan[68], and other cyclic amino-acids[34,66,69].

3. CHEMICAL METHODS OF CONVERTING CARBOHYDRATES TO CARBOCYCLIC COMPOUNDS

The possibility of converting carbohydrates and their derivatives into alicyclic and aromatic compounds by the usual methods of organic chemistry has long attracted the attention of many workers.

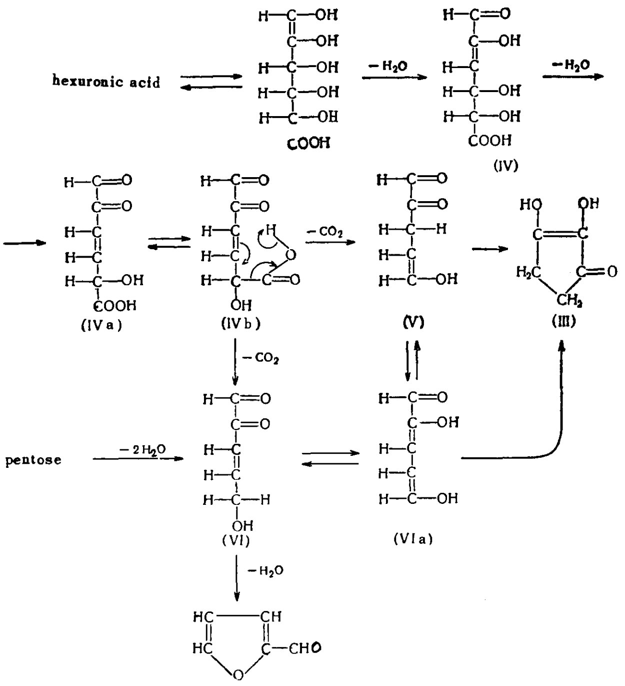
The conversion of carbohydrates to compounds of the cyclopentane series, which was first achieved by Reichstein and Oppenauer in 1933,[70,71] is of great interest. By heating hexuronic acids or pentoses with dilute sulphuric acid to 150° in an autoclave, they consistently obtained a yellow crystalline compound with m.p. 213°–213.5°. Because of the presence of an enediol grouping adjacent to a carbonyl group, the chemical properties of this compound are very similar to those of ascorbic acid, but, unlike ascorbic acid, it was found to be a cyclopentane derivative and was named reductic acid (III):



(III)

It was found that lactones and esters of hexuronic acid, polyuronides, methyl-3-oxo-β-D-glucopyranoside[72], 2,5-diethoxytetrahydrofurfural diethylacetal[73], and several other compounds are easily converted to reductic acid when heated with water or a weakly acid solution at high pressure (100°–150°). Furfural, succinic, fumaric, pyruvic, α-ketoglutaric acids, and several compounds of unknown structure were obtained as by-products of this reaction. In the acid cleavage of galacturonic acid the yield of furfural and reductic acid depends largely on the nature of the mineral acid: orthophosphoric acid promotes the formation of reductic acid (yield up to 41%)[74,75] and hydrochloric acid promotes the formation of furfural.

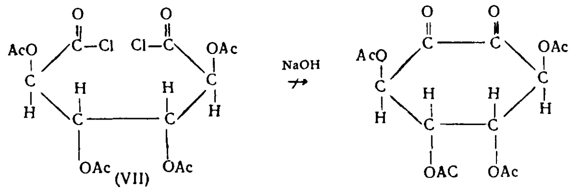
Stutz and Deuel[74] suggest that the mechanism by which reductic acid is formed comprises the stepwise dehydration of tautomeric enol forms of hexuronic acids to β,γ-unsaturated acids (IV, IVa, IVb) which are then decarboxylated to α-ketoglutaric dialdehyde (V);[73,76] this cyclises in the tautomeric form to give reductic acid (III) or furfural. The synthesis of reductic acid from pentoses is similar, the same intermediate (V) being formed in the dehydration:



However, the decarboxylation of the unsaturated acid (IVb) as presented in the scheme, with the transfer of a proton to the third carbon atom, is unrealistic. It is most probable that (IVb) is decarboxylated in the usual way to the unsaturated pentosone (VI), an intermediate in the dehydration of pentoses, the enol form of which (VIa) cyclises to reductic acid.

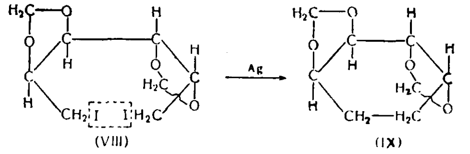
The ease with which pentoses are converted to cyclopentane derivatives (reductic acid) suggests the possibility of a similar process occurring in nature. In fact, cyclopentane compounds are important constituents of petroleum, a product of geological changes in the remains of carbohydrate-containing plants; these might be formed by the cyclisation of pentoses at high temperatures and pressures.

In plants and living organisms carbohydrates are readily converted to inositol, and many unsuccessful attempts have been made to effect this conversion by chemical means. The first experiments on those lines were undertaken by Diels and Löflund in 1914.[77] These workers hoped that by splitting off a molecule of chlorine from tetraacetylmucyl chloride (VII) the cyclohexane ring would be closed by the reaction



However, neither this method nor the thermal decomposition of tetraacetylmucyl azide led to the desired result[77].

A successful cyclisation was first achieved in Micheel's laboratory[78] by heating a toluene solution of 1,6-dideoxy-1,6-diiodo-*O*-dimethylenemannitol (VIII) to 165°–170° for 8 h with molecular silver. *O*-Dimethylenetetrahydroxycyclohexane (IX) was obtained from (VIII) in this way:

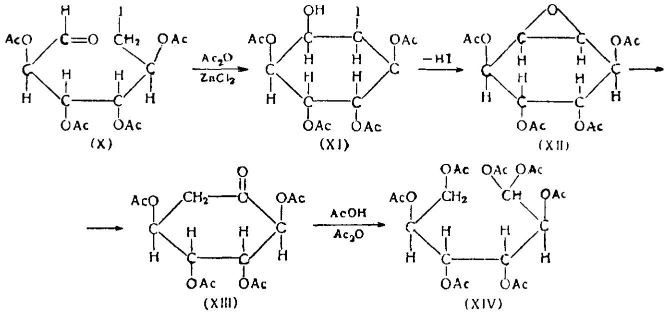


Wolfrom and Usdin[79] examined the possibility of cyclising 1,6-dibromogalactitol hexaacetate to inositol derivatives by heating it with active metals (Ag, Zn, Mg, Ca, Na), but their results were negative. They showed, however, that the tendency of carbohydrates to cyclise depends on their spatial configuration.

Cyclisation of aldoses by intramolecular aldol condensation, which has not yet been effected in one stage *in vitro*, is of particular interest. Attempts to carry out an aldol condensation of glucose in an alkaline medium[80] led only to isomerisation of the carbon chain and the formation of saccharinic acids. Reducing sugars are known to undergo a variety of conversions in an alkaline medium, forming numerous carbohydrate and non-carbohydrate products, but no carbocyclic compounds whatever[81,82] have been found. Negative results were obtained in attempts to cyclise 1,2,3,4-tetraacetyl-6-chloroglucose and 6-cyano-6-deoxyglucose in alkaline solution[16]. However, intramolecular aldol condensation of hexoses was successful when the hydrogen atom at C_6 was activated by substituting iodine, carboxyl, or the nitro-group for the hydroxyl.

Micheel and Ruhkopf[83] made a detailed examination of the possibility of cyclising 2,3,4,5-tetraacetyl-6-deoxy-6-iodo-aldehydo-D-galactose (X) by heating it with acetic anhydride in the presence of anhydrous zinc chloride. Under these conditions, the compound cyclises smoothly to form an unstable inositol derivative (XI); this is then converted to the epoxy-compound (XII), which isomerises to deoxyinosose tetraacetate (XIII). The isomerisation of compound (XII) is a special case of intramolecular oxidation-reduction disproportionation fairly frequently encountered in carbohydrate chemistry.

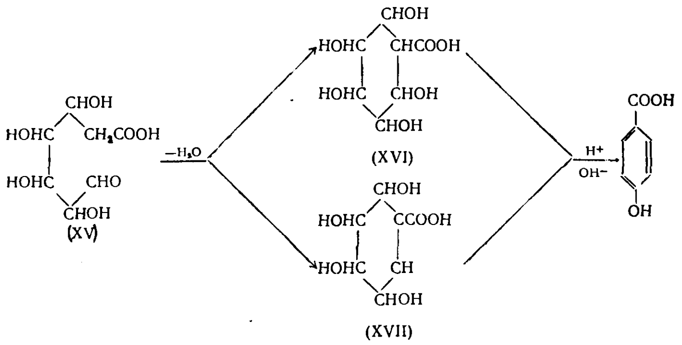
Compound (XIII) is unstable in acetic acid and, according to the authors, it is easily decyclised to form aldehydo-D-galactose heptaacetate (XIV) with an open carbon chain:



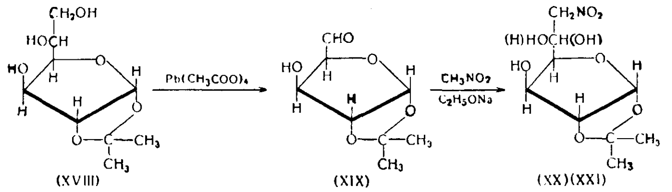
In our opinion, the results of this work are not entirely convincing and need to be confirmed.

Prey and Szabolcs[84], studying possible routes for the conversion of carbohydrates into carbocyclic compounds in living matter, carried out the intramolecular condensation of 6-deoxyhepturonic acid (XV). This conversion was achieved by prolonged heating of an aqueous solution of the

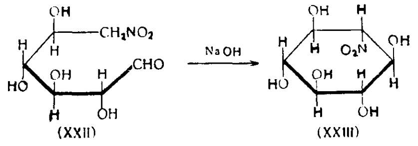
6-deoxyhepturonic acid (90°, 24 h) with an excess of the ion-exchange resin Amberlite IRA-400. Chromatography of the reaction mixture on the same resin yielded a small quantity of pentahydroxycyclohexanecarboxylic acid (XVI) and tetrahydroxycyclohexenecarboxylic acid (XVII), which were dehydrated by mineral acids or alkalis to form *p*-hydroxybenzoic acid:



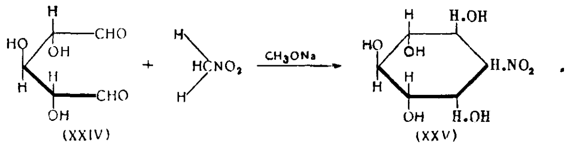
The nitromethane method proposed by Grosheintz and Fischer[85,86] was shown to be the most promising for converting aldoses to inositol. In this method D-glucose is treated with acetone in the presence of sulphuric acid and 1,2-monoacetone-D-glucose (XVIII) is obtained; this is oxidised by lead tetraacetate in benzene solution to 1,2-monoacetone-D-*xylo*-trihydroxyglutaric dialdehyde (XIX), which is then condensed with nitromethane in the presence of an alcoholic solution of sodium ethoxide[85]. When the aldehyde group of the acetonated dialdehyde (XIX) is condensed with nitromethane, a new asymmetric centre arises, and a mixture of the isomers 1,2-monoacetone-6-deoxy-6-nitro-D-glucofuranose (XX) and 1,2-monoacetone-6-deoxy-6-nitro-L-idofuranose (XXI) is formed:



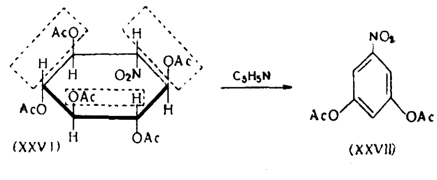
The mixture of acetonated deoxysugars cannot be separated by fractional crystallisation; however, repeated acetonation of the mixture yields the diacetone derivative of deoxynitro-L-idose, which can easily be separated from the unchanged 1,2-monoacetone-6-deoxy-6-nitro-D-glucofuranose (XX). When (XX) is hydrolysed, 6-deoxy-6-nitro-D-glucose (XXII) is formed, and in the presence of a solution of sodium or barium hydroxide, this cyclises to give, from the mixture of isomers, crystalline-2-deoxy-2-nitroinositol (XXIII) in 40% yield, corresponding in spatial configuration to 2-deoxy-2-nitroscyllitol[86]



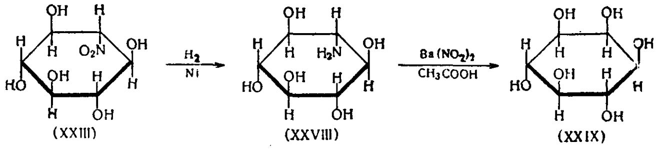
Brocca and Dansi[87] described the cyclisation of D-*xylo*-trihydroxyglutaric dialdehyde (XXIV) to a mixture of isomers of 2-deoxy-2-nitroinositol (XXV), which occurs in one step when the dialdehyde is treated with nitromethane in the presence of sodium methoxide:



The cyclic character of the deoxynitroinositols was demonstrated by the quantitative conversion of their pentaacetates (XXVI) to diacetyl-5-nitroresorcinol (XXVII), which is readily formed when (XXVI) is treated with hot pyridine:

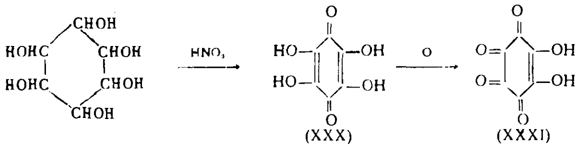


2-Deoxy-2-nitroscyllitol (XXIII) can be converted to *meso*-inositol without difficulty: it is hydrogenated catalytically in the presence of Raney nickel to give 2-amino-2-deoxyscyllitol (XXVIII)[86] in 69% yield; on treatment with barium nitrite solution in acetic acid, the amino-group of (XXVIII) is replaced by hydroxyl, and *meso*-inositol (XXIX)[88] is formed by a Walden inversion:

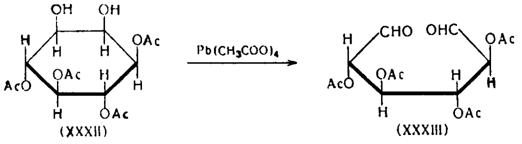


Posternak and coworkers used this method[89] to synthesise *meso*-inositol labelled with ^{14}C in position 2, starting from 1,2-monoacetone-D-*xylo*-trihydroxyglutaric dialdehyde (XIX) and labelled nitromethane, $^{14}CH_3NO_2$.

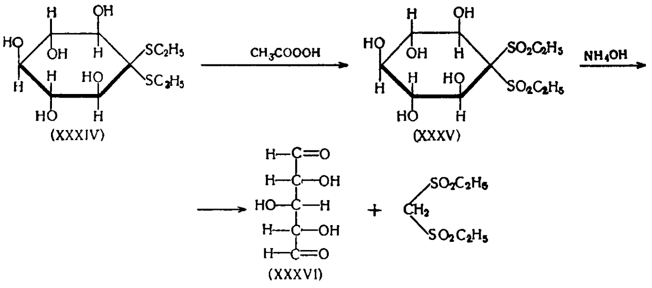
It has been pointed out above that *meso*-inositol is an intermediate in plant metabolism, being readily converted to polyhydric phenols. A similar conversion of *meso*-inositol and its derivatives to di- and tri-hydric phenols has been successfully carried out under laboratory conditions[15,87,90]. In general, the exceptionally easy aromatisation of the ring is characteristic of inositol and other cyclitols. Quercitol, for example, when heated under reduced pressure decomposes to form quinone, hydroquinone, and pyrogallol; when it is reduced with hydriodic acid, benzene, phenol, hydroquinone, and quinone[91] are obtained. On heating with nitric acid, inositol is oxidised to tetrahydroxyquinone (XXX), and then to rhodizonic acid (XXXI), which also has an aromatic structure:



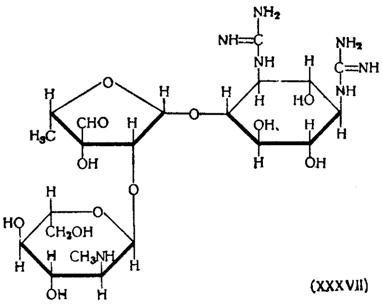
The reverse conversion of inositol to the dialdehyde is achieved fairly easily under laboratory conditions by various methods based on oxidative ring cleavage. Oxidation of tetraacetyl-*meso*-inositol (XXXII) to the acetylated dialdose (XXXIII) proceeds smoothly when (XXXII) reacts with lead tetraacetate[92]:



MacDonald and Fischer developed a simple method of opening the inositol ring[93] by cleaving the disulphone (XXXV) with ammonia, the disulphone being obtained by oxidising *meso*-inosose diethylmercaptal (XXXIV). The dialdehyde (XXXVI) obtained in this way contains one carbon atom less than the initial cyclitol:



The nitromethane method of closing six-membered rings has been successfully used to establish conclusively the structure and synthesis of the streptidine part of the streptomycin molecule. Detailed structural studies showed this antibiotic to be *N*-methyl-*α*-L-glucosaminido-*β*-L-streptosidostreptidine (XXXVII)[94]

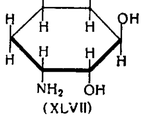


When heated with dilute acids, streptomycin hydrolyses to streptidine and streptobiosamine[95].

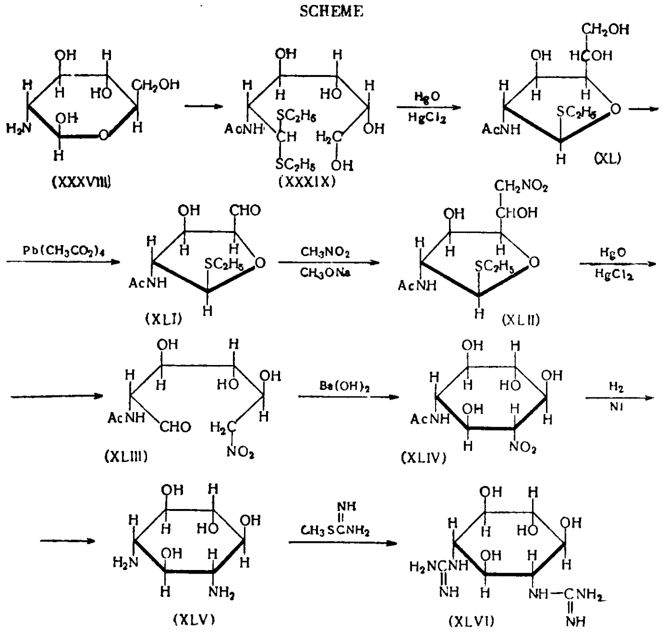
Wolfrom[96,97] synthesised the streptidine part of the streptomycin molecule in 1950 by cyclising D-glucosamine by the nitromethane method. Natural D-glucosamine (XXXVIII) (which has a known configuration), with its amino-group protected by acetylation, is converted to the diethylmercaptal (XXXIX) by treatment with ethylmercaptan; mercuric chloride and mercuric oxide in aqueous solution converted the mercaptal into *S*-ethyl 2-amino-*α*-D-glucothiofuranoside (XL), and then the amino-derivative of the dialdehyde (XLI) was obtained after glycol cleavage with lead tetraacetate. This was condensed with nitromethane in the presence of sodium methoxide by the method described above[67], and the nitrosaccharide (XLII), formed after the ethylthio-group had been hydrolysed (to yield XLIII), was cyclised by aldol condensation in the presence of barium hydroxide.

When the nitro-derivative of inositol (XLIV) is reduced catalytically, a mixture of isomeric diamino-compounds is formed, from one of which the diamine (XLV), identical with streptamine obtained by saponification of streptidine in an alkaline medium, is isolated. Condensation of streptamine with *S*-methylthioisourea yields streptidine (XLVI) (see scheme below). The streptidine synthesised in this way was identical with the compound obtained by hydrolysing streptomycin.

An optically inactive analogue of streptidine, 1,3-diamino-4,5,6-trihydroxycyclohexane [deoxystreptamine (XLVII)] is obtained by acid hydrolysis of the new antibiotics neomycin, kanamycin, and paromomycin, of which it is a constituent, linked by a glucoside bond[98,99].

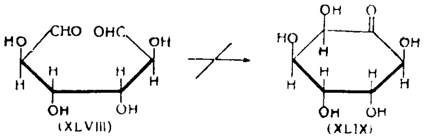


SCHEME

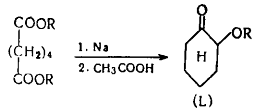


Besides the work cited above on the cyclisation of the carbon chain of carbohydrates by splitting out halogen in a reaction of the aldol-condensation type, attempts at ring closure by an acyloin-condensation reaction should be mentioned.

Wolfrom and Usdin[79], who used galactodialdohexose (XLVIII), obtained by reducing tetraacetylmucyl chloride (VII), showed that the acyloin condensation with the formation of the expected inosose (XLIX) does not occur:



In 1950, Sheehan and coworkers[100] showed that it was possible to cyclise dimethyl adipate to adipoin (L) by the acyloin method.

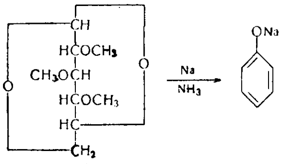


(L)

where R=H, CH₃.

However, the attempt by Brocca and Dansi[101] to carry out a similar cyclisation by boiling dimethyl 2,4,3,5-*O*-dimethylene-D-glucarate in toluene solution with potassium was unsuccessful.

In 1939, Shorygin and Shorygina[27] made the first successful attempt to convert carbohydrates directly to aromatic compounds. By treating 2,3,4-trimethyllaevoglucosan (LI) with sodium in liquid ammonia, they obtained phenol in 34% yield. They put forward a reaction scheme for this conversion, based on the cleavage of the ether bonds of 2,3,4-trimethyllaevoglucosan with sodium:



(LI)

Bright yellow transient intermediate products (probably organosodium compounds) are formed in the reaction. Shorygina and Perfil'eva[102] improved the reaction procedure and increased the yield of phenol from 50 to 56%; the yield of phenol is directly proportional to the quantity of sodium used in the reaction, the optimum quantity of sodium required for the cleavage of the three groups of trimethyllaevoglucosan corresponding exactly to 6 g-atoms per gramme-molecule of (LI). In experiments with amounts of sodium less than the amount required by the equation, unreacted trimethyllaevoglucosan was obtained, and an excess of sodium did not increase the yield of phenol. These facts are of great importance as regards confirmation of the authors' reaction scheme. By-products of the aromatisation of (LI) include the dihydric phenols resorcinol and catechol, which were isolated from the reaction mixture by paper chromatography[102].

It appears that the group of carbohydrate compounds capable of being aromatised under the conditions of the Shorygin reaction is somewhat limited, since when sodium, alone or in liquid ammonia, reacts with methylglucoside or methyl-2,3,4,6-tetramethyl-D-glucoside, no phenol or phenolic compound is formed[103].

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ADVANCES IN THE SYNTHESIS OF POLYSACCHARIDES

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ADVANCES IN THE SYNTHESIS OF POLYSACCHARIDES

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CONTENTS

I. INTRODUCTION

The synthesis of high-molecular-weight polysaccharides from various monoses or low-molecular-weight polyoses is one of the most complex problems of modern carbohydrate chemistry and also one which holds out most promise. The considerable interest in this problem is due to the following reasons.

1. The efforts to synthesise polysaccharides analogous in structure and properties to the more important natural polysaccharides, in particular cellulose and amylose, in which the glucose units are united by α- or β-(1 → 4)glycosidic linkages. Successful syntheses of this kind will help elucidate many problems associated with the structure and properties of these most important natural high-molecular-weight compounds and their derivatives.
2. The possible synthesis of new synthetic materials with valuable properties, which could be used for various purposes, particularly in medicine and biology. By changing the molecular weight, chemical structure (for instance the type of linkage between the elementary units of the macromolecule) and especially the branching of synthetic polysaccharides the properties of this new type of synthetic polymers can be varied within wide limits and new fields for their application found.
3. Simulation of many complex biological systems, particularly with a view to studying complex biological and biochemical processes and the physicochemical and biological properties of mucopolysaccharides (heparin, chondroitin, etc.).

Although work on the synthesis of polysaccharides (the so-called "reversion") started as early as the seventies of the last century, the most important results in this field were obtained in the last few years.

By using the basic methods and principles of modern synthetic polymer chemistry, particularly polycondensation and conversion of cyclic compounds into linear polymers, it was possible to obtain polysaccharides with molecular weights from several thousand to one million. Application of modern physicochemical and physical methods for the study of high-molecular-weight compounds has led to great advances in the field of these typical polyelectrolytes and their derivatives.

The problem of the preparation of synthetic analogues of cellulose and amylose, which have a linear, stereoregular structure, and whose macromolecules contain but one type of glycosidic linkage [α- or β-(1 → 4)], has so far remained unsolved. Obviously the synthesis cannot be effected by using monomeric monoses, containing 4–5 reactive functional groups, as starting material in the homopolycondensation. Other methods, starting from bifunctional monomers, must be used.

Systematic studies of this kind are only just starting, in the USSR as well as abroad. We think, nevertheless, that very interesting results have already been obtained in this new and complex branch of the chemistry of synthetic polymers. We have therefore undertaken to review briefly the current state of this problem.

II. METHODS FOR THE PREPARATION OF SYNTHETIC POLYSACCHARIDES

We already pointed out that two methods are available at present for the synthesis of polysaccharides, *i.e.* polycondensation and conversion of cyclic compounds into linear polymers.

A. SYNTHESIS OF POLYSACCHARIDES BY POLYCONDENSATION

Of all the various modifications of polycondensation, only homopolycondensation can be used in the synthesis of polysaccharides, since every monose required in this reaction contains two types of functional groups: hydroxyl groups and the aldehyde group in the form of a hemiacetal.

Interaction between these functional groups results in the glycosidic linkages between the units of the polymer macromolecule. Depending on the position of the hydroxyl group in the monose molecule, various types of glycosidic linkages may be formed (1 → 1, 1 → 2, 1 → 3, 1 → 4, 1 → 6).

The polycondensation of monoses can be effected not only in anhydrous media (as in the case with other polymers), with continuous elimination of water formed in the reaction, but also in aqueous solutions in the presence of acid catalysts, as for instance in the hydrolysis of crude polysaccharides. In contrast to homopolycondensation proceeding without a catalyst, *e.g.* of polyamides, where the only factor which controls the reaction rate and the molecular weight of the product is the temperature, the synthesis of polysaccharides is always carried out in the presence of acid catalysts.

1. Polycondensation in Solution

(a) The polycondensation of monoses in aqueous solutions in the presence of acid catalysts has been known for a long time. In the seventies of the last century it was observed that glucose can undergo polycondensation to form high-molecular-weight polysaccharides. In 1872 Musculus[1] described the dextrin-like products formed by the action of concentrated mineral acids on glucose. Other research workers reported similar results[2-5]. Tollens (ref.6, p.10) showed somewhat later that polycondensation (reversion) occurred in 20% aqueous glucose solutions in the presence of hydrochloric acid. The work of Wohl[7] and Ost (ref.6, p.11) belongs to the same period. In their study of the products of polycondensation obtained by the action of concentrated hydrochloric acid upon 25% aqueous glucose solution, the authors isolated a product, $[\alpha] = +122°$, with a reducing power 7–9 times lower than that of glucose, which they named "glucosin". On hydrolysis with diluted acid this product was converted quantitatively into glucose, but it resisted enzymic hydrolysis.

Interesting investigations of the structure of the products of glucose polycondensation in the presence of hydrochloric acid were carried out by Fischer[8] during this period. Willstätter and Zeichmeister[9] studied the reversion of glucose in hydrochloric acid solutions by measuring the change in the specific rotation. Silin and Sapegina[10] studied the polycondensation of monoses in the presence of dilute acids. All this work was of great practical importance for the development of methods of saccharification in the industry of starch and molasses. Smirnov[11] recently carried out investigations along the same lines. Sharkov and Liprandi (ref.6, p.12) studied the effect of 80% sulphuric acid on glucose by measuring the change in the reducing power of glucose with time. Sharkov and Sartania (ref.6, pp.13–15) later investigated the effect of 80% sulphuric acid on glucose, galactose, mannose, fructose, and xylose. The polycondensation products had a reducing power 6–7 times smaller than the initial monoses. They showed that the higher the concentration of the monose in solution, the faster and the more efficient its polycondensation. In aqueous alcoholic solution the degree of polycondensation is considerably higher than in aqueous solution. Sharkov and Smirnova[12], who studied the polycondensation of glucose in the presence of concentrated sulphuric acid, arrived at a similar conclusion.

Odintsov and Preobrazhenskii[13,14] also studied the polycondensation of glucose in concentrated sulphuric acid and on the whole confirmed the results of Sharkov and his collaborators; they established in addition that the products of polycondensation are more stable to high temperatures in the presence of concentrated sulphuric acid than glucose itself. The average degree of polymerisation of the products of glucose polycondensation in sulphuric acid, according to end group analysis, was 4–5.

The kinetics of glucose polycondensation in the presence of hydrogen chloride of varying concentration have been studied in great detail by Fram[15,16]. He showed the reversible character of this reaction, made an attempt to determine the molecular size distribution of the reaction products, and studied the structure of the resulting polysaccharides. He carried out the polycondensation of methyl-substituted glucoses with a view to determining the reactivity of various hydroxyl groups in the glucose molecule. The methylated reaction products were fractionated by high-vacuum distillation. The primary alcoholic group at carbon atom six in glucose was established to be the one mainly engaged in polycondensation.

Pogosov and Rogovin[17,18] studied the polycondensation of glucose in hydrogen fluoride solutions. At hydrogen fluoride concentrations lower than 75% and at room temperature this process proceeds very slowly, the average degree of polymerisation of the resulting sugars, determined from the iodine number, being lower than 2. Polycondensation proceeds more readily at hydrogen fluoride concentrations 80% and higher. The polysaccharide obtained from these solutions had the average degree of polymerisation 10–12 (from end group analysis).

Ricketts[19] recently studied the polycondensation of glucose in concentrated hydrochloric acid containing a small amount of concentrated sulphuric acid. The reaction mixture was left at room temperature for seven days. After purification and dialysis the syrup-like product had an average degree of polymerisation of 20 and $[\alpha] = +106°$. On complete hydrolysis it yielded only glucose; isomaltose was isolated chromatographically after partial hydrolysis. Periodate oxidation established the presence of 70% of α-(1 → 6) glycosidic bond. Hurd and Cantor[20] and Fetzer[21] studied the products of polycondensation of glucose in the presence of aqueous acid solutions. By methylation and subsequent molecular distillation of methylglucose, Montgomery and others[22,23] isolated 40% of monoses, 28% of bioses and 4% of trioses. From the mixture of bioses Miller[24] isolated after acetylation gentiobiose acetate. In addition to gentiobiose he found a disaccharide of uncertain structure which did not ferment with yeast. Coleman later showed[25] this disaccharide to have the structure like gentiobiose but with an α-glycosidic linkage (isomaltose).

Moelwyn-Hughes[26] calculated the activation energy for the formation of the glycosidic bond to be 33 500 cal. Since this value is considerably higher than the energy of the cleavage of the glycosidic bond (28 000 cal), the rate of polycondensation increases faster with increasing temperature than the rate of hydrolysis.

The polycondensation of a number of carbohydrates in aqueous solutions in the presence of acid catalysts has been studied recently. The resulting products were analysed chromatographically. Bishop[27] studied the polycondensation of xylose in hydrochloric acid solution. The degree of polymerisation of the resulting xylose polymer was 10. Ball and Jones[28], who also studied the polycondensation of xylose, obtained the same results. Hough and Pridham[29] studied the polycondensation of arabinose.

Jones and Nicholson[30] investigated the composition of products formed by the polycondensation of L-arabinose and D-mannose in 6 *N* HCl during 96–168 h.

Separation of the reaction products in a cellulose chromatographic column, followed by the paper chromatography of separate fractions, showed them to be predominantly disaccharides with different types of glycosidic linkage between the monoses.

Taufel *et al.*[31,32] studied the polycondensation of D-glucose, D-xylose, D-galactose, D-arabinose, lactose, maltose, and cellobiose in acetic acid solution in the presence of small amounts of hydrochloric acid. By using paper chromatography to separate the polycondensation products, oligosaccharides were detected in addition to bioses, but their structure was not studied in detail.

Peat *et al.*[33] used paper chromatography to study the composition of the products of polycondensation of glucose formed in the presence of 0.33 *N* sulphuric acid and in 90% formic acid. Disaccharides of various structures predominated among the reaction products, which also contained laevoglucosan, formed by intramolecular elimination of water from glucose. Micheel and Groses[34] studied the polycondensation of glucose in dimethylsulphoxide solution in the presence of hydrogen chloride at room temperature. The products detected by paper chromatography were gentiobiose, maltose, isomaltose, cellobiose, other oligosaccharides, and polysaccharides. The polysaccharides were insoluble in methanol. The structure of the oligo- and poly-saccharides was not investigated.

Using absorption chromatography on charcoal-zeolite columns, Thompson and his collaborators[35] succeeded in isolating from the products of the polycondensation of glucose in 0.082 *N* hydrochloric acid the following bioses: isomaltose, gentiobiose, maltose, cellobiose, nigerose, sofrose, β-trehalose, and anhydromonose (laevoglucosan).

The analytical data on the quantitative composition of the biose fraction of the glucose polycondensation products show[33,35] that disaccharides formed by the condensation of the primary hydroxyl group at carbon atom 6 with the aldehyde group of another molecule of monose predominate in the mixture. This can be explained by the higher reactivity of primary hydroxyl groups in acid media, particularly in the formation of a glycosidic linkage[36].

It is clear from the foregoing that polycondensation in aqueous solutions does not yield products of very great molecular weight. The average degree of polymerisation of the polycondensation products did not exceed 15–20. Such results are fully understandable since the polycondensation is reversible and in aqueous solution the equilibrium is shifted towards the hydrolysis of the high-molecular-weight synthetic polysaccharides.

(b) The polycondensation of glucose in the presence of anhydrous acid catalysts with a view to shifting the reaction equilibrium towards the formation of high-molecular-weight polysaccharides was effected by a number of research workers. Schlubach and Lüers[37] were the first to show liquid hydrogen chloride to be, at room temperature, an active catalyst in the polycondensation of sugars. Under such conditions glucose yields polyglucosans, which on hydrolysis can be converted again to glucose; thus only glycosidic bonds exist between the units of the synthetic polysaccharide. Fructose gave the so-called polyfructosans[38] whose structure has not been studied in detail. Helferich and coworkers[39-41] studied the action of anhydrous hydrogen fluoride on glucose and trimethylglucose, but did not succeed in identifying the polycondensation products. In their study of the effect of anhydrous hydrogen fluoride on cellulose Freudenhagen and Cadenbach[42] obtained a polysaccharide formed by the polycondensation of the hydrolysis products (the so-called cellan). Cellan weakly reduced Fehling solution and was not hydrolysed by enzymes. The use of methylation to determine the structure of the polycondensation products was unsuccessful. Sharkov and his collaborators (ref.6, p.20) obtained similar results in their study of the action of hydrogen fluoride on cellulose.

By fractional precipitation of the products of glucose polycondensation in the presence of hydrogen fluoride, Rogovin and Posogov[18,36] recently obtained a series of fractions of different molecular weight and specific rotation. They studied the structure of the biose fraction and showed the bioses to contain primarily the α-(1 → 6) glycosidic linkages.

In all cases the average degree of polymerisation did not exceed 25, although products of higher molecular weight might have been expected in polycondensations carried out in the presence of anhydrous acid catalysts. It is clear, however, that high-molecular-weight products cannot be obtained without a continuous removal of water from the reaction system.

(c) New methods for the synthesis of polysaccharides by polycondensation have recently been suggested. Several amongst them, for instance the solid-phase reaction, have acquired great significance for the chemistry of synthetic polymers in general.

Polycondensation at elevated temperatures with continuous removal of water under high vacuum was the first method used for the preparation of synthetic polysaccharides of molecular weight 50 000 to a million. It should be noted that the polysaccharides obtained under these conditions have a higher molecular weight than other types of synthetic polymers obtained by the same method (*e.g.* polyamides, polyesters, etc.).

These new methods of synthesis may be divided into a number of groups, which are considered below.

2. High-Vacuum Polycondensation of Glucose

The preparation of high-molecular-weight branched polyoses, with a degree of polymerisation from 1 to 10, by high-vacuum polycondensation of various sugars was first described in the patent by Mora and Pacsu[43]. They showed that heating sugars individually or in mixtures, in an inert solvent or without solvent, in the presence of small amounts of an acid catalyst (*e.g.* 0.01–5 wt.% H_3PO_4 with respect to the glucose) between -80° and +110°, at pressures from 10^{-5} to 100 mm Hg (reaction times from 2 min to 72 h), yields vitreous polymers not containing any decomposition products. These polymeric carbohydrates had a molecular weight from 2500 to a million. Various polymer fractions were separated by dialysis or by fractional precipitation. These polymers were suggested for use as blood plasma substitutes instead of dextrans, which are synthesised enzymically.

In a series of communications Mora and his collaborators[44-46] described in detail the experimental technique and the composition of the resulting synthetic polysaccharides. They concluded[44] that to obtain polysaccharides of a high degree of polymerisation (> 300), the homopolycondensation should be effected under the following conditions: (*a*) catalyst concentrations at which there can be no decomposition of polysaccharide in a side-reaction; (*b*) uniform heating of the reaction mixture to fairly high temperatures; (*c*) high concentration of the monomer in the reaction mixture; and (*d*) the absence of oxygen or other reagents which could cause the decomposition of the resulting polymer.

The high-vacuum polycondensation, giving rise to products of high-molecular-weight and of varying degree of branching, has been carried out in three ways: (a) by the polycondensation of molten glucose heated by an infra-red lamp in the presence of an acid catalyst; (b) by the polycondensation of molten glucose as under (a) but in the presence of tetramethylsulphone which, being a plasticiser for glucose, lowers its melting point; and (c) by a two-stage polycondensation. In the last case the solid polymer formed in the first stage of the process is cooled, ground up, and heated again as under (b). In all three modifications phosphoric acid (0.168 wt.% with respect to the glucose) was used as a catalyst. To obtain a uniform reaction, small amounts of acid had to be distributed uniformly within the mass of monosaccharide by prolonged agitation of glucose with the acid in a ball mill.

The number-average molecular weights of certain polysaccharide fractions obtained under the above conditions are collected in Table 1.

TABLE 1. Number-average molecular weights and specific rotations of certain synthetic polysaccharide fractions obtained according to the Mora method[44].

Method of polycondensation	Temp., °C	Number-average mol. wt. (determined by the end-group method)	$[\alpha]_D^{25}$ in 1 *N* HCl, degrees
Modification (a)	140	15 000	71.1
	140	16 800	73.3
	150	22 750	70.0
	150	21 250	82.0
Modification (b)	155	16 200	71.2
	155	8 250	69.7
	175	32 800	85.2
	175	20 000	82.8
Modification (c)	150	17 500	63.6
	150	15 100	65.7
	170	20 000	67.8
	170	16 200	68.6

The branched polysaccharides, isolated by precipitation with methanol, were white and readily soluble in water. To separate the low-molecular-weight fractions, the polysaccharides were dialysed. They were also subjected to hydrolysis in 1 *N* HCl in order to determine the yield of glucose (96–100% of theoretical). Glucose was identified as the ozazone. The hydrolysis products were analysed chromatographically in order to determine the extent of partial decomposition and the formation of side-products during the polycondensation of glucose under the above conditions. Only traces of laevulinic acid[47,48] and hydroxymethylfurfural were detected on the chromatograms. The reaction mechanism proposed for the polycondensation of glucose is illustrated in Fig.1, [44] which shows the role of hydrogen ions and water in mutarotation, hydrolysis, and polycondensation. Mutarotation is accompanied by the formation of a free aldehyde group, which at equilibrium is present to the extent of about 0.2 mole %.[49] The open--chain form rapidly undergoes ring-closure to give the stable α- or β-forms (only the α-form is shown in the first part of the scheme). It is clear that the carbonium ion at carbon atom 1 could react with any hydroxyl group in another molecule of glucose, for instance with the primary hydroxyl group at carbon atom 6 (see Fig.1). The probability of such an interaction is very low in dilute solutions, but the process can be accelerated by the continuous removal of water from the system. It was shown earlier that the mutarotation proceeds according to a rearrangement mechanism[50,51], which applies in the presence of both acids and bases[52,53]. Phosphoric acid has a relatively low dissociation constant (4.8×10^{-3}) and the dissociated acid is more nucleophilic. It is very probable therefore that phosphoric acid may play a double role in the reaction and serve at high temperatures as an ion carrier. The concentration of phosphoric acid used in the synthesis (0.164%) was chosen empirically. Other acids could obviously also catalyse this process[43], but phosphoric acid has a number of advantages, being non-volatile and stable to oxidation at high temperatures. Glucose is most resistant to decomposition at pH 3. It is clear from Fig.1 that the formation of the glycosidic bond proceeds according to the A-R-B$_{f-1}$ scheme[54] (where A = glucosidic hydroxyl; B = non-glucosidic hydroxyl).

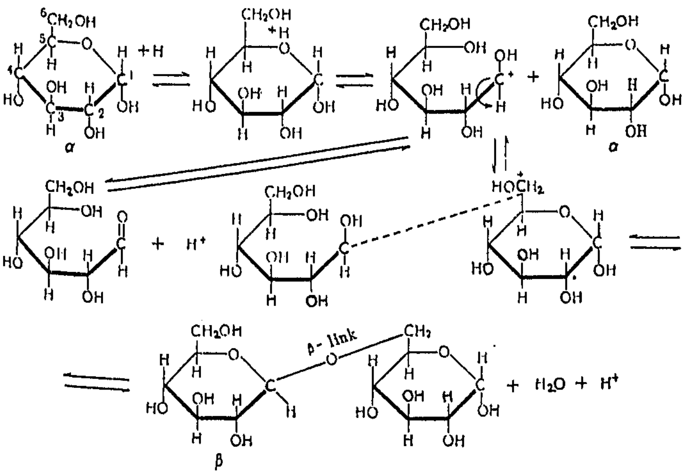

Fig.1. Mutarotation, hydrolysis, and condensation (reversion) of glucose.

The formation of the 1 → 1 bond is energetically unfavourable, as already pointed out by Moelwyn-Hughes[26], and the bond is in fact not found in the reaction products.

Although it could be expected that the amount of α- and β-linkages in the synthetic polysaccharide should correspond to the equilibrium concentrations of glucose isomers (in accordance with Fig.1), the high specific rotation of the preparations indicated the predominance of α-linkages between the units of the polysaccharide macromolecule.

Mora[45] suggested a structure for the polymer (see Fig.2), based on his results of the periodate oxidation of the synthetic polysaccharides.

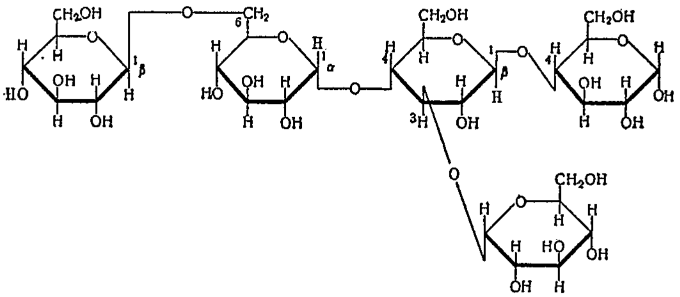

Fig.2. The possible structure of the synthetic polysaccharide.

3. Solid-Phase Polycondensation of Glucose

In 1945 Lenk[55] described a method for the polycondensation of glucose in the solid phase, by heating it with boric acid or its anhydride. The product kept its crystalline structure throughout the reaction and weakly reduced Fehling solution. Lenk's data were recently confirmed by a number of workers[56] who used metaboric acid (HBO_2) as a catalyst. The polycondensation was carried out at 135°–140°. The resulting polyglucosans were completely soluble in water. The amount of catalyst used was 5 wt.% with respect to the glucose. To obtain polysaccharides, both the acid and monose had to be dry. The highest degree of polymerisation obtained under such conditions was 17, and the specific rotation was +64°. It was established by infra--red spectroscopy that the resulting polysaccharides contained both α- and β-linkages. The presence of gentiobiose and isomaltose was detected chromatographically in the products of partial hydrolysis. Methylation followed by hydrolysis gave a number of methyl-substituted glucoses, which were found by paper chromatography to contain a large proportion of 2,3,4-trimethylglucose. This is an indication of the predominance of the 1 → 6 linkage in the polymer.

Qualitative paper chromatography also detected considerable amounts of 2,3,6-trimethylglucose, *i.e.* 1 → 4 linkages are also present in these polysaccharides. The conclusions drawn from this work can be briefly summarised as follows.

The polysaccharides obtained by solid-phase polycondensation in the presence of metaboric acid do not contain chemically bound acid. Since hydrolysis yielded only glucose, the polysaccharide units are bound solely by glucosidic bonds. The polymer is considerably branched, and mainly contains 1 → 6 and 1 → 4 linkages between the units of the macromolecule. It contains both α- and β--glucosidic bonds, without either of them predominating.

4. Polycondensation in the Presence of Dehydrating Agents

A number of investigations in recent years were devoted to polycondensation of glucose in the presence of thionyl chloride. London and his collaborators[57,58] subjected glucose to polycondensation at 110° for one hour in the presence of thionyl chloride. Thionyl chloride served to bind the water formed in the reaction, generating hydrogen chloride, itself a catalyst in glucose polycondensation.

This method for the removal of water appeared, however, to be less effective than the continuous removal of water in a high vacuum. This is revealed by the fact that the average degree of polymerisation of the products did not exceed 20. Periodate oxidation showed that 58% of all the glycosidic bonds were of the 1 → 6 type. From infra--red absorption spectra, it followed that the units were mainly linked by α-(1 → 6) glucosidic bonds, less than 5% being of the α-(1 → 3) type. This polysaccharide (of relatively small molecular weight) has been used as an inhibitor of blood coagulation.

Kent[59] carried out the polycondensation of glucose at 100°–150° in the presence of thionyl chloride containing traces of water or alcohol. The mean degree of polymerisation of the resulting polysaccharides was 25. The polymer is completely hydrolysed by 1 *N* HCl, yielding glucose.

Ricketts and Rowe[60] carried out the polycondensation of glucose, galactose, maltose, lactose, and a glucose–galactose mixture, by passing dry hydrogen chloride as a water-binding agent through powdered carbohydrates, and stirring. The resulting paste was left for five days. After neutralisation and dialysis, the degree of polymerisation was found to be 20. After partial hydrolysis by dilute acid, the polysaccharide was chromatographed on paper. The α-(1 → 6) bonds were found to predominate.

5. Polycondensation of Glucose in the Presence of Polymeric Cation-Exchangers

It was shown recently that cation-exchangers can be used for the hydrolysis of water-soluble polysaccharides[61,62]. Such investigations are very promising from the theoretical as well as the practical standpoint. Hydrolysis of polysaccharides in the presence of a polyelectrolyte, which is insoluble in the reaction mixture and can easily be removed from the reactions products, may become one of the most efficient industrial methods for the hydrolysis of water--soluble polysaccharides, *e.g.* starch. The amount of catalyst is practically unchanged in this process. Although the cation-exchangers catalyse the cleavage of the glycosidic bond, under a different set of conditions they may serve as catalysts for the formation of that bond. The synthesis of polysaccharides from monosaccharides in the presence of cation-exchangers was first carried out by the Hungarian scientists Zemplen and Kisfaludy[63]. If 280 g of glucose, 160 ml of water, and 20 g of polymeric benzenesulphonic acid resin are heated to 70° for 72 h, a polycondensation equilibrium is established. The authors separated gentiobiose from the complex mixture of reaction products.

Colla and Lee[64] used a series of polymeric cation--exchangers for the synthesis of polysaccharides from monoses, *e.g.* the following: Zeokarb-215, Zeokarb-225, IR-100(H), and IR-125(H).

The equivalent amounts of glucose and a cation--exchanger were mixed and heated to 100° for 15 min. In the solution of the resulting polysaccharides isomaltose was identified by paper chromatography. The yield of polysaccharides increased on increasing the reaction time. The composition of the reaction products has not been studied in detail.

Recently, Japanese workers[65] isolated a biose from the products of polycondensation of glucose in the presence of a cation-exchange resin.

B. SYNTHESIS OF POLYSACCHARIDES BY THE CONVERSION OF RINGS INTO LINEAR POLYMERS

In addition to the polycondensation of glucose in a high vacuum, another method has been developed for obtaining polysaccharides, namely the conversion of rings into linear polymers. By this method polymers are obtained from three-membered rings (ethylene oxide, ethyleneimine, epoxy compounds, etc.), as well as seven-membered rings, *e.g.* caprolactam. The principles of the conversion of cyclic compounds into linear polymers were systematically studied in the polymerisation of caprolactam and other heterocyclic compounds by Knunyants, Rogovin, Strepikheev *et al.*[66-68]. The same method was used for the synthesis of polysaccharides from anhydromonoses, *e.g.* laevoglucosan.

By this method branched polymers can be obtained owing to the presence in the monose molecule of several free hydroxyl groups. So far, only one type of strained-ring monose, laevoglucosan, has been employed in this reaction, but there is no reason why a series of different monoses, whose polymerisation would result in new types of synthetic polysaccharides, should not be used in a systematic study.

Pictet and his collaborators showed 40 years ago[69-79] that in a high vacuum, and in the presence of catalysts, anhydrosugars are capable of polymerisation. For instance, on heating laevoglucosan (1,6-anhydro-β-D-glucopyranose) in the presence of platinum black, dimers, octamers, and other polysaccharides are formed. It has been shown[74] that a small fraction of the reaction products does not pass through a semipermeable membrane and must consequently have a rather high molecular weight. Somewhat later the Pictet method was used for the synthesis of oligosaccharides from laevoglucosan[80,81]. At that time modern physicochemical methods for studying polymers were not available, and the high-molecular-weight fractions were therefore not investigated.

Carvalho *et al.*[82] recently made an attempt to polymerise laevoglucosan using procedures developed by Pictet[69-79] and other workers[80,81]. They carried out the polymerisation at 100°–130°, and used 0.001 to 0.05 mole of catalyst per mole of monomer. The catalysts employed were HCOOH, CH_3COOH, HCl, oxalic acid, H_3PO_4, $ClCH_2COOH$, and $ZnCl_2$. Some experiments were carried out in the presence of solvents (dimethyl sulphoxide or tetramethyl sulphone). At 120°, and in the presence of monochloroacetic acid, an amber-coloured polymer, readily soluble in water, was obtained. In spite of its relatively high molecular weight (38 000–90 000) the preparation had low viscosity, which was an indication of the spherical form of the macromolecule, *i.e.* of extensive branching. Investigation of the structure of this product by periodate oxidation gave various positions for the glycosidic bonds, 1 → 6 and 1 → 4 predominating. The specific rotation was +90°, which is evidence for the prevalence of α-glycosidic linkages. Carvalho *et al.*[82] suggested that the polymerisation of laevoglucosan proceeded *via* the formation of an intermediate anhydro-compound of the α- or β-(1 → 2)-anhydroglucopyranose type. This is consistent with the data obtained in other investigations on the conversion of cyclic compounds into polymers[83,84]. The mechanism of the polymerisation and the structure of the resulting synthetic polysaccharides suggested by Carvalho are given in Fig.3.

According to the scheme in Fig.3, on ring opening, reaction takes place between the resulting free bond and one of the three hydroxylic groups of another monomer molecule. As a result, as already shown by Pictet[70] in the hydrolysis of synthetic polysaccharides, only glycosidic bonds are formed between the polysaccharide units.

Wolfrom *et al.*[85] described a method for the thermal polymerisation of laevoglucosan in the absence of catalysts.

They showed earlier[86] that heat treatment converts the α-(1 → 4) glycosidic bond in starch into α- and β-D-(1 → 6) glycosidic linkages, a few β-D-(1 → 2) linkages being formed simultaneously. Considerable amounts of 1,6-anhydro-β-D-glucopyranose (laevoglucosan) were formed under such conditions. Since this process takes place almost instantaneously at 200° in the absence of water or acid, clearly neither hydrolysis nor polycondensation occur in this case. The polymer obtained in the thermal polymerisation of laevoglucosan was, after partial hydrolysis, subjected to chromatographic analysis. The acetates of the following sugars were isolated: gentiobiose, isomaltose, maltose, cellobiose, and laevoglucosan. It was thus established that the polysaccharides contained the following linkages: α- and β-(1 → 6); α- and β-(1 → 4); and β-(1 → 2). A possible reaction scheme of the polymerisation of pyrodextrins is given in Fig.4.[85]

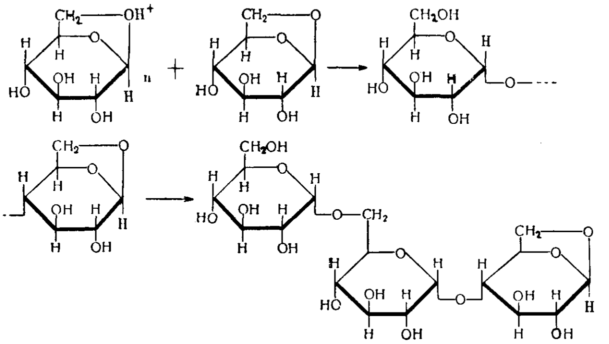
Fig. 3. Polymerisation of laevoglucosan in the presence of acid catalysts.

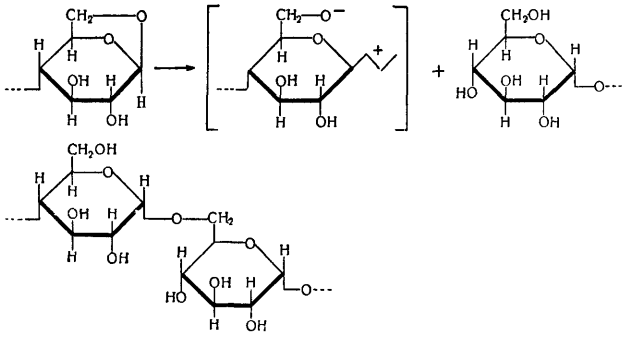
Fig. 4. A reaction scheme for the thermal polymerisation of laevoglucosan.

Korshak[172] recently studied the polymerisation of laevoglucosan and its ethers in dioxane solution in the presence of a series of catalysts. The most effective catalysts were ferric chloride, aluminium chloride, benzenesulphonic acid and the boron fluoride-ether compound. The work included a detailed investigation of the physicochemical properties of polymers and of the mechanism of polymerisation in the presence of the boron fluoride-ether compound.

To sum up, no method for the polycondensation of monoses or the polymerisation of anhydromonoses has as yet become available which would yield polysaccharides with a regular linear structure similar to that of cellulose, amylose, and other natural high-molecular-weight polyoses. By the methods available at present polysaccharides of high molecular weight, but also extensively branched are obtained. The formation of branched polysaccharides is fully understandable since the starting monoses contain 4–5 reactive functional groups. That is why new methods of synthesis should be developed for the preparation of linear polyoses containing only one type of linkage, *e.g.* 1 → 4, or monoses containing only two reactive functional groups should be used.

The highly branched polysaccharides contain exclusively glycosidic linkages between the units, which is confirmed by the composition of hydrolysis products.

Chromatographic and optical analyses showed that α-(1 → 6) glycosidic bonds predominate in synthetic polysaccharides. This corroborates the observation made previously[87] that in acid media the primary hydroxyl groups are more reactive than the secondary, and that in alkaline media the contrary is true. This is the reason for the prevalence of 1 → 6 linkages (isomaltose or gentiobiose type) in the polycondensation products.

Konkin[88] and others[18,89] showed that the 1 → 6 linkage is more resistant to the action of hydrolysing agents than the 1 → 4 linkage. The hydrolysis rate of disaccharides containing 1 → 6 linkages is almost half that of maltose. These data also show that the 1 → 6 linkage is more readily formed in polycondensation in acid media, and that is considerably more difficult to cleave than other types of glycosidic linkage.

Irrespective of their molecular weight, synthetic branched polysaccharides are readily soluble in water†. Synthetic polyoses are atactic polymers, in contrast to natural polysaccharides which have an isotactic or syndiotactic structure. It should be noted, however, that many of the preparations obtained have not been investigated by modern chemical and physicochemical methods.

III. NEW METHODS FOR THE INVESTIGATION OF SYNTHETIC POLYSACCHARIDES

Thanks to the application of new methods of study, the composition and structure of several synthetic polysaccharides have recently been determined. Although isomaltose was discovered by Fischer at the beginning of the twentieth century, the structure of this disaccharide has till recently been the subject of a good deal of controversy[91]. Only by selective partition in adsorption chromatographic columns or by the application of paper chromatography was it possible to show that the product which Fischer considered as a biose of strictly determined structure, and which he named isomaltose, was not a homogeneous product, but consisted of stereoisomeric (1 → 6)-bioses. Isomaltose was isolated by partition chromatography and its chemical structure was established[35,92].

For almost 50 years mainly the classical methods have been used for the demonstration of the structure of carbohydrates[92-94] (ref.67, pp.512–520).

Although these methods retain their significance today, and have scored considerable achievements in this complex field of organic chemistry, they have often been unable to provide the necessary data on the structure of various bioses and especially the high-molecular-weight polysaccharides.

Many new physicochemical and physical methods have recently come to be widely used in polymer chemistry for the investigation of the structure of various polysaccharides, particularly the synthetic ones. Below we discuss the results obtained by some of these methods in determining the chemical and physical heterogeneity of polysaccharides, their molecular form, molecular weight, and the type of linkage between the units.

(a) Determination of the chemical heterogeneity of bioses and higher polyoses. Separation by chromatography has at present acquired great significance. The chromatographic separation of various isomeric bioses formed in the polycondensation of glucose has lately been elaborated and used by a number of workers[29,95]. Especially good separation has been achieved in columns packed with activated charcoal or zeolite[96,98].

In certain cases solutions of polysaccharide acetates, rather than those of the polysaccharides themselves, were used, since the former are more readily separated. Oligosaccharides of high molecular weight were not simply and successfully separated in columns until 1957–1959, when cellulose preparations were used as sorbents[99,100].

Paper chromatography is the simplest method for determining the chemical heterogeneity of low-molecular-weight polysaccharides. Many workers have lately used exclusively this method for the analysis and identification of complex product mixtures obtained in the polycondensation of monoses[30-34,56,101]. A wide variety of solvents and developers was used. Irrespective of the composition of the reagents used, fairly accurate and reliable results were obtained. Good results were also obtained in the application of this method for the separation of the products of the partial hydrolysis of synthetic polysaccharides[60].

(b) Determination of the molecular size distribution in synthetic polysaccharides. The usual fractionation methods are employed in the majority of cases for the determination of the molecular size distribution in these polymers: (1) fractional precipitation by the addition of methanol or ethanol to aqueous solutions of synthetic polysaccharides (Mora *et al.* used this method with success[44,45,102]); (2) fractional dissolution (a sample of the preparation is treated with aqueous ethanol or methanol of varying concentration[103]); (3) dialysis for the separation of low-molecular-weight fractions.

Very few data are available so far on the solubility of various mono- and poly-saccharides in organic solvents and their mixtures. One paper[104] contains data on the good solubility of carbohydrates in dimethyl sulphoxide and tetramethyl sulphone. Without suitable solvents the synthetic polysaccharide preparations cannot be isolated nor purified for subsequent investigations. The separation of catalysts from the resulting synthetic polysaccharides presents special difficulties. The methods used by various workers were relatively complex and involved considerable losses of the reaction products. One of the authors of this review[105] recently worked out a simple method for the separation of mono- and poly-saccharides of various degrees of polymerisation from inorganic impurities by extraction with anhydrous pyridine.

(c) Determination of the form of the macromolecule. The products obtained in the polycondensation of monoses are highly branched and the determination of the form of the macromolecule is of considerable importance both from the viewpoint of the physical chemistry of these polymers, as well as biological simulation, since the form of the macromolecule has a considerable effect on the biological properties of polymers.

To determine the form of the macromolecules of his synthetic polysaccharides, Mora[106] used the usual methods of polymer chemistry for the determination of the degree of branching: (a) comparison of number-average molecular weights (determined by the osmotic and end-group methods) with weight-average molecular weights (determined by viscosimetric and light-dispersion methods); (b) oxidation of polymer preparations by periodic acid[107,108].

(d) Spectroscopic methods for the determination of types of linkage in synthetic polysaccharides. The type of linkage between the units in polyoses (α or β), and the presence of pyran or furan rings, as well as of free hydroxyl groups in them, have recently been determined simply and fairly accurately by physical methods[27,57,109].

It was established[57] that the characteristic absorption band of the α-glycosidic linkage is 844 ± 8 cm^{-1}, and of the β-glycosidic band 891 ± 7 cm^{-1}. These values have been checked on various synthetic glucosans and on natural polysaccharides.

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† Using the same methods Mora ***et al.***, [90] recently obtained a polymer of 2-deoxyglucose, which is sparingly soluble in water and does not hydrolyse. It has not been studied in detail.

In his study of the infra-red absorption spectra of dry synthetic polysaccharide films, Durand[56] established that the polymers obtained by solid-phase polycondensation of glucose in the presence of metaboric acid contain, alongside other types of glycosidic linkage, a considerable number of the α-(1 → 6)-glycosidic bond, with its characteristic absorption maximum at 760–960 cm^{-1}. Finan and Reed[110] recently described the use of the mass-spectroscopic method for the determination of α- and β-glycosidic bonds in various sugars (maltose, cellobiose, laminaribiose, etc.). It was shown that the energy of dissociation of methyl-β-D-glucopyranoside is 0.6 eV higher than the energy of dissociation of methyl-α-D-glucopyranoside.

Electrophoresis in the presence of borate buffers[33,111] gave good results in the separation of various isomeric bioses and polyoses.

Enzymic analysis can also be used for the determination of α- and β-glycosidic links between polysaccharide units, as well as the number of terminal aldehyde groups[112-114].

The most successful of all the chemical methods recently used is periodate oxidation combined with mild hydrogenation. Individual stable polysaccharide fragments have been obtained by this method. By further study of these fragments, the structure of the polyose could be determined. All these questions have recently been discussed in reviews[112,113].

IV. PRINCIPAL USES OF SYNTHETIC POLYSACCHARIDES

After the discovery of the most important biological polysaccharides such as heparin, chondroitin, etc., and the investigations of the role they play in living organisms, attempts were made to prepare their synthetic analogues and substitutes[116]. As a result of the systematic investigations of synthetic polysaccharides and especially their derivatives containing a sulphate or carboxyl group, a number of preparations were obtained which could find practical applications in the following fields: (1) as blood plasma substitutes; (2) as substitutes for heparin and chondroitin in biological processes (heparin can inhibit the coagulation of blood by forming an inactive complex with thrombokinase); (3) as inhibitors of a series of enzymic processes; (4) as selective adsorbents for the separation of proteins and other compounds; (5) as water-soluble polyelectrolytes.

The first polysaccharide preparations used for biological purposes were derived from cellulose. In 1936 Chargaff *et al.*[115] and later Karrer[116] prepared cellulose sulphates which had heparin-like properties (against thrombosis).

In 1943 Kenyon *et al.*[117] showed that the products of cellulose oxidation containing a carboxyl group in position 6 had styptic properties. A detailed investigation has been published recently on the preparation of monocarboxycellulose and its application in medicine[118]. The same preparations were also used as blood plasma substitutes and as carriers of various physiologically active preparations[119].

Since cellulose sulphates were found to be toxic, the soluble cellulose ethers, *e.g.* monoglycolic ether and others[120,121] have been tested. The sulphates of glycogen and starch[122,123], dextran[124], polyvinyl alcohol[125], xylan[126], and chitin[116] have similar properties.

The majority of these substances are toxic owing to their precipitating effect on fibrinogen. That is why, in addition to preparations obtained by enzymic processes (dextrans), attempts were made to synthesise the water-soluble polysaccharides, and obtain from them blood coagulation inhibitors and other biologically important compounds. London *et al.*[57] prepared a sulphate derived from synthetic polyglucosans with $\gamma = 176$. This preparation had the heparin-like property of acting as blood coagulation inhibitor.

Similar products were obtained by Kent and others[59,60]. Their preparations had small molecular weights (degree of polymerisation 20–30), and could only be used as blood anticoagulants. They were not suitable as plasma substitutes, where polymers with molecular weights of 70 000–100 000 are required[127]. In contrast to these preparations, the polysaccharides obtained by Mora *et al.*[45] had high molecular weights and a varying degree of branching. By their fractionation a series of preparations of varying molecular weight and degree of branching was obtained.

Since many biological preparations have a constant mean molecular weight (*e.g.* enzymes), the molecular weight of the synthetic polysaccharide used and the configuration of its macromolecule should obviously have a considerable effect on its biological properties. Mora[45] showed that polyglucosans whose molecular weight is less than 75 000 are inactive biologically and can only be used as blood anticoagulants.

In one of their communications, Mora and his collaborators[128] described synthetic polysaccharide preparations obtained by high-vacuum polycondensation, which had different molecular weight and degrees of branching and in which hydroxyl hydrogen was substituted by sulphuric acid residues to different extents. The preparation of dextran sulphates had been described earlier[124,129-132]. The preparations were obtained in the form of sodium salts and were converted to acids on ion-exchange resins, *e.g.* Amberlite IR-120(H). Preliminary investigations showed that they had the same anticoagulant action as heparin[128], under the same conditions[133,134].

On interaction with macroanions proteins form insoluble complexes[135-137]. The insoluble complexes between proteins and polysaccharide sulphates, which are macroanions, were used for the fractionation of the former[137]. Macroanions also react with enzymes and inhibit various biochemical processes[137].

Mora[138] explains this inhibiting effect by the formation of inactive complexes of the protein with polyelectrolyte, a process which seems to be similar to the precipitation of antigens by antibodies. By titrating a synthetic polysaccharide, (mol.wt. 18 300) containing three free sulphate groups in a single unit, with a protein containing a fixed amount of basic groups (*e.g.* polymixin B), it was established that the two reacted in a stoichiometric ratio.

Adrenocorticotropic hormone in aqueous solution at pH 3.4 was not precipitated on addition of sulphuric acid solution, but on titration with a solution of polysaccharide sulphate the precipitate of the hormone-polysaccharide complex appeared at pH 1. Precipitates are also formed in reactions of synthetic polysaccharide sulphates with protamine, lysozyme, ribonuclease, and neomycin B[138].

Carboxy-derivatives of synthetic polysaccharides were tested as blood anticoagulants[139]. They were prepared by oxidation of synthetic polysaccharide with sodium periodate, followed by chlorite oxidation of the resulting dialdehyde to dicarboxy-derivatives[140,141]. By changing the reaction conditions, preparations with varying amounts of carboxyl groups (from 3 to 28%) could be obtained. The preparations had weak anion-exchanging properties. The advantage of these preparations over polysaccharide sulphates is their lower toxicity. Their molecular weight is practically the same as that of the starting polysaccharides. The carboxy-derivatives of polysaccharides were also used as inhibitors of various enzymes, such as lysozyme, ribonuclease, and other polyampholytes.

Competitive inhibition of enzymes by derivatives of synthetic polysaccharides containing acid groups. The nature of the interaction between macromolecules carrying opposite charges, which alters the solubility of the initial polymers, is of great importance in certain enzymic reactions. This is the main basis of the inhibition of enzymes by polyelectrolytes[137], demonstrated clearly on lysozyme[142], ribonuclease[143-147], hyaluronidase[148-151], etc.[152-158]. Since polyelectrolytes react with proteins to form insoluble complexes, this method is widely used for the fractionation of proteins in serum[135,159-161]. Polyelectrolytes are often polyampholytes, and the pH of the medium is very important.

In recent years systematic investigations have been undertaken on the interaction of various synthetic polyelectrolytes with serum albumin[135,159-161], γ-globulin[160], β-lipoprotein[136,162], fibrinogen[163], and other proteins and nucleic acids[164-169].

This work established the importance of the influence of the chemical composition and properties of polyelectrolytes on the inhibition of enzymes *in vivo* and *in vitro*[137]. Synthetic polysaccharides of varying degree of polymerisation and branching obtained by varying the reaction conditions, were used in model studies of the competitive inhibition of enzymic processes. Mora *et al.*[170] made a study of the reaction of synthetic polysaccharide sulphates of varying molecular weight and extent of branching with lysozyme, ribonuclease, protamine, pancreatic peptide, polymixin B, neomycin, and cytochrome *c* from the albumin serum of man. The competitive inhibition of hyaluronidase and ribonuclease by these polysaccharide derivatives has also been studied. It was established that synthetic polysaccharide sulphates are stronger inhibitors than those used earlier[142], such as glutamyl peptide and DNA (deoxyribonucleic acid). Data on the inhibiting action of polyglucosan preparations on lysozyme activity are given in Table 2.

TABLE 2.* Inhibition of the activity of 60 g of lysozyme by synthetic polysaccharide derivatives[170].

Degree of substitution γ	Polyglucosan sulphate ($PGSO_3^{2-}$)								Carboxy-derivs. of polyglucosan ($PGCOO^-$)	
	B		a		b		C		F	G
	300		270		120		60			
	amount of preparation, μg	% inhibition	amount of preparation, μg	% inhibition	amount of preparation, μg	% inhibition	amount of preparation, μg	% inhibition	amount of preparation, μg	% inhibition
	10	100	10	100	10	100	20	100	50	100
	5	80	5	98	5	68	10	91	25	70
	2.5	66	2.5	65			5	41		

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* Preparations B, a, b, C, F, and G differ in molecular weight and extent of branching. For particulars about these preparations see refs.45 and 128.

It is clear from Table 2 that with increased branching (*e.g.* preparation a) the inhibiting effect of these preparations increases. With a higher extent of branching preparations of lower molecular weight can be used to obtain complete inhibition. The inhibiting activity of several highly branched preparations is four times higher than that of heparin. Similar results were obtained in investigations of the effect of branching of synthetic polyoses on the inhibition of ribonuclease activity[171].

The inhibiting effect of synthetic polysaccharide sulphates, being a result of the interaction of acid groups in the polysaccharide with basic groups in the protein, can be removed by substituting the protein in the protein-polysaccharide sulphate complex with another, more basic protein. For instance, if the ribonuclease-polyglucose sulphate is acted upon by lysozyme, the inhibiting effect of the sulphate is counteracted owing to its interaction with lysozyme which is a stronger base. Free ribonuclease is thereby made available again, with unaltered enzymic activity.

Carboxy-derivatives of polysaccharides showed under similar conditions a lower inhibiting activity owing to their low degree of dissociation.

In vivo carboxy-derivatives of synthetic polysaccharide preparations cause detoxification of basic macromolecules, *e.g.* polymixin B, which is more effective the higher the extent of branching and the higher the content of carboxyl groups. The activity of adrenocorticotropic hormone increases in the presence of carboxyl-containing polyglucosans[140].

The studies made so far on the synthesis of polysaccharides and their biological uses have not exhausted the numberless possibilities for the preparation of synthetic polysaccharides nor the fields of their application. Systematic studies in this interesting and complex field of chemistry and biochemistry are still in the process of development, and will undoubtedly lead to further remarkable practical and theoretical achievements.

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THE CAUSES OF THE STABILITY OF EMULSIONS

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CONTENTS

A great number of investigations has been devoted to the causes of the stability of emulsions to aggregation, nevertheless, at the present time, there is no single opinion even on the causes of the stabilility of the classical emulsions stabilised by ordinary soaps. An attempt is made in the present paper, on the basis of a critical comparison of the accumulated experimental material, to discuss the question of the stability of emulsions and, in this way, to arrive at some general conclusions.

I. STABILITY OF EMULSIONS STABILISED BY SOAPS

An analysis of the scientific literature shows that, if theories of only historical interest discussed in detail in special monographs[1-3] are not taken into consideration, the stability of emulsions stabilised by soaps has been interpreted generally from two viewpoints: either from the so-called physical theory of stability, which specifies the presence of an electrical double layer on the surface of the globules, or from the presence round the globules of a coating of stabiliser possessing structural and mechanical properties. Both conceptions start from premises on the formation of adsorbed films; however, the properties and structure of the films, and also the very basis of stability, according to these theories, are completely different. We shall consider these two theories separately.

Stability of emulsions as a result of the presence of an electrical double layer round the globules. This theory of the stability of emulsions arose from general ideas on the stability of colloid systems developed as early as the beginning of the present century by Hardy[4]. According to this conception, the stability of colloid and micro-heterogeneous systems to aggregation is a consequence of the formation on the surface of the particles of an electrical double layer of ions, which produces an energy barrier obstructing the approach of similarly charged particles to a distance where the intense molecular forces of attraction operate. This layer, the external surface of which generally possesses a diffuse character, usually arises on the surface of the particles as a result of selective adsorption of one of the ions of an electrolyte present in the system. This idea was used by Ellis[5] and Powis[6] to explain the stability of dilute emulsions, and has subsequently been widely used also to explain the stability to aggregation of concentrated emulsions stabilised by soaps[7,8]. At the present time, such prominent scientists as Kruyt[9], Verwey[10], Overbeek[11], Van den Tempel[12], Becher[13], etc., prefer to explain the stabilisation of emulsions by ionic materials on this basis.

A persuasive argument for the correctness of this approach is the behaviour of emulsions stabilised with soaps when electrolytes of different valencies are added to them. Dilute emulsions were shown by Powis[6] to obey the Schultze–Hardy rule. In the Soviet Union, Kharin and Takking[14] have come to the same conclusions.

Martin and Hermann[15] have shown that the Schultze–Hardy rule is also applicable to emulsions of xylene stabilised by sodium oleate. Somewhat later, Van den Tempel[12], investigating the stability of normal emulsions stabilised with sodium salts of esters of sulphosuccinic acid, and with sodium laurate, to the action of electrolytes, also found that his results were in complete agreement with the Schultze–Hardy rule, according to which the concentration of a cation necessary to ensure a predetermined rate of coagulation of a sol with negatively charged particles is determined by the charge, and to a considerably smaller degree, by the specific nature of the cation. Voyutskii and Panich[16], studying the influence of electrolytes on the ζ-potential of particles of synthetic latices stabilised with salts of naphthenic acids, also found an extremely marked influence of the valency of the cation on the threshold concentration for coagulation. According to their results, the threshold concentration for coagulation was generally inversely proportional to the sixth power of the valency of the cation, in agreement with the formula deduced by Deryagin and Landau from the physical theory of the stability of lyophobic sols, which gives greater precision to the Schultze–Hardy rule.

Another indication that emulsions are stabilised by the electrical double layer formed on the surface of the hydrocarbon droplets is the dependence of the emulsifying power of soaps on the nature of their cation observed by Kremnev and Kagan[17]. These authors established that, for normal emulsions, the aqueous phase of which consisted of 0.32 *N* solutions of the oleates of various alkali metals, the critical thicknesses δ of the stabilising layers of systems of limiting concentration and the relative emulsifying power of the corresponding soaps had the values given in Table 1.

The relative values of the critical thicknesses δ of the layers of emulsions of limiting concentrations obtained using oleates with different cations are remarkably similar to the ratios of the coagulation thresholds determined by the same cations when they are added to typical lyophobic sols with negatively charged particles[9,18]. This can be seen, for example, from a comparison of the data of Table 1 with the values for the coagulation threshold γ of suspensions of various clays for various cations found by Jenny and Reitemeier (see ref. 18) and given in Table 2.

The similarity observed is most simply explained by a general cause — an increase in the condensation of the electrical double layer as a result of an increase in polarisability and a diminution in the hydration of the ions with an increase in their true radius. Finally, complete correlation cannot be expected here in consequence of the universally known low accuracy of the determinations of γ and their poor reproducibility.

TABLE 1. Critical thicknesses of the stabilising layers δ and relative emulsifying power of various salts of oleic acid.

Emulsifier	δ, Å	Relative emulsifying power
Sodium oleate	100	1
Potassium oleate	50	2
Rubidium oleate	35	2.85
Caesium oleate	20	5.0

TABLE 2. Values of the coagulation threshold (γ) of suspensions of various clays by different cations.

Cation	Ca-clay		H-clay	
	γ, mM	γ, % of γ for Na^+	γ, mM	γ, % of γ for Na^+
Na^+	4.5	100	2.7	100
K^+	3.0	66	1.5	55
Rb^+	1.9	42	1.2	44
Cs^+	1.2	26	0.7	25

The fact that a diminution in the critical thickness of the stabilising layer and a parallel increase in the emulsifying power is observed when the true radius of the ion of the alkaline metal increases is explained, finally, by an increase in the adsorption of the soap (the adsorbability of soaps rises in parallel with their hydrophobic properties from sodium soap to caesium soap). As a result of this increase in adsorption, the charge density at the inter-phase boundary rises, and the electrical double layer retains its capacity for preventing the agglomeration of the particles at a lower layer thickness.

A third argument in favour of the view that the stability of emulsions is determined by electrical forces of repulsion is the presence in emulsions stabilised by ionic materials of an isoelectric point and the possibility of reversing the charge on their particles. This was noted for dilute emulsions in the early investigations of Ellis[5] and Powis[6]. The same dependence has been established for natural latex by Belgrave[19], Sarrut[20], Fullerton[21], and Rhodes and Secar[22], and for synthetic latices by Voyutskii and coworkers[16]. During the charge reversal, the latex passes through the isoelectric point and the system may coagulate. To prevent this, the charge-reversing electrolyte must be added to the latex as rapidly as possible, and a protective colloid should be added to the latex first. Latex with particles on which the charge is to be reversed must not be too concentrated. It can be seen that to reverse the charge on an emulsion, all the conditions under which charge-reversal of typical lyophobic sols proceeds must be preserved. It must be noted that the change in the ζ-potential of the globules of latices, which are ideal models of emulsions, on changing the pH or adding indifferent electrolytes to the system, obeys laws characteristic for typical lyophobic colloids. A great amount of material on this question has been given in our special review[23].

Finally, the idea that the stability of emulsions stabilised by soaps is determined by the presence of an electrical double layer on the surface of the globules is favoured by the remarkable fact that the emulsifying power of soap solutions falls at fairly high concentrations[24]. In certain cases, it is absolutely impossible to prepare emulsions using highly concentrated soap solutions[25]. It has also been shown[17] that when the concentration of soap in an emulsion is increased the degree of dispersion and, consequently, the stability of emulsions of limiting concentration are reduced to a slight extent. This phenomenon is, of course, connected with the condensation of the electrical double layer in consequence of a high concentration of the stabilising electrolyte.

In a consideration of the stability of emulsions stabilised by soaps starting from the assumption that an electrical double layer is formed round the globules, a number of questions arises. These questions reduce fundamentally to the following three:

1. Why cannot stability be imparted to emulsions by low-molecular-weight inorganic electrolytes which stabilise ordinary lyophobic sols?
2. Why do the salts of the lower fatty acids not possess stabilising properties? If, in the stabilisation of emulsions, everything reduced to the formation of an electrical double layer, then an appropriate increase in the concentration of these salts, which are capable of being adsorbed at an oil–water interface, could, it would appear, produce stable emulsions.
3. Why does the concentration of emulsions (for example, by evaporation) lead to their stabilisation when such an increase in the concentration of a lyophobic sol generally causes its coagulation?

There is no difficulty in answering the first question. Inorganic polarising ions cannot be adsorbed on the non-polar surface of hydrocarbon droplets in sufficient amount for stabilisation. The low adsorption of such ions on the surface of the globules can lead only to their imparting a comparatively weak electrical charge to the latter, as was found in the well-known experiments by Ellis and Powis with dilute emulsions.

The answer to the second question is that, to attain the necessary adsorption for the stabilisation of an emulsion, the concentration of relatively low-molecular-weight soaps in the inter-globular liquid must be so high that considerable condensation of the electrical double layer and rupture of the emulsion will at once take place. According to Donnan[26], who first put forward such an explanation for the lower homologues of the series (up to sodium laurate), the absence of marked emulsifying power is connected with the predominance of the coagulating action of sodium ions, exceeding the capacity for emulsification and reduction of the surface tension. Moreover, it may be considered that the salts of the lower fatty acids, the molecules of which have short hydrocarbon radicals, are completely lacking in emulsifying power and act rather as ordinary electrolytes. The observations of Yurzhenko and Ivanchev[27] are in complete agreement with this; they made a detailed study of the influence of added salts of various fatty acids on emulsion polymerisation. While the addition to the system of salts of fatty acids with more than six carbon atoms in the chain was equivalent to an increase in the concentration of emulsifier, conversely the addition of salts of the lower fatty acids caused the sample to coagulate, leading to an increase in the mean radius of the latex globules and, at high concentrations, to a completely non-stable system.

Finally, the explanation of the possibility of concentrating emulsions leads to the fact that salts of the higher fatty acids, due to the presence of long hydrocarbon chains in their molecules, are very strongly adsorbed. Thus, for example, in rubber emulsions, soap is found almost completely in the adsorbed state on the surface of the globules[28]. Thus, comparatively small amounts of soap will be found in the dispersion medium of even concentrated emulsions, and, consequently, its ionic strength will be relatively low if, of course, saturation of the adsorbed layer is not reached.

Moreover, since the salts of fatty acids are weak electrolytes, the transition from ionised soap to molecular soap incapable of condensing the electrical double layer will take place to an ever increasing degree in the inter-globular liquid as the concentration in the emulsion is increased. Under these conditions, the increase in the concentration of emulsifier which takes place as the emulsion is concentrated cannot in any way fundamentally affect its stability.

The situation is different when the concentration of typical lyophobic sols is increased. The stabilising inorganic electrolytes in a lyophobic sol are mainly in the inter-micellar liquid. Moreover, inorganic electrolytes are generally strong electrolytes and, consequently, cannot change their degree of ionisation with an increase in the concentration of the sol. All this, of course, must lead to coagulation of a lyophobic sol when it is concentrated excessively.

The possibility is not excluded that, although an increase in the soap concentration in the emulsion converts the electrical double layer into a non-ionised layer, the latter being sufficiently hydrated to ensure stability to aggregation in the system. This supposition is quite reasonable if one considers the outstanding polarity of the carboxyl group in which hydrogen has been replaced by an atom of an alkali metal. There are indications in the work of Deryagin[29,30] of the hydration of the electrical double layer formed by the soap molecules after the compression of this layer to the limit and of the stabilising action of the polymolecular hydrate layer arising in this way.

Of course, the papers cited answer the questions posed only in a very general, qualitative form: special investigations are necessary to establish a quantitative basis for the answers given. In recent years, the correctness of the explanation of the stability of emulsions to aggregation as being due to the presence of electrical double layers on the surface of the globules has been confirmed by an experimental test, accompanied by quantitative calculations of the forces acting between the particles.

Van den Tempel[31] has investigated the flocculation and coagulation of emulsions of the oil-in-water type as functions of the concentration of a uni-univalent electrolyte added to them. Calculation of the repulsion energy between the oil droplets of the initial emulsion showed that a potential barrier due to electrical forces must exist between approaching surfaces which exceeds the value of kT by a factor of several thousand. Obviously, the energy of the Brownian motion under these conditions is insufficient to cause direct contact between the surfaces of the drops and hence their coalescence. Therefore, on adding small amounts of a uni-univalent electrolyte to the emulsion, only flocculation takes place. The globules in such a flocculated emulsion are still separated by an aqueous film and are at a distance of at least 100 Å apart. This corresponds to a second shallow minimum on the potential curve which always occurs if the attractive forces diminish more rapidly than the repulsive forces with increasing separation. This minimum is located between 100 and 200 Å for the concentrations of electrolytes used in Van den Tempel's work. More complete contact of the particles under these conditions is still prevented by a fairly high potential barrier of an electrostatic character. Coalescence of the droplets sets in only at comparatively high concentrations of electrolyte as a result of a diminution in the thickness of the aqueous film and its rupture.

In his investigation, Van den Tempel showed that a theory which included only electrostatic repulsion and van der Waal's attraction predicted a far more rapid diminution of the thickness of the aqueous film with an increase in the concentration of electrolyte than is found by experiment. Thus, the experimental results indicated the presence, in addition to the electrostatic forces, of repulsive forces of a different nature acting at distances between the surfaces of the globules of less than 125 Å. The author suggests that such forces are due to steric factors.

It is material that, even earlier, Deryagin and Titievskaya[29], studying the effect of pressure on the thickness of a soap film between two bubbles of a foam, also found evidence for repulsive forces with a small radius of action and evidently of non-electrostatic origin. As mentioned above, Deryagin and Titievskaya consider that these forces are connected with the presence of polymolecular hydrate films in the monolayers of stabiliser. Quite recently, Voropaeva, Deryagin and Kabanov[32] have detected non-electrostatic repulsive forces due to the formation of solvate layers on the surface when two crossed platinum wires are brought to contact in electrolyte solutions.

The recently published investigation of Schenkel and Kitchener[33] is of great importance for the comprehension of the reasons for the stability of emulsions. The investigation was carried out with an aqueous suspension of spherical particles of cross-linked polystyrene with a diameter of 10 μ bearing sulpho-groups on the surface. As the authors pointed out, the dimensions and shape of the particles used, the nature of the disperse phase, and the nature of the ion-forming groups make this suspension a good model of an emulsion. Of course, in this case, due to the solid nature of the dispersed phase, coalescence, which is typical of true emulsions, does not occur on coagulation. In their investigation, Schenkel and Kitchener determined the conditions which control the stability, slow aggregation, and rapid aggregation of this model suspension in solutions of KNO_3, $CaCl_2$, and $LaCl_3$ at various concentrations. The authors determined these states of the suspension from their sedimentation velocity and the volume and nature of the precipitate formed. The values of the zeta-potential of the particles of the disperse phase in the corresponding solutions were also determined by microelectrophoresis. Taking into account the fact that, for the given system, the ψ_0-potential is approximately equal to the ζ-potential, Schenkel and Kitchener calculated, making all necessary corrections, the energy of repulsion of the electrical double layers and the van der Waal's attraction between the particles, and constructed the corresponding potential curves. These permitted a quantitative check on the applicability of the physical theory of coagulation to the given case. We shall not enter into the experimental details of this thorough investigation but will consider only the fundamental conclusions that follow from it.

The action of electrolytes on the model suspension proved remarkably similar to the action of electrolytes on typical colloidal systems. The transition from a stable suspension to the conditions of slow, and then rapid, aggregation had an identical character. In both cases, the valency of the counter-ion had a typically powerful influence on the system. However, the potential energy curves found showed that the particles of the suspension repelled one another extremely strongly if they approached to a distance of about 100 Å. For example, the repulsion energy of particles at this distance in KNO_3 solution with a concentration corresponding to the beginning of flocculation must amount to at least 1.2×10^{-10} erg. Since the mean energy of the Brownian motion of the particles kT is approximately 4×10^{-14} erg, the energy barrier preventing contact of the particles is at least 3000 kT under these conditions. Consequently, aggregation, corresponding to the first minimum of the potential curve, is completely excluded in this case.

According to the physical theory of the stability of lyophobic colloids, when an energy barrier exists between two colloid particles, a small secondary minimum must also exist in the potential curve, corresponding to greater separations. This follows from the fact that the energy of the van der Waals attraction falls with the distance according to a power law, while the energy of electrostatic repulsion diminishes exponentially. For typical colloid systems, the minimum is very shallow compared with kT, except for systems containing rod-shaped or lamellar particles capable of forming tactoids and thixotropic gels. However, Verwey and Overbeek specially noted the possibility of aggregation corresponding to a second minimum in the potential curve for coarse dispersions.

The second minimum generally lies at a distance of the order of 1000–2000 Å on the potential curve. Fig. 1 shows the potential curves for different cases calculated according to the theory. Curve *a* represents the variation of the attractive energy alone; curve *b* characterises the resulting potential energy at the critical concentration; and curves *c* and *d* represent the resulting curves corresponding to the upper limit of the range of stability and lower limit of the range of rapid coagulation.

The theoretical curves enable the experimental observations to be explained extremely satisfactorily. In all regions of stability, repulsion continues to act at distances of up to 2000 Å and the secondary minimum is too low ($< 1\ kT$) to cause the combination of two particles into a single aggregate. At the critical concentration, the minimum becomes deeper and attains 4 kT, which is sufficient for the combination of two particles. Under these conditions, of course, there is always the possibility of the addition of a third approaching particle to the aggregate. On the other hand, dissociation of the particles, forming a pair, may also take place. This is due to the slow rate of aggregation in this region of electrolyte concentrations. Finally, at higher concentrations of KNO_3, there is a deep potential trough ($V \simeq -40\ kT$ at 240 Å) from which the particles cannot escape by using the energy of the thermal motion alone.

Schenkel and Kitchener put forward two qualitative observations in defence of this interpretation. In the first place, when particles which are not too coarse settle on a glass plate in 10^{-3} N KNO_3 solution, they keep up the Brownian motion. This indicates that the particles are not in direct contact with the glass. In a 10^{-2} N solution, the Brownian motion is no longer observed, providing a direct indication of a decrease in the distance between the particles and the glass. In the second place, a microscopic investigation of the suspension has shown that the precipitates, whether in the aggregated or non-aggregated state, can be redispersed by simple stirring. This indicates that the particles in the precipitate do not adhere firmly to one another.

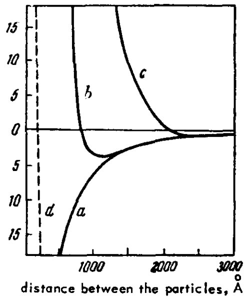

Fig. 1. Potential curves for different cases of the destabilisation of a polystyrene suspension[31].

From all that has been said, the conclusion must be drawn that the stability and aggregation of the model suspensions of polystyrene in KNO_3 solution is quite well explained by the theory based on the presence of a second minimum in the potential curve.

For experiments with $CaCl_2$ and $LaCl_3$ solutions, the region of critical concentration corresponds to lower electrolyte concentrations than those calculated theoretically. The authors explain this discrepancy by the complications arising on using polyvalent counter-ions for destabilising the system.

Stability of emulsions as a consequence of the structural and mechanical properties of the adsorbed layer. This theory of the stability of emulsions arises as a consequence of the viewpoint that highly stable colloidal and microheterogeneous systems can exist in a liquid medium only when the surface of the particles carries an adsorption–solvation layer possessing structural viscosity at low velocity gradients and forming a structural and mechanical barrier[34-36]. According to this theory, such layers must consist of adsorbed layers of orientated surface-active molecules which are almost saturated and form two-dimensional crystal-like structures. However, according to this theory, a particularly strong stabilising action is possessed by adsorbed colloidal layers which consist of peculiar jelly-lyogels which are strongly solvated by the dispersion medium and pass diffusely into the intermicellar liquid. Substances capable of forming such layers in hydrosols include proteins, alkali-metal soaps, and some other substances with sufficiently large organic ions.

According to Rebinder[37], the stabilising properties of structurally viscous (gel-like) absorbed layers in collisions between particles of the disperse phase is explained by the fact that the highly viscous layer between the particles cannot be squeezed out during the collision. Rebinder[38] considers that the structural and mechanical factor is the most powerful stabilising factor and has universal importance, and that its use is essential to obtain highly stable particularly concentrated disperse systems (for example, technical foams, emulsions, and suspensions).

It must be said that no direct and irrefutable proofs of the applicability of this theory to the explanation of emulsions stabilised by soaps have been given until recent times. Indications of the possibility of forming sufficiently strong, most frequently polymolecular, films of soap round the globules of an emulsion exist in many old papers of foreign workers[39-43]. However, all these lack a sufficiently conclusive experimental basis. Of Russian workers, Bromberg[44] has attempted to show the possibility of forming polymolecular layers of soap round the globules of emulsions of limiting concentrations†. However, Kremnev and Soskin[25] have pointed out a series of fundamental errors in Bromberg's calculations which make his results of doubtful validity.

The explanation of the stability of emulsions as due to the presence of a strong mechanical adsorbed layer round the globules encounters a series of insurmountable difficulties. First of all, it is now firmly established that the

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† In ordinary, not too highly concentrated, emulsions, according to Bromberg, there are protective films of soap molecules which are monomolecular and have a packing density corresponding to the condensed state.

globules of emulsions stabilised with soap are covered with a layer of the emulsifier, which is generally far from saturated. Fischer and Harkins[45] were apparently the first to establish this fact. Zwicker[46] gives data from which it follows that the surface of synthetic latex globules stabilised by soaps is only 40–60% covered by the stabiliser. Maron, Elder, and Ulewitch[47], and also Voyutskii and Panich[48], who studied the adsorption of the stabiliser on synthetic latex globules, came to the same conclusion. The non-saturation of the adsorbed layers on the surface of the latex globules is shown both by the calculated area per soap molecule under these conditions, and experimentally: generally a considerable amount of soap must be added to the latex before it appears in the non-adsorbed state, as can readily be determined by the change in surface tension of the system[49].

Particularly convincing data on the incomplete coverage of globules of emulsions by soap molecules are given in the numerous and extremely thorough investigations of Kremnev and his coworkers. In his 1946 paper[24] it was shown that the area occupied by a molecule of sodium oleate on the surface of a benzene globule in an emulsion in water of limiting concentration is ~ 100 Å^2‡ (as a matter of fact, the areas for one molecule of stabiliser given in the papers of Kremnev *et al.* must probably be increased still further, since they were calculated from the assumption that all the soap present in the system is adsorbed). Since this figure considerably exceeds the cross-sectional area of the carboxyl group, Kremnev quite correctly considers that highly rarefied gaseous layers of molecules of the stabiliser are present on the surface of the globules of emulsions. In the 1948 investigations[17], which were carried out with the oleates of various alkali metals, Kremnev and Kagan came to the conclusion that "the stabilising capacity of an adsorbed layer is not connected with the packing density and degree of rarefaction in it". The only exceptions are extremely rarefied coatings which no longer possess stabilising properties. In the same paper, as an example, the authors indicated that stable emulsions stabilised with an oleate can be obtained even when a molecule of the stabiliser on the surface of a globule corresponds to an area of 258 Å^2. In a more recent investigation (1951) Kremnev and Kuibina[50], on the basis of a large amount of experimental material, came to the conclusion that the stabilisation of emulsions by non-saturated layers of stabiliser (triethanolamine oleate or stearate) is not subject to any doubt. Finally, in a paper of 1958 on the interpretation of his experiments, Kremnev[51] again departs from the position that the stabilisation of the emulsions is brought about by adsorbed monolayers of soap. Only in one paper does Kremnev[52] consider that he has established the presence of a polymolecular layer of soap on the droplets of an emulsion of the oil–water type. However, this case relates to the system obtained by emulsifying molten paraffin wax in a hot soap solution. There is every reason to consider that dissolution of the emulsifier in the molten disperse phase takes place at elevated temperatures. As a result of this, the concentration of soap in the dispersion medium will be greatly reduced in comparison with the concentration of soap in the initial aqueous solution, which was used by Kremnev in his calculations of the thickness of the adsorbed layer. It is clear that all this makes Kremnev's conclusions concerning the polymolecularity of the adsorbed layer in the case of the paraffin-wax emulsion extremely doubtful.

As we shall see below, Kremnev has established that, in the case of inverse emulsions and emulsions obtained with the use of a non-ionic stabiliser, the stabilising adsorbed layer is extremely far from saturation.

Further, according to generally accepted opinion[53], amphipathic molecules are arranged at an oil–water boundary in such a way that the polar or ion-forming groups are turned into the water and the hydrocarbon radicals are immersed in the droplets of the emulsion. As Kremnev and Kuibina[50] correctly remark, it is hardly possible to imagine that, in unsaturated layer, amphipathic molecules lie flat or at an acute angle to the surface, as is the case at a liquid–gas interface. In other words, the hydrocarbon radicals of the molecules present at the phase-separation boundary must be dissolved in the hydrocarbon phase. Then, thanks to the solvation of the non-polar portions of the soap molecules by the hydrocarbon of the disperse phase, the interaction between the molecules of the emulsifier must be a minimum, in contrast to the case where the soap is present at a solution–air boundary. Attention has also been drawn to this fact by Harkins[54] and subsequently by Adam[55] and by Blakey and Lawrence[56].

Taubman and coworkers[57,58] have shown quite conclusively that the soap is present in the form of a two-dimensional gas at the surface of separation of two liquid phases, irrespective of the length of its hydrocarbon chain.

On the basis of the incompleteness of the stabilising layer on the surface of the globules of an emulsion, the orientation of the amphipathic molecules at the oil–water boundary, and the gaseous nature of the two-dimensional adsorbed layer, it is very difficult to imagine the existence on the surface of the droplets of a gel-like film of emulsifier, possessing mechanical strength and responsible for the stability of emulsions to aggregations. It was just these considerations that led Langmuir, and also Harkins[53], to renounce the ideal of the interphase layer in emulsions stabilised with soaps as a strong polymolecular film and forced them to consider it as a monomolecular layer of orientated amphipathic molecules attaining continuity only under limiting conditions. These recent ideas exclude, it seems to us, the possibility of explaining the stability of emulsions by the concept of a structural and mechanical barrier. In spite of this, a number of workers adhere to this explanation.

It is particularly remarkable that Kremnev, having done so much to establish the unsaturated nature of the adsorbed layer coating the globules of emulsions, speaks in some of his papers[50,59] of "the gel-like state" of the adsorbed layers, and of "the gelatinisation of the stabiliser concentrated on the droplets (through positive adsorption) with the formation of a two-dimensional gel", and so on. His statements that the stability of an emulsion may also be promoted by a layer of a certain thickness formed under the surface of the globule from the hydrocarbon radicals of the molecules of stabiliser dissolved in it is also completely incomprehensible. In the first place, such layers cannot possess any appreciable structural and mechanical properties on account of their rarefaction and the solvation of the hydrocarbon radicals. In the second place, if such layers, located under the surface of the globule, did possess a certain strength, this could not prevent coagulation, just as the high mechanical properties of the disperse phase of typical lyophobic colloid systems with solid particles cannot prevent coagulation.

Very recently, Orr and Breitman[60], using synthetic

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‡ The Russian text gives Å as the unit of area throughout. This is given as Å^2 here (Ed. of Translation).

latices with disperse phases of different natures stabilised with various cation-active soaps, have also shown that the area covered by the stabiliser is between 44 and 70% of the total surface of the latex globules. Also, Orr's opinion that part of the surface of the globules may remain uncovered with stabiliser in the presence of excess soap[61] is extremely interesting. More recently, he has explained this by the fact that, when a stabiliser is added to a latex, the critical micelle-formation concentration is always reached before a saturated monomolecular layer of the stabiliser is formed on the surface of the globules. After the critical micelle-formation concentration has been reached in the aqueous phase, the further addition of stabiliser can lead only to an increase in the number of micelles formed and not to an increase in the amount of molecularly dissolved soap, with which the soap adsorbed on the surface is in equilibrium. According to Orr, the critical micelle-formation concentration always corresponds to the maximum stability of latices. Besides, the correctness of this position had been shown earlier for emulsions by Cockbain and McMullen[62]. It is very important that Orr came to such conclusions on the basis of experiments with latices having disperse phases of very diverse nature. This indicates the possibility of applying the ideas which he has developed to all emulsions of the oil-in-water type also.

A number of other arguments can be brought against the explanation of the stabilisation of emulsions by the formation of adsorbed layers possessing definite structural and mechanical properties on the surface of the globules.

Firstly, in contrast to previous investigations, the accurate measurements of Blakey and Lawrence[56] and a number of other workers[63,64] carried out in very recent years have shown that even saturated layers of surface-active substances (with the exception, perhaps, of saponin) on a hydrocarbon–water interphase exhibit no plasticity and, generally, no increased viscosity. This agrees completely with all that has been said above on the rarefied nature of the adsorbed interphase layers and on the solvation of their molecules. Moreover, if an adsorbed layer with definite structural and mechanical properties is present at the interphase surface, this viscosity should certainly have been detected.

Secondly, if the molecules of the emulsifier formed a strong gel-like film on the globules through the energetic interaction or mechanical interlacing of their hydrocarbon chains, the stability of the emulsions should increase with an increase in the length of these chains. However, Kremnev and Kuibina[65], using normal emulsions obtained with salts of triethanolamine and various fatty acids, showed that the emulsifying power of these stabilisers and the stability of the emulsions obtained increased with an increase in the length of the fatty acid chain only up to 12 carbon atoms (which corresponds to triethanolamine laurate). On further increasing the length of the hydrocarbon radical of the molecule of the stabiliser, its emulsifying power and the stability of the emulsions remained unchanged or even decreased slightly. Similarly, Levi and Smirnov[66] found that the optimum emulsifying power was possessed by salts of alkenylsuccinic acids containing from 10 to 16 carbon atoms in the chain or salts of alkylphosphinic acids with 7–9 carbon atoms in the alkyl radical. A decrease or an increase in the length of the hydrocarbon chains led to a reduction in, or the complete loss of, their emulsifying action.

This relationship is, of course, an argument against the explanation of the stability of emulsions by the formation of a strong adsorbed layer on the surface of the globules, since the mechanical properties of this layer should increase extremely sharply at longer chain lengths, when the interaction between the hydrocarbon radicals increases and the possibility of forming a strong two-dimensional gel becomes greater.

On the other hand, such a relationship is very readily comprehensible if it is assumed that the stability of emulsions depends on the action of the electrical double layer. The rise in the emulsifying power of the emulsifier and the stability of the emulsions observed with an increase in the length of the hydrocarbon chain up to a definite limit is naturally explained in this case by a reduction in the solubility of the emulsifier and, hence, an increase in its adsorbability. As Donnan[26] has shown, an appreciable absorption of soap at an aqueous solution–paraffin oil boundary commences with sodium caprylate and rises sharply on passing to the laurate. The diminution in the stability of the emulsion after the hydrocarbon part of the molecule of soap has reached its optimum dimensions can readily be explained by the increase in the solubility of the soap in the hydrocarbon phase and the decrease in the electrical charge on the surface of the globule.

Thirdly, as experiment has shown, stable emulsions can be obtained using emulsifiers known to be incapable of giving mechanically strong adsorbed films. Here are included the crystalline nekals (alkali metal salts of alkylnaphthalene sulphonic acids), triethanolamine, and other quite widely-used stabilisers.

Fourthly and finally, the effect of electrolytes on emulsions stabilised with soaps also conflicts with the idea of a mechanical protective action of the adsorbed layers. If a gel-like layer is present on the surface of the globules, the addition of electrolytes which usually favour gel-formation, should increase the thickness and density of the surface film and thereby increase the stability of the emulsion. In actual fact, the addition of electrolytes leads to the coagulation of the emulsion; this coagulation, as we have seen, generally follows the Schultze–Hardy rule.

It has been shown in a number of papers that it is possible to increase the stability of concentrated emulsions to aggregation by imparting thixotropic structural properties to the dispersion medium[67–70]. For example, Kremnev[70] observed a marked increase in the stability of benzene emulsions whose aqueous phase contained cetyl alcohol in addition to sodium oleate. However, it would be incorrect to suppose that this phenomenon has anything in common with the effect of a structural and mechanical factor in the sense in which this is understood in the explanation of the stability of emulsions. In the investigations cited, the stability of the emulsions was determined by the transition of the whole system to the state of a thixotropic gel and not by the formation of a gel-like adsorbed layer on the surface of the globules changing diffusely to the dispersion medium. This point of view is confirmed both by the increase in the sedimentation stability of such emulsions and by the fact that measurement of the area occupied by a molecule of the emulsifier on the surface of the globule under these conditions, as Kremnev himself indicates, does not leave any doubt of the monomolecularity and even considerable incompleteness of the adsorbed layers.

II. STABILITY OF INVERSE EMULSIONS

Long ago the opinion was already widespread that emulsions of the water-in-oil type can be stabilised only by the strength of an interphase film. The existence of an electrical double layer on the surface of the globules was not considered, since the hydrocarbon phase possesses a low dielectric constant and therefore prevents ionisation[71,72].

However, the idea of the presence of a strong adsorbed film on the surface of the globules of inverse emulsions was shaken by a study of the properties of this layer. Kremnev and Kuibina[50], using water-in-benzene emulsions obtained with triethanolamine oleate as the emulsifier, showed that inverse emulsions are also stabilised by a highly unsaturated adsorbed layer. These authors also consider that the degree of rarefaction of the adsorbed layer is even far higher in inverse emulsions than in normal emulsions. According to their results, the area occupied by a molecule of triethanolamine oleate on the surface of the benzene droplets is from 130 to 210 Å^2, depending on the concentration of the stabiliser. Kremnev and Kuibina[65] came to the same conclusions in another investigation in which they prepared emulsions of water in benzene by stabilising them with alkali-metal oleates in the presence of electrolytes.

On the other hand, Fuoss and Krauss[73] showed that slight polarisation may take place even in non-polar oils. Salts of polyvalent metals and organic acids generally exhibit a degree of ionisation of the order of 10^{-8} in hydrocarbon media. Consequently, for a solution of such a salt in benzene with a concentration in the mM range, the ionic concentration will have a value of the order of 10^{-10} N. Under such conditions, the electrical double layer will, of course, be very diffuse — calculations indicate that the value of $1/\kappa$ must be a few microns. Hence, as Koelmans and Overbeek[74] indicate, the capacity of the double layer in such a non-polar liquid is extremely small and a very small charge is necessary to cause the presence of a considerable surface potential.

Koelmans and Overbeek carried out an analysis of whether the free energy of the electrical double layer in a hydrocarbon medium can provide the potential barrier of about 15 kT required, according to Verwey and Overbeek[75] to impart stability to the system. They assumed that, at low ionic concentrations, the change in the repulsive energy with distance can be represented approximately by Coulomb's law and that — in contrast to hydrosols, where, as a result of the screening effect of the counter-ions, the fall in the repulsive energy takes place far more abruptly — the repulsive potential falls relatively slowly with the distance in hydrocarbon media. Combining the energies of electrostatic repulsion and van der Waals attraction by Hamaker's method, they obtained a potential curve having a maximum, $v_{\max}$. The height of this maximum was not very sensitive to changes in the van der Waals constant a used in the calculation. This explained the comparatively slow decrease in the repulsive energy with distance. The values for $v_{\max}$ calculated for $a = 10^{-12}$ erg and expressed in units of kT at room temperature (4×10^{-14} erg) are given in Table 3.

TABLE 3. Maximum repulsion as a function of the dimensions of the particles r and the surface potential ζ.

ξ, mV	$\frac{v_{\max}}{kT}$		
	$r = 10^{-4}$ cm	$r = 10^{-5}$ cm	$r = 10^{-6}$ cm
25	13	—	—
35	26	1	—
50	62	4	—
75	152	11	—
100	256	20	1
150	662	54	4

In spite of the low ζ-potentials, systems with a hydrocarbon medium and with particles with a size of 1 μ and above may be stabilised as a result of the action of the electrical double layer. This may be ascribed to the fact that repulsion begins to play its role at distances where attraction is quite inappreciable. At the same time, the low value of the repulsive energy characteristic of particles with $r < 10^{-6}$ cm completely excludes the possibility of stabilising highly dispersed oleosols using an electrical double layer.

Van der Minne and Hermanie[75], studying the electrophoresis of suspensions in benzene, found a good correlation between the stability and the results of electrophoretic measurements, and showed by direct experiments that stabilisation of suspensions in hydrocarbons can be explained by the presence of an electrical double layer on the surface of the particles.

Quite recently this question was again subjected to detailed investigation by Albers and Overbeek[11]. Experiments with emulsions of water in benzene, stabilised with oleates and sulphonaphthenates of various multivalent metals, which are capable of ionising in a hydrocarbon medium, showed that, in such emulsions, there was no correlation between stability and flocculation, on the one hand, and the ζ-potential of the drops of water in benzene, on the other hand. Although the energy barrier for emulsions with particles having a radius greater than 1 μ and a ζ-potential greater than 25 mV is calculated to be higher than 15 kT, this barrier is not capable of preventing the separation of the system into the dispersion medium and a cream, and does not exclude subsequent flocculation and coalescence of the globules. Thus, the observations made in this work appear to contradict the work of Koelmans and Overbeek[74] cited. Albers and Overbeek explain this contradiction by the fact that the case developed by Koelmans and Overbeek[74] is true for extremely dilute suspensions and emulsions, but is inapplicable to the more concentrated emulsion with which they worked and, in any case, to a layer of cream. In both the latter cases, the attractive forces between the droplets of water causing them to draw together are so high that when the globules approach one another, the highly mobile solvated negative ions on their surface are readily pushed apart, thus permitting coalescence.

Albers and Overbeek did not only find that a rise in the ζ-potential of the globules does not increase the stability to aggregation of emulsions of the water-in-oil type, but they even found a clear inverse correlation between the ζ-potential and the coalescence. They explained the existence of this relationship as follows. The molecules of soap, on their adsorption on the interphase surface, are naturally orientated in such a way that their non-polar part is in the benzene and the ion-forming head is turned into the aqueous phase. Under these conditions, partial hydrolysis takes place, the degree of this hydrolysis depending on the nature of the soap. The hydrolysis products (being insoluble in water and in benzene) accumulate at the interphase boundary in the form of fine particles. Thanks to their generally hydrocarbon character, they are more readily wetted by benzene than by water and therefore their greater part is located in the external hydrocarbon medium, thereby stabilising the water-in-oil emulsion by purely mechanical means (for the stabilisation of the emulsions by protective layers of granules, see below). The greater the degree of hydrolysis which has taken place the lower, naturally, the ζ-potential at the interphase boundary. Hence the inverse correlation between the magnitude of the ζ-potential and the stability of the emulsion found in Albers and Overbeek's investigation is comprehensible.

In their next paper, Albers and Overbeek[11] made a detailed investigation of the reason why the presence of a fairly high energy barrier (greater than 15 kT) of electrostatic origin round the droplets of water-in-oil emulsions did not prevent the flocculation of these systems. The authors showed that, in consequence of the long-range action of the electrical forces in systems with an external hydrocarbon medium, it was necessary to omit the repulsive force between only two adjacent particles from the calculations. The behaviour of water-in-oil type emulsions can be understood only by taking the interaction between a large number of particles into consideration. Albers and Overbeek formulated their discussion in the following way. In a system in which the continuous phase is water, the thickness of the electrical double layer is only $\sim 10^{-3}$–$10^{-2}\,\mu$, so that electrostatic interactions can be observed only at extremely small distances between the particles. The potential energy of charged particles at particle separations greater than $10^{-2}\,\mu$ is thus practically zero.

The case is different in a system with a continuous hydrocarbon phase. In this case, the thickness of the electrical double layer is generally several microns. This thickness is of the same order as the distance between the globules in a moderately concentrated emulsion. Therefore, the globules of such emulsions already possess a certain amount of potential energy in comparison with that which they would have if they were at an infinitely great distance from one another. Consequently, the energy barrier is reduced in this case and the stability with respect to flocculation must also be reduced. This effect was shown earlier by Verwey[77].

A further reduction of the energy barrier in a system with an external hydrocarbon phase takes place in consequence of the combination interaction of more than two particles, as can be seen from Fig. 2, which shows the reduction in the energy barrier for particle *2* under the influence of two neighbouring particles — *1* and *3*. The broken lines represent the change in the energy of interaction with the distance between particles *1* and *2* in the absence of particle *3* and between particles *3* and *2* in the absence of particle *1*. The symbol E_1 denotes the energy barrier which must be overcome for particle *2* to approach particle *1* from infinity. This barrier diminishes to E_2 if particle *2* begins its movement from the position shown. It is reduced still more, to E_3, if its interaction with particle *3* is taken into consideration. The continuous line in the figure represents the resulting potential curve.

Since in systems with an external hydrocarbon phase, as previously mentioned, each globule of the water-in-oil type emulsion possesses a greater potential energy than if it were present at an infinitely great distance from the other particles, the flocculation of a certain number of globules to the bottom of the vessel causes the remaining globules to act like a compressed spring accelerating their movement downwards. Further, according to the authors, each globule tends to move downwards under the influence of the cumulative weight of all the globules present above it.

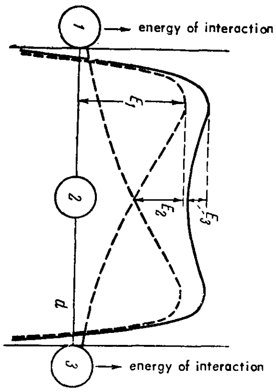


Fig. 2. Sketch explaining the decrease in the energy barrier between the particles of an emulsion of the water-in-oil type[11].

Thus, the sedimentation rate of a charged globule under these conditions will be some orders of magnitude higher than the rate of settling of a globule under the action of its own weight. Consequently, extremely rapid flocculation takes place and lasts until the concentration of the disperse phase above the precipitate is very low, that is, until the distance between the globules is greater than the thickness of the electrical double layer.

To confirm the correctness of their considerations, Albers and Overbeek carried out extremely thorough calculations and pointed out that a flocculated state is characteristic of water-in-oil type emulsions, or, as Pink[72] formulated it, the difference between emulsions of the normal and inverse types consists in the more rapid formation of creams in emulsions of the water-in-oil type.

As a result of all that has been said above, a number of investigators now adhere to the opinion that the stability of inverse emulsions may be due to the presence of an electrical double layer on the surface of the globules. However, it is still difficult to resolve finally whether inverse emulsions can be stabilised by electrostatic forces, since far fewer data have been accumulated for these systems than for oil-in-water emulsions.

In conclusion, we must dwell upon two further possible causes for the stability of inverse emulsions.

The first possibility consists in the adsorption on the surface of the water droplets of fairly long and flexible hydrocarbon chains, possessing polar end groups, dissolved in the external non-polar phase of the emulsion and capable of performing a micro-Brownian motion[74,79]. In this case, the stability is obviously determined by the thermal motion and the mutual repulsion of the hydrocarbon radicals having only one end attached to the globules of the emulsion, that is, with a factor having the character purely of entropy[9].

Repulsion in consequence of thermal motion of chains adsorbed in this way can, of course, only be observed where chains which are connected to two neighbouring particles interact. This means that van der Waals attraction will take place only at distances greater than twice the

TABLE 4. Van der Waal's attraction between spheres at a distance of 40 Å from one surface to the other.

a	$\frac{v_{\min}}{kT}$		
	$r=10^{-4}$ cm	$r=10^{-5}$ cm	$r=10^{-6}$ cm
10^{-12}	510.0	42.0	1.2
10^{-13}	51.0	4.2	0.1
10^{-14}	5.1	0.4	0.01

length of the chain of the stabiliser. Table 4 gives the values of the minimum total interaction $v_{\min}$ calculated by Koelmans and Overbeek[74] for the conditions of an inter-particle distance of 40 Å and various values of r and a. Since there is no reason to consider that the van der Waals constant in xylene differs appreciably from the constant in water ($a = 10^{-12}$), the values given in Table 4 show that the adsorbed chains cannot prevent coagulation if the length of the stabiliser molecule is not commensurate with the size of the particles.

In agreement with the considerations expressed, experiments have shown that suspensions with large particles and non-ionic stabilisers are never stable. The weak stabilisation observed increased with an increase in the length of the chain. The longer chains obviously keep the particles at greater distances and thus make the potential trough shallower. However, these results do not contradict the possibility of stabilising emulsions having a low degree of dispersion using the entropy factor by adding stabilisers with sufficiently long molecules (for example, high-molecular-weight stabilisers) to them.

The second possible cause of the stability of inverse emulsions consists in stabilising the droplets of water with a protective layer of granules formed from insoluble alkaline-earth metal soaps [11,50,80] or of the product of their hydrolysis [11]. In this case, the mechanism of stabilisation is completely analogous to the mechanism of the stabilisation of emulsions using powder emulsifiers.

III. STABILISATION OF EMULSIONS BY SUBSTANCES OTHER THAN SOAPS

Experimental data on the stability of emulsions stabilised by substances not having the nature of soaps are extremely sparse. The information given on this question in recent monographs devoted to emulsions is completely inadequate for the causes of the stability of these emulsions to aggregation to be deduced. Only in the last few years has there been a series of investigations enabling some conclusions to be drawn in this respect.

Let us turn first of all to investigations on emulsions stabilised by the so-called protective colloids. Kremnev and Soskin[25], who studied gelatine-stabilised emulsions of benzene-in-water of limiting concentration, showed that the thickness δ of the critical layer was ~ 800 Å in this case, *i.e.* eight times greater than the thickness of the corresponding layer when sodium oleate was used as the stabiliser. However, if the thickness of the adsorbed layer of gelatine in the dry state is calculated and the minimum thickness of a monolayer of gelatine is taken as 7–9 Å,[81-83] it is found that emulsions of limiting concentration are stabilised by extremely unsaturated gelatine films (δ_{gel} amounts to only 2.7–5.2 Å).

Kremnev and Soskin's conclusion that the adsorbed layer of protein at an oil–water interphase surface is not polymolecular was confirmed by Cockbain[84]. Cockbain investigated the distribution of blood albumin and sodium dodecyl sulphate between the interphase surface and the aqueous phase of an emulsion of n-decane; he showed that, in the absence of dodecyl sulphate the adsorbed layer of albumin was monomolecular. In the presence of dodecyl sulphate, its complex with the albumin was formed at the interphase surface and in the aqueous phase.

Saunders and Saunders[85], studying the action of methylcellulose on dilute latices, also observed that stabilisation of the system took place when the globules were covered with a monomolecular layer of the protective colloid. In the latter case, the system is far less sensitive to small additions of electrolytes.

Addition to dilute latices of amounts of methylcellulose insufficient to form a monomolecular layer, on the other hand, caused sensitisation of the system — reduction of the ζ-potential, the formation of aggregates, and a fall in the stability to electrolytes.

When considerable amounts of ionic emulsifying agents were present in the latices, the protective action of methylcellulose began at lower concentrations. When the interphase surface was completely covered by the emulsifier, the methylcellulose was not adsorbed and the stability of the latex was then, in the opinion of the authors, entirely determined by the electrical double layer due to the adsorbed emulsifier.

Nielsen *et al.*[86] investigated the influence of various protective colloids on the interphase viscosity at a water–styrene boundary and determined the stability of the hydrocarbon droplets to coalescence at this boundary. The experiments showed that the presence of protective colloids increases the life of the droplets to the greatest extent under conditions corresponding to a low solubility of a high-molecular-weight stabiliser. This was also shown in experiments with poly-(methacrylic acid) and its salts. The lower the pH of the solution, the lower was the solubility of the polymer and the greater the life of the droplets. Stabilisation by gelatine may serve as another example. Gelatine exhibited the greatest stabilising action at the isoelectric point. This is probably due to the increased adsorbability of the protective colloid under conditions where it is sparingly soluble.

As far as the results of viscosity measurements are concerned, an appreciable interphase viscosity was shown only by a solution of poly-(methacrylic acid) at low pH values. In the other cases, the interphase viscosity was small or completely absent. Very frequently, an increased interphase viscosity corresponded to a longer life of the droplets and, consequently, to better stabilisation. However, cases were also observed in which interphase viscosity was completely absent and the droplets possessed high stability to coalescence. In his paper, Nielson gives no indication of the nature of the adsorbed layer in the cases investigated, *i.e.* whether it was monomolecular or polymolecular.

For inverse emulsions of water in toluene stabilised with ethylcellulose, Kremnev and Shadrin[87], using a method of calculation similar to that used earlier[25], established that the adsorbed layer of emulsifier was not monomolecular but consisted of several layers of polymer molecules. However, this conclusion cannot be used as a confirmation that the stability of these emulsions is determined by a structural and mechanical factor. In view of what has been said on the stability of inverse emulsions, it is unlikely that the stability of systems containing protective colloids is determined by the entropy factor[9].

Here it is convenient to mention that, in connection with the action of the entropy factor, it is pointless to speak of the polymolecularity of the adsorbed layer and to establish its thickness from the amount of emulsifier adsorbed by unit interphase surface and the diameter of the molecular chain for, as Simha, Eirich, and Frisch have shown in a series of papers[88-92], chain molecules are generally adsorbed on the surface at one or more points, while the greater part of the chain continues to be in the dispersion medium and is capable of performing micro-Brownian motion.

It is interesting that similar views on the causes of the stability of gelatine-stabilised emulsions to aggregation were developed by Bromberg[93] as early as 1946. According to Bromberg, adsorbed films cannot possess a high mechanical strength even if the specific orientating influence of the boundary is taken into consideration and, therefore, the stability of emulsions cannot be determined by the structural and mechanical properties of the adsorbed layers. On the other hand, according to Bromberg, attempts to reduce the protective effect to the presence of diffuse hydrate layers are also unsatisfactory. Bromberg considers that the sole cause of the stability of emulsions in the presence of protective colloids is the osmotic swelling forces of the intermediate gel-like layers of gelatine. It is just these forces which prevent the free escape of water, and consequently, the approach of particles of the disperse phase to one another.

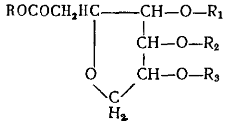
However, in the case of normal emulsions stabilised with protective colloids having molecules containing ion-forming groups, it can be fully admitted that the emulsions are stabilised by the formation of an electrical double layer on the surface of the globules as a result of the ionisation of these groups.

Recently, there has been a wide use in the production of emulsions of the so-called non-ionic emulsifiers, whose molecules consist of a fairly large hydrocarbon radical with several polar groups, generally hydroxyl groups, located at its end. When such emulsifiers are used, it is not very likely that stabilisation of the emulsions occurs as the result of the formation of an electrical double layer on the surface of the globules.

However, just as in the case of emulsions stabilised by ion-forming substances, there are no grounds for assuming the formation of a strong adsorbed layer or a two-dimensional gel on the interfaces of such emulsions. The stability of oil-in-water type emulsions stabilised with non-ionic substances is most simply explained by the orientation of the amphipathic stabiliser molecules at the interphase boundary in such a way that the hydrocarbon chain of the molecules is dissolved in the oil and the polar hydrated groups project into the water and form a fairly strong hydrate layer round the globule. It may be assumed that, to obtain a hydrate layer sufficient to stabilise an emulsion, the concentration of the polar groups at the hydrocarbon–water surface must be very great. This is indicated by some observations of Levy and Smirnov[66] who showed that monoglycerides acquire emulsifying properties only when a sufficient number of polar hydroxyl groups are present at the end of the chain.

It must be noted that, according to the same observations of Levy and Smirnov, the introduction of one or two ion-forming carboxylic groups into the molecule of a non-ionic stabiliser already containing a relatively large number of hydroxyl groups greatly increases its emulsifying properties. This indicates that ion-forming groups exert a far higher influence on emulsifying action than polar non-ionic groups.

In a recently published paper, Sata and Harisaki[94] investigated the stability of the drops of oil in water and of water in oil in the presence of the stabiliser Emasol, the molecules of which have the structure



where R is a hydrocarbon radical, and R_1, R_2, and R_3 are poly-(ethylene oxide) chains of different lengths. The authors showed that Emasol protects drops of oil in water from coalescence well, but is ineffective for drops of water in oil. They explain these properties of Emasol in the following way.

In the case of droplets of oil in an aqueous medium, the three hydrated poly-(ethylene oxide) chains of each molecule of stabiliser are directed into the aqueous phase forming a strong hydrate layer on the surface of the drops which does not break when the drops come into contact and prevents coalescence. In the case of droplets of water in an oleaginous medium, only the one hydrocarbon radical is directed into the external phase, and the droplets are insufficiently protected and therefore readily coalesce. Unfortunately, it is impossible to deduce from Sata and Harisaki's paper the state of the poly-(ethylene oxide) chains of the stabiliser in the aqueous medium on the surface of the oil droplets, and, in this case, the protective action may be ascribed both to the hydration of the chains and to the fact that they maintain their thermal motion (entropy factor).

In Orr and Breitman's investigations[60,61], which we have touched on above, they made attempts to determine the geometry of the molecules of a non-ionic stabiliser present on the surface of latex globules. The authors worked with non-ionic stabilisers in which the hydrophilic part of the molecule consisted of a single poly-(ethylene oxide) chain. In Orr and Breitman's opinion, at ordinary temperatures the hydrophobic part of the molecule of such a stabiliser is immersed in the particle of latex and the poly-(ethylene oxide) chain is turned into the water and arranged on the surface of the globule like a caterpillar, as is shown in Fig.3. The correctness of this viewpoint is confirmed by the observations of Rosch[95], who considers it quite possible that such a shrinkage of the poly-(ethylene oxide) chain is due to the electrostatic attraction of the dipoles which form the individual links of the chain. Orr and Breitman, using a Fischer–Hirschfelder model, calculated the dimensions of an individual fold of the chain in the non-hydrated state and found that each fold was 16 Å high and contained nine ethylene oxide residues. At higher temperatures, the hydrophilic part of the molecule of the stabiliser straightens out and the stabiliser becomes more oil-soluble, as a result of which its stabilising action

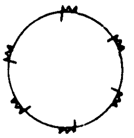


Fig. 3. Configuration of the molecules of a non-ionic stabiliser on the surface of a globule.

in oil-in-water systems falls sharply. The fact that heating aqueous solutions of non-ionic stabilisers leads to their precipitation agrees well with the assumption that dehydration of these stabilisers takes place at elevated temperatures.

The observation of Orr and Breitman that the addition of a non-ionic stabiliser increases the efficacy of ordinary ionic soaps is extremely interesting. These authors explain this by a decrease in the electrostatic repulsion of the soap ions due to the presence of molecules of the non-ionic stabiliser between them in the adsorbed layer and, consequently, a contraction of the area occupied by a soap ion. The observations of Orr and Breitman agree well with the results of a series of well-known investigations by Cockbain in which it was established that the use of mixtures of two stabilisers gives a positive effect only where a mixture of an ionic and a non-ionic stabiliser is used.

A particular case of the stability of emulsions takes place in stabilisation by solid emulsifiers. However, in view of the special mechanism of this stabilisation, this case requires special consideration. We shall mention only that in the case of emulsions of the water-in-oil type, for example, the presence on the surface of the globules of a protective layer, consisting of granules of a relatively hydrophobic solid emulsifier is still insufficient to ensure the stability of the system to aggregation. The globules of such an emulsion should adhere to one another when they collide for the same reasons which cause the unstabilised particles of the hydrophobic powder to adhere in water. Hence, the obvious conclusion that the stability of such emulsions may be due to the mosaic structure of the granules of the solid emulsifier. This ensures, on the one hand, adhesion of the granules to the internal phase and, on the other hand, formation on the surface of the granules turned towards the external phase of a sufficiently strong solvated layer or electrical double layer[3,9].

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AROMATIC HETEROCYCLIC *N*-OXIDES

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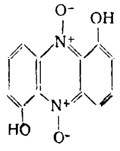
CONTENTS

INTRODUCTION

Heterocyclic *N*-oxides, a class of bipolar ammonium compounds, have been known for a relatively long time. In 1881, in their study of the reduction of the ethyl ester of *o*-nitrocinnamic acid, Friedländer and Ostermaier[1] isolated "oxycarbostyril", of empirical formula $C_9H_9NO_2$. It was not until 1914 that Friedländer established that this compound was carbostyril *N*-oxide[2], the first aromatic heterocyclic *N*-oxide to be synthesised. By the subsequent work of Meisenheimer[3,4] the heterocyclic *N*-oxides became easily obtainable. The interest in the chemistry of these compounds was later revived in an effort to find a method for introducing a substituent into a nitrogen-containing ring. One of such methods was the Chichibabin reaction, another involved quaternary ammonium salts, *e.g.* pyridinium salts. Methods employing *N*-oxides as starting material gave even better results[5]. The interest in heterocyclic *N*-oxides can also be accounted for by the discovery of such structures in certain biologically active natural products. For instance, the antibiotic iodinin[6] was shown by Kiprianov and his collaborators[7,8] to be 1,6-dihydroxyphenazine *N,N*-dioxide (I). Aspergillic acid, also an antibiotic, is a substitued pyrazine *N*-oxide (II).[9]



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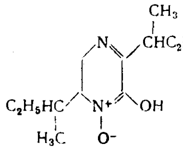


(II)

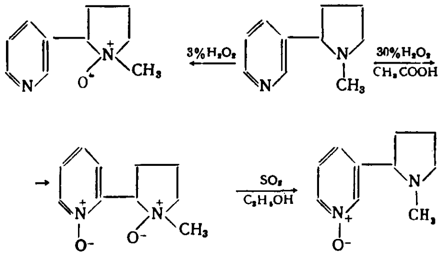
The chemistry of *N*-oxides has been the subject of several reviews. One of these reviews is devoted solely to the work of Japanese research workers[10]. Some have been published in journals that are not readily available[11,12], and others are only partly devoted to aromatic heterocyclic *N*-oxides[13,14]. The review by Katritzky[15], published in 1956, seems to be the best so far, but its author has himself, in the meantime, published over ten communications on the chemistry of *N*-oxides. Although a great deal of work has been done on this subject by Soviet workers, it has so far not been reviewed in Soviet literature. Hence the present review, in which are collected all the references which appeared through 1960. We shall only discuss the properties of the *N*-oxides of aromatic heterocyclic compounds, and not those of aliphatic amines, which have been treated in detail elsewhere[13].

I. METHODS OF PREPARATION OF AROMATIC HETEROCYCLIC *N*-OXIDES

1. Oxidation of Aromatic Heterocyclic Compounds

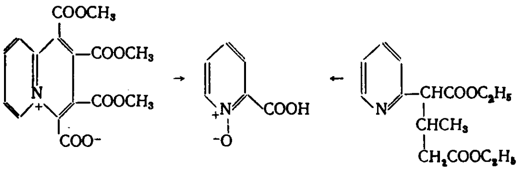
Oxidation of aromatic heterocyclic compounds is the most general method for the preparation of the *N*-oxides derived from them. Aliphatic amines are readily oxidised to *N*-oxides by hydrogen peroxide in neutral solution. Aromatic heterocyclic compounds, on the other hand, can only be oxidised in acid media, using peracids as oxidising agents. Meisenheimer first used a benzene solution of perbenzoic acid[3]. Monopernaphthoic[16,17], performic, and peracetic[18] acids have also been used.

The Japanese work showed that peracetic acid can successfully be replaced by a mixture of hydrogen peroxide and an organic acid, acetic acid being the best[10]. *N*-oxides are also prepared by using inorganic acids, *e.g.* sulphuric or phosphoric, but in that case the yields of the reaction products are very low[18]. However, addition of 0.3% sulphuric acid and 0.1% sodium phosphate to the reaction mixture has a favourable effect[19]. The oxidation of heterocyclic rings containing nitrogen with hydrogen peroxide in glacial acetic acid is described in textbooks[20] and can be used to prepare the *N*-oxides of numerous heterocyclic compounds, including various natural products[13]. The oxidation of natural products such as nicotine, which contain two nitrogen atoms, one in an aromatic, and another in a non-aromatic ring, is particularly interesting. Nicotine forms two monoxides and one dioxide. As shown by Gol'dfarb and Zvorykina[21], and somewhat later by Taylor and Boyer[22], individual nicotine *N*-oxides are best prepared by utilising the different ease of oxidation of aliphatic tertiary amines and heterocyclic nitrogen-containing rings and the different ease of reduction of the isomeric *N*-oxides:



All the *N*-methylanabasine *N*-oxides and aminonicotine *N*-oxides were prepared similarly[23,24].

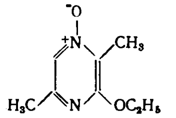
In spite of its universality, the direct oxidation of aromatic heterocyclic compounds containing nitrogen in the ring is occasionally complicated by side-reactions. Firstly, the formation of *N*-oxides may be accompanied by other oxidations. It was recently shown, for instance, that on oxidation, quinaldine and lepidine yield, in addition to *N*-oxides, products of oxidation at carbon atoms, namely 3-hydroxyquinaldine[25] and 3-hydroxy-4-methylcarbostyril[26] respectively. Similarly, the oxidation of quinoxaline and its derivatives yields large amounts of the 2,3-dihydroxy derivatives of quinoxaline[18]. If the compound undergoing oxidation contains readily oxidisable groups, the *N*-oxides of the oxidised compounds are formed. The oxidation of pyridine-2-aldehyde yields the *N*-oxide of picolinic acid[27], while that of the esters of 2- and 4-pyridylacetic acids yields 2- and 4-pyridine carboxylic acid *N*-oxides[28,29]. It should be noted that the oxidation of 3-pyridylacetic acid proceeds normally[29]. The increased mobility of hydrogen atoms in *α*- and *γ*-methylenic groups, discussed below, is clearly responsible for this difference in behaviour. The formation of *N*-oxides is sometimes preceded by oxidative degradation; picolinic acid *N*-oxide is obtained[28,30] by oxidation of compounds (III) and (IV).



(III) (IV)

Some readily oxidisable groups need to be protected before the oxidation is undertaken. For instance, 2-aminopyridine should first be acylated and then oxidised. 2-Aminopyridine *N*-oxide is obtained on saponification[31,32].

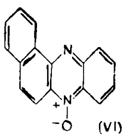
Low yields of *N*-oxides and even the complete failure of the oxidation can sometimes result from steric hindrance. This was the case in the oxidation of *α*- and especially di-*α*-substituted derivatives. For instance, 2,6-diphenylpyridine *N*-oxide can only be obtained in very low yields[33]. Although pyrazine yields its *N,N'*-dioxide on oxidation 2,5-dimethylpyrazine yields, owing to steric hindrance, a mixture of dioxide and monoxide, while 2,5-dimethyl-3-ethoxypyrazine forms the monoxide (V) only[34,35].



(V)

Steric hindrance increases with the size of the substituents. While 2,3-dimethylquinoxaline can be oxidised to the dioxide, its 2-methyl-3-isopropyl analogue only forms the monoxide, and 2,3-diisopropylquinoxaline is unable to form an *N*-oxide[36].

Certain substituents in the peri-position can also cause steric hindrance. 8-Nitroquinoline[37], certain 8-alkoxyquinolines[38], and 2-(4'-methoxyphenyl)- and 2-(4'-chlorophenyl)-8-methylquinolines[39,40] could not be oxidised, while the corresponding 6- and 7-substituted derivatives formed *N*-oxides. Quinoxalines which are 5- and 3-substituted and 1-carboxyphenazine only formed the monoxides[18,41], 5,8-dichloroquinoxaline[18] resisted oxidation, and 1,2-benzophenazine and its derivatives readily formed monoxides (VI) but could be oxidised to dioxides only with difficulty[42,43].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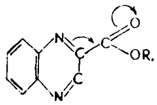
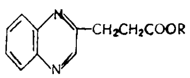


(VII)

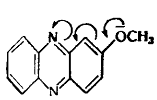


(VIII)

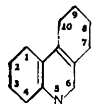
The introduction of a substituent in the nucleus affects the course of oxidation if it causes a change in the electron density of the electron pair carried by the nitrogen atom. Electron-accepting substituents, conjugated with nitrogen, lower the electron density and thereby render oxidation more difficult. The stability to oxidation of the derivatives of *β*-quinoxalinecarboxylic acid (VII) can easily be explained by the drift of the electrons towards the carboxyl group[44,45].

This view is supported because β-quinoxalinepropionic acid (VIII), in which such conjugation is out of the question, undergoes oxidation more readily[46]. The electron density at the nitrogen atom is lowered also by the presence of a nitro- or a cyano-group at position 6 of the quinoxaline 2,6-Pyridine and 2,5-pyridinedicarboxylic acids are so stable to oxidation that they are employed to stabilise peracids. oxidation that they are employed to stabilise peracids. Conversion of acids to their sodium salts lowers the electron-accepting power of the carboxyl group, and the corresponding *N*-oxides can be obtained in 75-80% yield[47].

Electron-donating substituents, on the contrary, increase the electron density at the nitrogen atom, and facilitate the oxidation. The predominant formation of 10-oxide in the oxidation of 2-methoxyphenazine (IX) is caused by the increased electron density at nitrogen atom 10.



(IX)



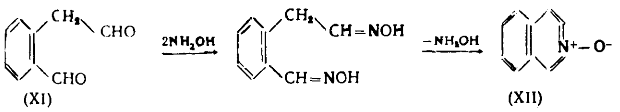
(X)

In the oxidation of 2-methyl- and 2-chloro-phenazine, 5- and 10-oxides are formed in equal amounts, while 1-chlorophenazine yields entirely the 5-*N*-oxide, owing to steric hindrance[48].

Both steric and electronic influences are observed in complex condensed systems containing several substituents. Phenanthridine (X) readily forms the *N*-oxide, as do its 6-methyl- and 6-ethyl-derivatives. The oxidation of 6-phenyl-and 6-nitro-phenthridine is more difficult, and 3,8-dinitro-6-phenylphenanthridine *N*-oxide could not be obtained[49]. It may also be noted that while pyrazine forms a dioxide, pyridazine and pyrimidine can only be oxidised to monoxides[50,51,52]. Purines, consisting of a condensed pyrimidine and iminazole ring, are oxidised by peracetic acid to monoxides derived from the pyrimidine ring[53,54].

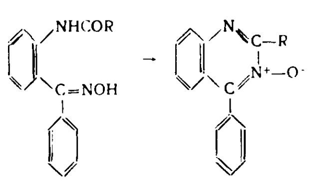
2. Cyclisation of Hydroxylamine Derivatives

The dioximes of 1,5-dicarbonyl compounds can undergo cyclisation with elimination of one molecule of hydroxylamine, to form *N*-oxides. Glutaconic and homophthalic (XI) aldehydes react in this way with hydroxylamine forming pyridine[55] and isoquinoline *N*-oxides (XII)[56].

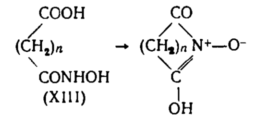


(XI) (XII)

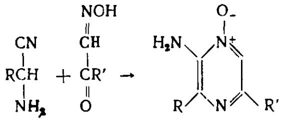
By dehydration of *o*-acylaminobenzophenone oxime the substituted quinazoline 3-oxide is obtained[57].



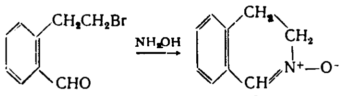
Other hydroxylamine derivatives, for instance those of type (XIII),[58] where n = 2,3, can similarly undergo ring-closure.



In a number of cases the intermediate oxime could not be isolated[59]. The monoximes of α,β-dicarbonyl compounds, themselves incapable of cyclisation, can be condensed with aminonitriles to form 2-aminopyrazine *N*-oxides[60]:

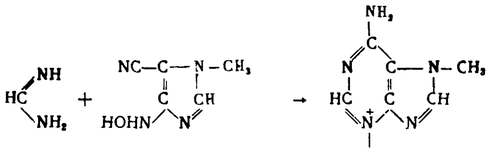


It is noteworthy[61] that the reaction of hydroxylamine with *o*-2-bromoethylbenzaldehyde (XIV) yields dihydroisoquinoline *N*-oxide (XV), resulting from intramolecular alkylation of the intermediate oxime[61].



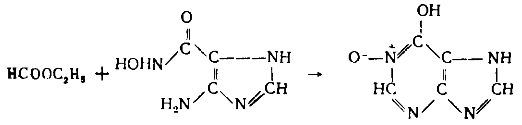
(XIV) (XV)

The individual *N*-oxides of heterocyclic compounds containing several nitrogen atoms in the ring, in particular, purine *N*-oxides, have been obtained by transformations of the hydroxylamine derivatives. The reaction of 1-methyl-4-hydroxylamino-5-cyanoimidazole (XVI) with formamidine acetate yields 92% of 7-methyladenine 3-oxide (XVII)[62].



(XVI) (XVII)

Purine 1-oxides can also be obtained by other methods. The reaction of 4-aminoimidazole-5-hydroxamic acid (XVIII) with ethyl formate results in hypoxanthine 1-oxide (XIX).[63]



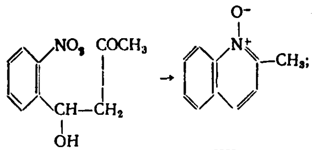
(XVIII) (XIX)

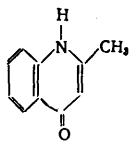
1-Oxides of 2-azapurines are formed from compounds of type (XVIII) on treatment with nitrous acid[64].

3. Reductive Cyclisation of Nitro-Compounds

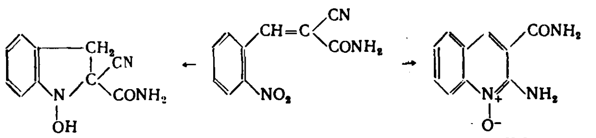
As already mentioned, certain hydroxylamine derivatives form *N*-oxides readily even though the intermediate oxime cannot be isolated. For instance, the hydroxylamine derivatives formed in the reduction of aromatic nitro-compounds containing various carbonyl functions in the *ortho*-position undergo ring closure forming aromatic heterocyclic *N*-oxides. This was in fact the first reaction to be discovered for the preparation of aromatic heterocyclic *N*-oxides.

Heller and his collaborators [65,66], who made a study of reductive cyclisation, incorrectly considered the reduction of methyl 2-hydroxy-2-(*o*-nitrophenyl)ethyl ketone (XX) to yield the carbonyl compound (XXII), whereas in fact the product obtained was quinaldine *N*-oxide (XXI).

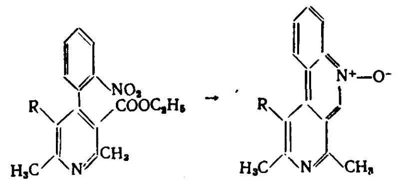

(XX) (XXI)


(XXII)

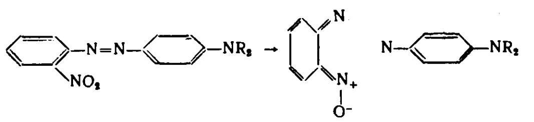
The products of the reduction of *o*-nitrobenzylidenemalonic acid derivatives (XXIII) were similarly taken for dihydroindole derivatives (XXIV). [66] Later work by other authors showed that this reductive cyclisation yields quinoline *N*-oxides (XXV): [67]


(XXIV) (XXIII) (XXV)

This reductive cyclisation can also be used for the synthesis of other types of oxides. For example, 2,6-dimethyl-3-ethoxycarbonyl-4-*o*-nitrophenylpyridine (XXVI) and its derivatives yield on reduction diazaphenanthrene 9-oxides (XXVII). [68]


(XXVI) (XXVII)

The *N*-oxides of compounds containing two [69] or three [70] nitrogen atoms in the ring can similarly be obtained, *e.g.* the substituted benzotriazole *N*-oxides (XXVIII).

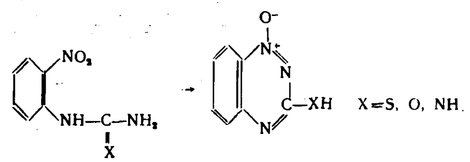

(XXVIII)

Ammonium sulphide [1], zinc in acetic [66,71] or hydrochloric [72] acids, and hydrazine [70] are the usual reducing agents in this reaction. Catalytic reduction on palladium has also been described [73]. The intermediate hydroxylamines have been isolated in certain cases [72].

4. Cyclisation of Nitro-Compounds

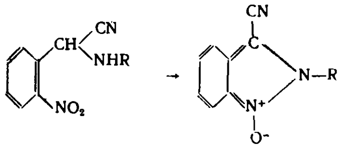
The reaction of aromatic nitro-compounds with aromatic amines in the presence of strong alkali (the Wohl–Aue reaction) yields, among other products, the *N*-oxides of the phenazine series [74]. When the Wohl–Aue reaction is carried out at 120°–125° the main product is the appropriate phenazine *N*-oxide. At higher temperatures (140°–160°) phenazine is the main product [75]. The *N*-oxide group is formed with partial reduction of the nitro-group [76]. Recent work on the structure of iodinin has aroused great interest in *N*-oxides of the phenazine series, and the Wohl–Aue reaction and its mechanism have been studied in great detail by Soviet workers [75,77–80].

If the nitro- and the amino-groups are present in the same molecule, intramolecular cyclisation can result from the transfer of the unshared electron pair of the amino-group to the nitro-group. For instance, the cyclisation of the *o*-nitrophenyl derivatives of urea, thiourea, and guanidine (XXIX) yields benzotriazine *N*-oxides (XXX): [81–83]

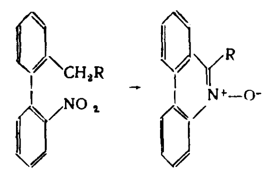


(XXIX) (XXX)

The ring closure in α-amino-*o*-nitrophenylacetonitriles [84] occurs similarly:

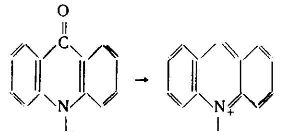


The formation of derivatives of phenanthridine *N*-oxides (XXXII) by the cyclisation of 2-alkyl-2′-nitrobiphenyl (XXXI) [85,86] is somewhat different in character. This cyclisation is only possible if the substituent R is a cyano-, carbamido-, or methoxycarbonyl-group; in other words, if the substituent increases the mobility of the hydrogen atom in the adjacent methylene group. If this is not the case (R = H, OH, Br), an *N*-oxide is not formed. The reason why a carbonyl group does not allow the reaction is not understood.


(XXXI) (XXXII)

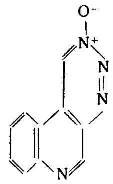
5. Other Methods of Preparation of *N*-Oxides

Certain particular cases of the formation of various aromatic heterocyclic *N*-oxides by routes other than the above have been reported in the literature. For instance, acridine *N*-oxide (XXXIV) has been prepared by reduction of *N*-hydroxyacridone (XXXIII) with sodium amalgam[87].

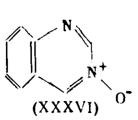


(XXXIII) (XXXIV)

Pyrylium salts react with hydroxylamine forming *N*-oxides[61]. On treatment with nitrous acid, 3-aminolepidine forms 1,2,3,9-tetraazaphenanthrene 3-oxide (XXXV)[88]. Finally, by reaction with hydroxylamine, quinazoline forms a monoxide (XXXVI)[89].



(XXXV)



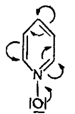
(XXXVI)

II. SOME PHYSICAL PROPERTIES OF AROMATIC HETEROCYCLIC *N*-OXIDES

The presence of a positively charged ammonium nitrogen considerably changes the properties of aromatic rings containing nitrogen. The *N*-oxides are solid, salt-like compounds, soluble in water. Nevertheless, the salt-like character of aromatic heterocyclic *N*-oxides is considerably less pronounced than that of the *N*-oxides derived from aliphatic amines. The melting and boiling points of *N*-oxides are lower in the heterocyclic than in the aliphatic series. Besides, the former are more soluble in organic solvents. Their infra-red spectra are also different. The N^+-O^- bond in the aliphatic series is characterised[90] by the frequency 950–970 cm^{-1}, while the *N*-oxides of aromatic heterocyclic compounds absorb intensely[51,91,92] in the 1240–1290 cm^{-1} region.

The difference between aromatic and heterocyclic *N*-oxides is especially pronounced in their dipole moments (Table 1).

The small differences in dipole moments between aromatic rings containing nitrogen and their corresponding *N*-oxides are worthy of note since such differences are considerably greater in the aliphatic series. The anionic centre, *i.e.* the negatively charged oxygen, is undoubtedly conjugated with the aromatic ring. Linton[93] pointed out that the conjugation in the molecule of pyridine oxide must involve the following scheme:



(I)

TABLE 1. Dipole moments of amines and their *N*-oxides[93-95].

Compound	Dipole moment		Bond polarity	Compound	Dipole moment		Bond polarity
	amine	*N*-oxide			amine	*N*-oxide	
Trimethylamine	0.65	5.02	3.3	Acridine	1.96(1.84)	4.08	2.02(2.62)
Pyridine	2.22	4.24	3.01	Quinoxaline	1.92	2.53*	1.86
Quinoline	2.15	4.00	2.80	Phenazine	0.0	1.76*	1.76

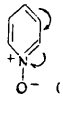
* Dipole moments of monoxides.

The low dipole moment of pyridine *N*-oxides is due to conjugation. The shift of electrons from the oxygen atom to the ring balances the dipole moment of the *N*-oxide group. The conjugation is even higher in condensed aromatic heterocyclic compounds, and as a result, the polarity of the N^+-O^- bond is lowered. This is clear from the work of Pushkareva *et al.*[94,95] who compared the polarity of the N^+-O^- bonds in the *N*-oxides of pyridine, quinoline, acridine, quinoxaline, and phenazine (see Table 1). The polarity of the N^+-O^- bond is inversely proportional to conjugation.

TABLE 2. Dipole moments of 4-substituted pyridines and their *N*-oxides.

Substituent	Dipole moment	
	pyridine	pyridine *N*-oxide
$-H$	2 22	4.24
$-CH_3$	2.61	4.74
$-OCH_3$	2.96	5.08
$-N(CH_3)_2$	4.31	6 78

In addition to the above-mentioned conjugation (I) in the molecule of pyridine *N*-oxide, there also occurs a shift of electrons in the opposite direction.



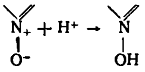
(II)

Katritzky and his coworkers[96] established the presence of this shift by comparing the dipole moments of a number of γ-substituted pyridines and their *N*-oxides. They found that by introducing electron-donating substituents into γ-position the dipole moment is increased, and more so in *N*-oxides than in unoxidised pyridines. This is clear from Table 2. The competition between the two types of conjugation can induce either a surplus or a deficiency of electrons at position 4 of the reacting molecule[96,97]. This is confirmed by the chemical behaviour of *N*-oxides, which we discuss below.

III. CHEMICAL PROPERTIES OF AROMATIC HETEROCYCLIC *N*-OXIDES

1. Reactions of the *N*-Oxide Group

Addition of a proton.



$$\overset{+}{\mathrm{N}}{-}\mathrm{O}^- + \mathrm{H}^+ \rightarrow \mathrm{N}{-}\mathrm{OH}$$

The basic properties of *N*-oxides are chiefly due to the negative charge on the oxygen atom. It is clear from Table 3 that the basicity of an *N*-oxide is lower than that of the corresponding amines.

The *N*-oxides of aromatic heterocyclic compounds form stable salts only with strong inorganic acids, and with picric and picrolonic acids[29]. Certain *N*-oxides do not form picrates[100]. The basicities of a number of substituted *N*-oxides are well represented[98] by the Hammett equation with $\rho = 2.09$.

Reduction. In contrast to aliphatic *N*-oxides, pyridine *N*-oxide, and its derivatives can be reduced only with difficulty. This is due to the decrease in the negative charge on the oxygen atom resulting from conjugation of the *N*-oxide group with the ring. The reduction potentials of various heterocyclic *N*-oxides vary, as can be seen from Table 4. Clearly, increased condensation of aromatic nuclei, and electron-accepting substituents, facilitate reduction. Nuclear electron-donating substituents, on the contrary, inhibit reduction. Pushkareva and Nechaeva[102] showed that the reduction potentials of *N*-oxides vary in the same sense as the dipole moments: the lower the dipole moment, the more easily is a compound reduced.

TABLE 3. Basicity of certain aromatic heterocyclic compounds and their *N*-oxides[98,99].

Compound	Basicity (pK_a)	
	parent base	*N*-oxide
Pyridine	5.29	0.79
Quinoline	4.94	0.70
Isoquinoline	5.4	1.1

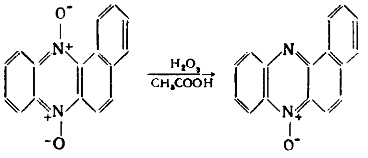
TABLE 4. Reduction potentials of *N*-oxides.

N-Oxide	Reduction potential		*N*-Oxide	Reduction potential	
	pH 3.5 (ref. 10)	pH 7.0 (ref. 101)		pH 3.5 (ref. 10)	pH 7.0 (ref. 101)
Trimethylamine	—0.4562	—	Quinoline	—1.0692	—1.164
Dimethylaniline	—0.7047	—1.018	Acridine	—	—0.854
Pyridine	—1.2786	—1.364	Quinoxaline*	—	—0.650
2,4,6-Collidine	—1.3924	—	Phenazine*	—	—0.218
4-Phenoxypyridine	—1.2820	—			

* Reduction potentials of monoxides.

Inspection of the reduction potentials shows that reducing agents such as sulphur dioxide and potassium iodide will not reduce pyridine *N*-oxide, but will reduce quinoline *N*-oxide[44]. In a number of cases iron in acid media[103,104], and sodium[104] or sulphide[105] in liquid ammonia were found to be satisfactory reducing agents. *N*-Oxides not containing reducible groups can satisfactorily be hydrogenated with palladium in alcoholic solution[107]. The reaction proceeds at normal pressure and room temperature. Reductions with Raney-nickel, on the other hand, require increased pressure. Since weaker reducing agents have, as a rule, no effect on the *N*-oxide group, they can be used for the selective reduction of reducible groups bound to the nucleus, for instance the nitro-group. The selective reduction of an *N*-oxide group can be carried out with any oxygen acceptor, most often with phosphorus trichloride[10]. This reaction proceeds under mild conditions, merely by heating the *N*-oxide and phosphorus trichloride in chloroform or ethyl acetate[109]. Quinoline *N*-oxide is somewhat harder to reduce than pyridine *N*-oxide, but the yield may be increased by using phosphorus tribromide instead of trichloride. Derivatives containing halogen in the nucleus, or in which radicals attached to the ring (*e.g.* the nitro-group) have been replaced by halogen, are obtained as by-products in the reaction of *N*-oxides with phosphorus trichloride. For instance, the reduction of 4-nitropyridine *N*-oxide with phosphorus trichloride yields 4-chloropyridine besides 4-nitropyridine[109], while the reduction of 4-nitroquinoline *N*-oxide with phosphorus tribromide yields 2-bromo-4-nitroquinoline as a by-product[110]. Triphenyl phosphite can also serve as oxygen acceptor, but compared to phosphorus halides, it requires more vigorous reaction conditions[111-113].

A rather unusual method for reducing *N*-oxides consists in prolonged heating in acid solution in the presence of oxidising agents. Heating a substituted quinoline *N*-oxide in sulphuric acid in the presence of chromic oxide results in the reduction of the *N*-oxide group[66]. Even more unusual is the behaviour of benzophenazine *N,N'*-dioxide (I). On being heated in acetic acid in the presence of hydrogen peroxide, namely under the conditions normally used to prepare *N*-oxides, this compound undergoes reduction to the monoxide[43].



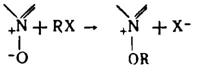
(I) (II)

The re-oxidation of the monoxide (II) is prevented by steric hindrance.

The oxidising properties of *N*-oxides are used for their detection. On heating *N*-oxides with dimethylaniline the solution becomes intensely coloured owing to the formation of crystal violet[114].

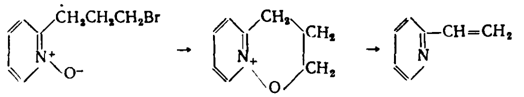
Heterocyclic *N*-oxides can be determined quantitatively by titanometric titration[115].

Alkylation.



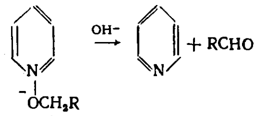
$$\overset{+}{\mathrm{N}}{-}\mathrm{O}^- + \mathrm{RX} \rightarrow \overset{+}{\mathrm{N}}{-}\mathrm{OR} + \mathrm{X}^-$$

N-oxides react with alkylating agents, especially in polar solvents such as acetonitrile or nitrobenzene, yielding *O*-alkyl derivatives which are effectively quaternary salts with a discrete anion. If, however, the compound contains an amine nitrogen in addition to an *N*-oxide group (*e.g.* the monoxides of quinoxaline and phenazine), *N*-alkyl derivatives are formed instead[115,117]. The internal alkylation of α-(3-bromopropyl)pyridine *N*-oxide (III), which results[118] in the formation of a bicyclic quaternary salt (IV), is noteworthy:



(III) (IV) (V)

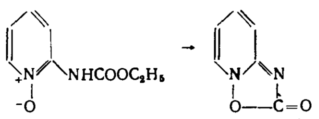
In common with aliphatic alkoxyalkyl ammonium salts, heterocyclic ammonium salts containing an alkoxy radical (VI) are decomposed by alkali forming an aldehyde and a reduced base:



(VI)

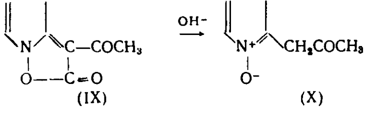
This reaction can be used for the preparation of aldehydes from alkyl halides. Substituted benzaldehydes were thus obtained in 90% yield from substituted benzyl chlorides[119]. The decomposition of the cyclic quaternary compound (IV) similarly yields vinylpyridine (V) and formaldehyde.

Intramolecular acylation. 2-Ethoxy-carbonylaminopyridine *N*-oxide (VII) splits off a molecule of alcohol when heated to 140° and undergoes ring closure[120,121] forming pyridino(1′ : 2′ – 2 : 3)-1-oxo-2,4-diazol-5-one (VIII).



(VII) (VIII)

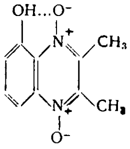
Compounds of this type are also formed in the reaction of 2-bromopyridine *N*-oxide with sodioacetoacetic ester. 2-Pyridineacetoacetic ester *N*-oxide, initially formed, is unstable and undergoes cyclisation[122] to 4-acetylpyridino-(1′: 2′ – 2 : 3)isoxazol-5-one (IX).



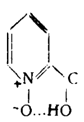
(IX) (X)

Both these bicylic compounds are unstable and undergo decarboxylation under the action of alkali, the compound (IX) yielding 2-acetonylpyridine *N*-oxide (X).

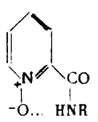
Formation of an intramolecular hydrogen bond. The *N*-oxide oxygen atom has a tendency to form an intramolecular hydrogen bond. Such a bond exists in 5-hydroxy-2,3-dimethylquinoxaline 1,4-oxide (XI), as shown by the relative solubilities in organic solvents of this dioxide and of its 6-hydroxy isomer[19]. The refractoriness of certain *N*-oxides (XII) towards reduction has been ascribed to the presence of hydrogen bonds, which was demonstrated by the preparation of chelate compounds with copper[123,124]. Moreover, the hydrogen bond in the derivatives of picolinamide *N*-oxide (XIII) was detected spectroscopically[125].



(XI)



(XII)



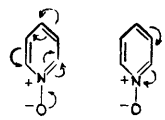
(XIII)

In addition to the foregoing reactions, the *N*-oxide oxygen atom is capable of reacting with various nucleophilic reagents, *e.g.* acid anhydrides. The resulting compounds are unstable and undergo rearrangement into compounds substituted in the nucleus. We shall discuss this type of reaction in the following section.

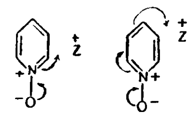
2. Substitutions in Aromatic Heterocyclic Compounds

By virtue of the electron-accepting property of the nitrogen atom, heterocyclic compounds containing nitrogen in the ring are very reluctant to undergo electrophilic substitution reactions.

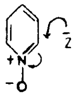
If electrophilic substitution does occur, the substituent is directed to the β-position, which has the greatest electron density (as compared with the α- and γ-positions). Reaction with nucleophilic reagents is somewhat easier, when the substituent is directed to position 2 (more rarely, 4). The conversion of a heterocyclic amine (for instance, pyridine) into its *N*-oxide is accompanied by appreciable changes in electronic structure. It has already been pointed out that two types of conjugation are possible in the molecule of an *N*-oxide. The *N*-oxide group can act as an electron-donating as well as an electron-accepting group:



The electrophilic reagent Z⁺ can easily attack the nucleus at the α- or γ-positions, where the electron density is higher owing to the positive tautomeric effect. Substitution in the γ-position should proceed especially readily, as the conjugation effect at the α-position is partly compensated by the oppositely directed inductive effect of the adjacent nitrogen atom.



On the other hand, because of the electron withdrawing effect, a nucleophilic reagent is also capable of attacking the nucleus of an *N*-oxide:



The nucleophilic substitution occurs primarily in the α-position, where the tautomeric and the inductive effect are superposed. The nucleophilic reagent can also attack the oxygen atom first, the resulting compound subsequently undergoing rearrangement to form a product substituted in the ring.

These general theoretical considerations, applied to the *N*-oxide of the simplest heterocyclic compound, namely pyridine, have been confirmed by quantum-mechanical calculations. The localisation energies in different positions of the molecule of pyridine and its *N*-oxide, calculated by Jaffe[126], are collected in Table 5†. The energies of localisation were computed by a theoretical treatment of the basicity constants of various derivatives of pyridine and its *N*-oxide.

It follows from Table 5 that both nucleophilic and electrophilic substitution should proceed more readily in the molecule of the *N*-oxide than in the parent base. Position 2 is the most reactive in nucleophilic substitutions, and position 3 in electrophilic substitutions, in the molecule of pyridine, whereas in the *N*-oxides position 4 is the most reactive in both cases.

TABLE 5. Charge localisation energies in pyridine and its *N*-oxide.

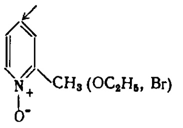
Compound	Position	Localisation energy, kcal/mole	
		electrophilic substitution	nucleophilic substitution
Pyridine	2	2.712	2.312
	3	2.487	2.378
	4	2.637	2.228
Pyridine *N*-oxide	2	2.634	2.689
	3	3.218	2.357
	4	2.474	1.714

Substitution in aromatic heterocyclic *N*-oxides, mainly in pyridine *N*-oxide, are considered below. Although the general picture of chemical properties may be somewhat changed when the derivatives of pyridine, or the condensed systems, are considered, the general assumptions remain unaltered.

Nitration. *N*-Oxides undergo nitration readily; the details of procedure can now be found in "Organic Syntheses"[127]. The main product of the nitration of pyridine *N*-oxide is 4-nitropyridine *N*-oxide; 2-nitro-pyridine is formed as a by-product, in amounts from 0.4 to 7.6%, depending on the reaction temperature. 2-Nitropyridine *N*-oxide can be obtained by the oxidation of the amino-group in 2-aminopyridine *N*-oxide with hydrogen peroxide in 30% oleum[128]. 3-Nitropyridine *N*-oxide can likewise be obtained by the oxidation of 3-aminopyridine with peracetic acid[129].

The nitration of quinoline *N*-oxide also yields predominantly the 4-isomer, but simultaneous nitration of the benzene ring gives the 5- and 8-nitro-derivatives in amounts depending on the reaction temperature[10,130]. In contrast to pyridine *N*-oxide, no 2-isomer is formed in the nitration of quinoline *N*-oxide. According to Ochiai[131,132] the nitration of quinoline and quinaldine *N*-oxides with benzoyl nitrate in aprotic solvents (chloroform, dioxane) yields mainly the 3-nitro derivatives.

The *N*-oxide group has a strong *ortho-para*-directing effect. Hertog and his collaborators[133-137] showed that the nitration of 2-picoline, 2-ethoxypyridine, and 2-bromopyridine *N*-oxides yields 4-nitro-derivatives (XIV). The directing effect of the *N*-oxide group must therefore be stronger than that of the methyl or ethoxy group, or bromine. This has been confirmed[138] by the nitration of the approprate 3-substituted derivatives (XV).



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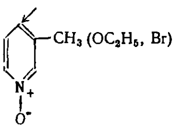

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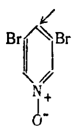

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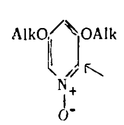
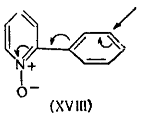


(XVII)

3,5-Dibromopyridine *N*-oxide also undergoes nitration in position 4 (XVI). However, 3,5-dialkoxypyridine *N*-oxide yields the 2-isomer (XVII), probably owing to steric hindrance. The directive effect of the hydroxyl group is greater than that of the *N*-oxide group, and 2-hydroxypyridine *N*-oxide, for instance, yields the 5-nitro-derivative.

In the nitration of 2- or 4-substituted phenylpyridine *N*-oxides (XVIII), the nitro-group takes up the *meta*-position in the phenyl radical[139].



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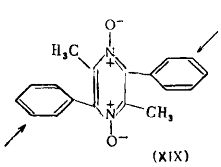

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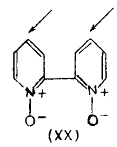

(XX)

Meta-substitution is caused by the withdrawal of electrons from the phenyl radical towards the *N*-oxide group. In this case the *N*-oxide group, or rather the pyridyl-*N*-oxide radical, is a *meta*-directing substituent, whose electron-accepting properties are weaker than those of a positively charged pyridinium group[140]. The nitration of 2,5-dimethyl-3,6-diphenylpyrazine 1,4-dioxide (XIX) proceeds likewise[141]. The nitration of 2,2'-bipyridyl 1,1'-dioxide (XX) yields the 4,4'-dinitro derivative[142].

It has been shown that 2- and 4-phenylpyridine *N*-oxides undergo nitration not in the form of salts, but in the form of bases[139,140].

Other electrophilic substitutions. Attempts to halogenate or sulphonate pyridine *N*-oxide were unsuccessful[143]. The *N*-oxides of pyridine derivatives containing electron-donating groups, however, are capable of being halogenated. 2-Hydroxypyridine and 4-hydroxypyridine *N*-oxides undergo bromination forming 3,5-dibromo derivatives[137,144]. The iodination of these compounds proceeds similarly[144]. 4-Bromoquinoline *N*-oxide was also obtained, although in small yield, by direct bromination[145]. Acridine *N*-oxide is brominated[146] in position 9. According to some Japanese workers[147] the mercuration of pyridine and quinoline *N*-oxides yields the 4-mercuri-derivatives. Ammers and Hertog, however, who made a detailed study of this reaction, report[148] that the mercuration of pyridine *N*-oxide gives 2- and 2,6-derivatives.

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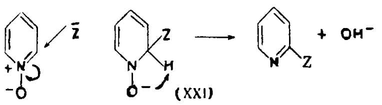
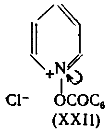
† The localisation energy is the energy required for the localisation of a charge at any position in the molecule. In the opinion of several authors, this energy represents a considerable part of the activation energy.

Action of organomagnesium compounds. In the reaction of aromatic heterocyclic compounds with strong nucleophilic agents the substituent takes up the α-position in the ring. Aromatic heterocyclic *N*-oxides also react with nucleophilic reagents, forming α-substituted derivatives. This latter reaction seems to proceed *via* an intermediate formation of compound (XXI).



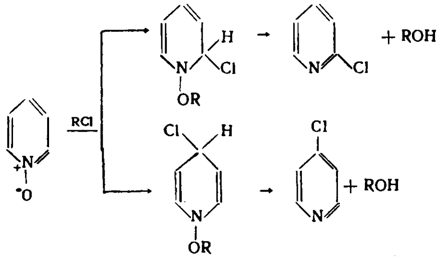
The Grignard reagents belong to this group of nucleophilic reagents. The reaction of phenylmagnesium bromide with pyridine *N*-oxide proceeds vigorously and yields 2-phenylpyridine and 2,6-diphenylpyridine[149]. The *N*-oxides of quinoline and its derivatives similarly yield α-phenyl quinolines[150]. The substituent was never found in the γ-position.

Owing to the positive charge carried by the nitrogen atom, aromatic heterocyclic *N*-oxides react more readily than the unoxidised bases with organomagnesium compounds. The decreased electron density of the *N*-oxide oxygen atom favours nucleophilic substitution in α-position. Therefore, if benzoyloxypyridinium ion (XXII) is reacted with phenylmagnesium bromide instead of pyridine *N*-oxide, the yield is greatly increased[151]. We shall see that the benzoyloxypyridinium ion can take part in other nucleophilic substitutions.



(XXII)

Reactions with sulphuryl chloride and phosphorus oxychloride. Although the direct chlorination of *N*-oxides does not yield satisfactory results, the reaction with sulphuryl chloride or phosphorus oxychloride gives the chloro-derivatives in good yields. For instance, pyridine and quinoline *N*-oxides react with sulphuryl chloride forming 2- and 4-chloro-derivatives[16,152]. Similarly results are obtained by the use of phosphorus oxychloride[153] and phosphorus pentachloride[154] It may be noted that the α- and γ-isomers are formed in almost equal amounts, in sharp contrast with reactions involving Grignard reagents, where there is selective α-substitution. For example, the reaction of pyridine *N*-oxide with sulphuryl chloride yields 2- and 4-chloropyridines in the ratio 57 : 43, and quinoline *N*-oxide yields the 2- and 4-isomers in the ratio 38 : 62. The chlorination mechanism seems to be the following[151]:

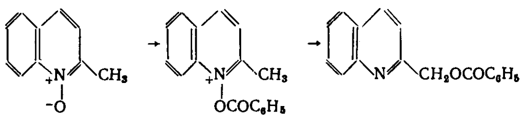


where R = $POCl_2$, PCl_4, SO_2Cl.

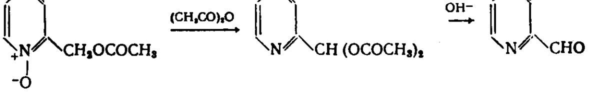
The substituents already present in the nucleus can modify the main course of the reaction and favour the formation of 4-isomers[155], as well as of polychloro-derivatives. Magidson and Rubtsov[156] showed that 6-methoxyquinoline *N*-oxide reacts with sulphuryl chloride forming di- and tri-chloro-derivatives of 6-methoxyquinoline.

The above reaction mechanism does not cover all cases of the reaction of *N*-oxides with inorganic acid halides. Cases are known in which the chlorination is not accompanied by reduction. 3,5-Diethoxypyridine *N*-oxide reacts with sulphuryl chloride forming a mixture of the *N*-oxides of 2,6-dichloro- and 2,4,6-trichloro-3,5-diethoxypyridine[157]. Nor does the above mechanism account for the formation of β-chloro-derivatives in the reaction of 5-nitroquinoline *N*-oxide with phosphorus oxychloride[37]. The chlorination of picoline *N*-oxides yielding products containing halogen in the side-chain also remains unexplained[158].

Action of organic acid anhydrides. The benzoyloxypyridinium ion has already been shown to be unstable, readily releasing the $PhCOO^-$ group which is capable of substituting hydrogen in the nucleus of the heterocyclic compound. Henze[159] studied the benzoylation of *N*-oxides (quinaldine *N*-oxide in particular), but was unable to identify the resulting 2-benzoyloxymethylquinoline[160].

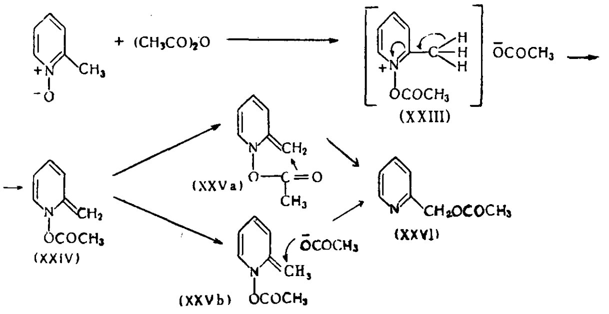


It was later shown that aromatic heterocyclic *N*-oxides react with acetic anhydride to form the esters of C-hydroxy compounds. Thus pyridine *N*-oxide gave 2-acetoxypyridine[10]. Pyridine *N*-oxide, like other heterocyclic *N*-oxides containing alkyl substituents in position 2 or 4, undergoes acetyloxylation in the alkyl group[161,162]. The anhydrides of other acids, benzoic[163] and acid chlorides, *e.g.* *p*-toluenesulphonyl chloride[164], act similarly. The *N*-oxides of the pyridine, quinoline, isoquinoline[165], pyrimidine[166], benzimidazole[167], and other series all react with acid anhydrides. This reaction is widely used in the chemistry of heterocyclic compounds for the synthesis of alcohols[17,166–170], and carbonyl compounds[171,172]. In the latter case *N*-oxides of 2- (or 4-) pyridylalkanoles or their esters are treated with acetic anhydride:



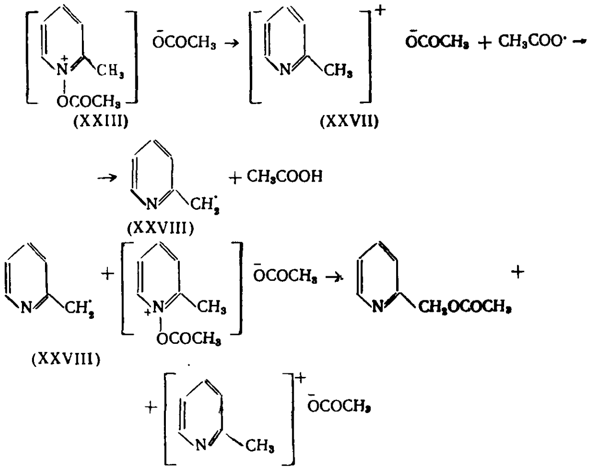
It has recently been shown that the reaction proceeds more vigorously and the resulting ester is easier to saponify if the acetic anhydride is replaced[173]. Several mechanisms have been suggested for the reaction of *N*-oxides with acid anhydrides. We shall discuss them below, using as an example the reaction of α-picoline *N*-oxide with acetic anhydride. The first stage of the reaction consists in the formation of *N*-acetoxy-2-methylpyridinium acetate

(XXIII). In the opinion of the supporters of the ionic reaction mechanism, (XXIII) spontaneously loses a proton forming the anhydronium base (XXIV), which subsequently either undergoes intramolecular rearrangement



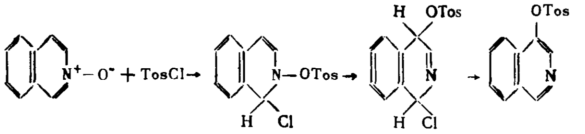
(*via* the intermediate compound XXVa), or is attacked by the acetate ion on the carbon of the methylene group (forming intermediate compound XXVb). In either case the final reaction product is 2-acetoxymethylpyridine (XXVI).

According to the radical mechanism, *N*-acetoxy-2-methylpyridinium acetate (XXIII) is also formed, homolytic decomposition of the N^+-O^- linkage then yields an acetoxy radical and the ion radical (XXVII). (XXVII) loses a proton yielding the 2-picolyl radical (XXVIII) which, by reacting with the *N*-acetoxy-2-methylpyridinium ion, forms the final product and regenerates the radical (XXVII):



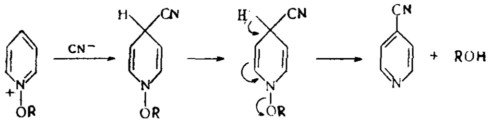
A great many facts speak in favour of the radical mechanism. The reaction has an induction period which is followed by vigorous evolution of heat. Boekelheide[174] demonstrated the formation of free radicals in the course of the reaction by introducing styrene into the reaction mixture and isolating its polymerisation product. It was subsequently shown, however, that the presence of free radicals cannot be taken as direct evidence in favour of the free-radical mechanism[175,176]. The addition of inhibitors of free-radical processes into the reaction mixture stopped the polymerisation of styrene, but had no effect on the yields of 2-acetoxymethylpyridine. This led to the opinion[175,176] that the free radicals are formed by a side-reaction, the main reaction proceeding by an ionic mechanism. The reaction with butyric anhydride in the presence of sodium acetate provided unambiguous evidence of the intramolecular character of the process, and identified the XXVa as an intermediate, since 2-pyridylmethyl butyrate was the only product.

The above mechanisms for the reaction of *N*-oxides with acid anhydrides do not cover all the aspects of this interesting reaction. They do not explain why the acetoxy-group sometimes assumes the β-position in the pyridine[177], quinoline[178], and isoquinoline[165] rings. In practice, the β-hydroxy-derivative is often formed in considerable amounts, as for instance in the reaction of isoquinoline *N*-oxide with the *p*-toluenesulphonyl chloride[165,179,180]. Ochiai[179] suggested the following mechanism for this reaction:



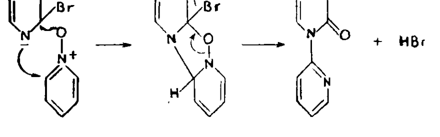
It is noteworthy that, although pyrimidine *N*-oxide and its methyl analogues react with acetic anhydride to form *C*-acetoxy-derivatives[168], purine oxides under these conditions suffer cleavage of the pyrimidine ring, yielding derivatives of imidazole[181].

Reactions with the cyanide ion. It was shown in 1936 that acridine *N*-oxide reacts with potassium cyanide forming 9-cyanoacridine[182]. Quinoline *N*-oxide reacts with a benzoyl chloride–potassium cyanide mixture forming 2-cyanoquinoline[183]. The reaction of the cyanide ion with *N*-oxides has recently been shown to be general[184]. For instance, the reaction of *N*-alkoxypyridinium salts under mild conditions with potassium cyanide yields 4-cyanopyridine (42%). The authors assumed that the first stage of this reaction consists of the addition of a cyanide ion to the quaternary pyridinium salt to form an *N*-alkoxyanhydronium base, which subsequently eliminates the alkoxy-group forming 4-cyanopyridine.



Quaternary *N*-alkoxyquinolinium and *N*-alkoxyisoquinolinium salts also react with the cyanide ion yielding 2-cyanoquinoline and 1-cyanoisoquinoline, respectively, in quantitative yields. Electron-accepting substituents in the pyridine ring do not inhibit this reaction. *N*-Alkoxy-4-cyanopyridine reacts with potassium cyanide forming 2,4-dicyanopyridine.

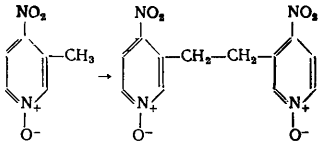
Reaction with α-bromopyridine. Heating pyridine *N*-oxide with α-bromopyridine at 100° yields 1-(2-pyridyl)-2-pyridone[185-187]. The reaction mechanism suggested by the authors is the following:



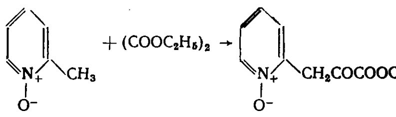
Villers and Hertog[188] ascribed the same mechanism to the reaction of 2-pyridyl *p*-toluenesulphonate with pyridine *N*-oxide, which also yields 1-(2-pyridyl)-2-pyridone. The same compound was observed as a by-product in the reaction of *p*-toluenesulphonyl chloride with pyridine *N*-oxide[189].

3. Effect of the *N*-Oxide Group on the Reactivity of Substituents in Aromatic Heterocyclic Compounds

The hydrogen atom in the methyl groups of α- and γ-picoline, quinaldine, or lepidine is characterised by remarkable reactivity which is caused by the conjugation of σ-electrons with the electrons in the ring. The mobility of the hydrogen atom is increased by transition to the corresponding quaternary compounds. Similarly, the mobility is higher in aromatic heterocyclic *N*-oxides. 2-Picoline and 4-picoline and quinaldine *N*-oxides react with aromatic aldehydes in the presence of basic reagents forming ethylene derivatives[190]. The increased mobility of the hydrogen atom in *N*-oxides as compared with non-oxidised compounds is brought out by the fact that 3-ethyl-4-nitropyridine *N*-oxide[191,192] and 2,5-dimethylpyrazine dioxide[50] react with benzaldehyde, while the corresponding non-oxidised bases do not. The mobility of the hydrogen atom in 3-methyl-4-nitropyridine *N*-oxide is evidenced by the fact that in alkaline solution this compound undergoes oxidative dimerisation and forms 4,4′-dinitro-3,3′-bipicoline 1,1′-dioxide[193].

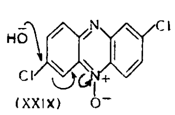


In contrast to the corresponding bases, 2- and 4-picoline *N*-oxides enter the Claisen condensation[28,194,195]. For instance, 2-picoline *N*-oxide undergoes condensation with ethyl oxalate forming a derivative of pyruvic acid:



Nevertheless, the electron-accepting power of the *N*-oxide group in quinaldine *N*-oxide is insufficient to cause the hydrogen mobility required for reaction with *p*-nitrosodimethylaniline[196].

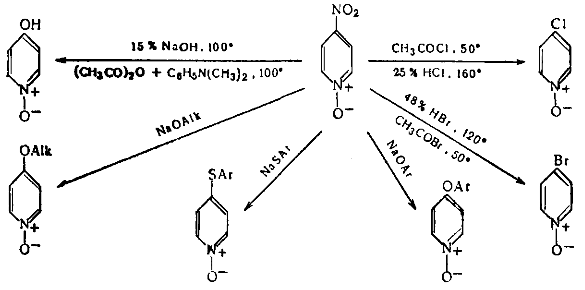
The ability of the *N*-oxide group to lower the electron density at the α- and γ-positions in the ring results in an increased mobility of halogen substituents in these positions. The halogen atoms in *N*-oxides, *e.g.* pyridine *N*-oxide, are more active than in the corresponding bases. 2-Bromopyridine *N*-oxide reacts with the sodium derivatives of malonic, acetoacetic, benzoylacetic, and cyanoacetic esters, while 2-bromopyridine itself is inactive in this reaction[112]. The halogen substituent in phenazine *N*-oxides is especially reactive: it hydrolyses on boiling with alkali[197-199], and is replaced by an amino-group on heating with amines[200]. In these reactions the *N*-oxide group activates the halogens in *meta*-positions, and not those in *para*-positions[201]. This behaviour is typically shown by compound (XXIX).



(XXIX)

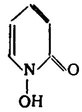
The *N*-oxide group also activates nitro-groups in positions α and γ of the heterocyclic compound. Such nitro-groups can easily be replaced by various reagents. As the nitro-group is readily introduced into position 4, its replacement is one of the preparative methods for obtaining 4-substituted aromatic heterocyclic compounds.

Typical replacements of the nitro-group in 4-nitropyridine *N*-oxide are summarised below[10,103]. The nitro-group in 4-nitronicotinic acid *N*-oxide can similarly be replaced[202].

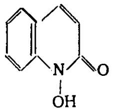


The nitro-group in 4-nitroquinoline *N*-oxide can be replaced under milder conditions, *e.g.* by chlorine, on boiling with hydrochloric acid. The reduction of nitro-substituted *N*-oxides is sometimes accompanied by replacement of the nitro-group.

The effect of the *N*-oxide group on the properties of 2- and 4-hydroxy- and amino-groups is most interesting, as is the comparison of the structure of these substituted *N*-oxides with those of the corresponding non-oxidised bases. In his comparative study of the spectra of the *N*-oxides of 2-hydroxy-, 3-hydroxy-, and 2-benzyloxy-pyridines, and of *N*-benzyloxy-2-pyridone, Shaw established that 2-hydroxypyridine *N*-oxide has the *N*-hydroxy-2-pyridone structure (XXX)[203]. 2-Hydroxyquinoline *N*-oxide has a similar structure (XXXI)[204].



(XXX)



(XXXI)

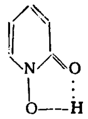
It could be assumed that 4-hydroxypyridine *N*-oxide also had the pyridone structure, but the experimental evidence is that both hydroxy- and oxo-forms were present. For instance, 4-hydroxypyridine *N*-oxide reacts with diazomethane forming a mixture of *N*-methoxy-4-pyridone and 4-methoxypyridine *N*-oxide[205]. 2-Amino- and 4-amino-substituted *N*-oxides were shown to have an amine, not an imine structure. They can easily be diazotised and coupled with β-naphthol[10]. 4-Aminopicoline *N*-oxides take part in the Skraup reaction[206].

Katritzky *et al.*[23,125,207,208] established the structure of the hydroxy- and amino-derivatives of pyridine *N*-oxide on the evidence of basicity and spectral studies, and also investigated the structure of the *N*- or *O*-alkyl derivatives corresponding to both tautomeric forms. It was shown that 2- and 4-aminopyridine *N*-oxides exist in the form of amino-derivatives, that 4-hydroxypyridine *N*-oxide consists of a mixture of equal amounts of the hydroxy- and oxo-forms, and that only 2-hydroxypyridine *N*-oxide exists in the pyridone form. Quantitative relationships are collected in Table 6.

TABLE 6. Correlation between the benzenoid and quinonoid structures.

Compound	Ratio of benzenoid to quinonoid structure			
	4-Amino	2-Amino	4-Hydroxy	2-Hydroxy
Pyridine *N*-oxide	10^7	10^8	1	—
Pyridine	$2\cdot10^3$	$2\cdot10^5$	$4\cdot10^{-4}$	$3\cdot10^{-8}$

The pyridone form of 2-hydroxypyridine *N*-oxide is stabilised by a strong hydrogen bond, which makes it impossible to calculate the quantitative ratio of hydroxy- and oxo-forms. The *N*-oxides of the mercaptopyridines exist mainly in the thione form[209]



IV. USES OF AROMATIC HETEROCYCLIC *N*-OXIDES

N-Oxides are widely used as intermediate products in the synthesis of various heterocyclic derivatives. Many such uses have already been discussed. It may now be noted that they are intermediates in the synthesis of certain alkaloids, *e.g.* ricinine[210], alstyrine[211], and 2-ethylisonicotinic thioamide[212]. Pyridinealkanol *N*-oxides are used in a convenient method for obtaining pyrrocolines[213,214]. The specific synthesis of isomeric alkylphenazinium salts using phenazine *N*-oxide is worthy of note[215].

The conversion of heterocyclic rings into corresponding *N*-oxides can be employed for the separation of high-boiling compounds. The lutidine fraction was separated by oxidation to 2,6- and 3,4-lutidine *N*-oxides followed by reduction to the corresponding bases[216]. The separation of the quinoline fraction has been done similarly[217]. Separation can be carried out either by fractional distillation *in vacuo* or chromatographically[218].

Aromatic heterocyclic *N*-oxides are not very important biologically. It has already been mentioned that the antibiotics iodinin and aspergillic acid are *N*-oxides. Attempts to enhance the biological activity by preparing *N*-oxide structures of this type have met with slight success[219]. Nicotinic and isonicotinic acid *N*-oxides are physiologically less active than the corresponding bases[220]. On conversion to *N*-oxides the activity of a number of tuberculostatic compounds (pyridine derivatives) usually drops[221,222]. Purines *N*-oxides are at the moment attracting attention as potential antimetabolites and as possible products of the biological transformations of purines[223,224].

Certain authors report bactericidal action in the *N*-oxides of certain heterocyclic compounds which are otherwise inactive[169,125]. Finally, certain *N*-oxides, *e.g.* 4-nitroquinoline *N*-oxide, have recently been shown to possess carcinogenic activity[226,227].

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CYANOETHYLATION, DECYANOETHYLATION, and TRANSCYANOETHYLATION

P. F. Butskus

CONTENTS

INTRODUCTION

The β-cyanoethyl group $-CH_2CH_2CN$ is most frequently introduced into compounds containing a mobile hydrogen atom by reacting them with acrylonitrile. The cyanoethylation with acrylonitrile has in the last 15–20 years been widely studied on many organic compounds. Alcohols, phenols, mercapto compounds, oximes, amides, aliphatic and aromatic amines, heterocyclic bases, phosphines, arsines, and compounds in which a mobile hydrogen atom is linked to carbon (certain hydrocarbons, polyhalogeno-alkanes, nitro-compounds, aldehydes, ketones, acid derivatives, compounds of the acetoacetic and malonic ester type, and sulphones) have all been cyanoethylated. Several hundreds of original publications and patents and several reviews have dealt with this subject[1-3]. Cyanoethylation is a very simple and convenient method for the preparation of a large number of compounds otherwise difficult to obtain, which are indispensable for the development of various fields of chemical industry.

Cyanoethylation with acrylonitrile proceeds according to the following scheme:

$$R{-}H + CH_2{=}CHCN \rightarrow R{-}CH_2CH_2CN.$$

Cyanoethylation is reversible. Hence by introducing a new compound capable of cyanoethylation into a system in equilibrium transcyanoethylation products can be obtained:

$$R{-}CH_2CH_2CN \xrightleftharpoons[+R-H]{-R-H} CH_2{=}CHCN \xrightleftharpoons[-R'-H]{+R'-H} R'{-}CH_2CH_2CN$$

In certain cases decyanoethylation occurs, when acrylonitrile is eliminated (sometimes as a polymer or as acrylic acid):

$$R{-}CH_2CH_2CN \rightarrow R{-}H + CH_2{=}CHCN.$$

Cyanoethylation and its reverse are base catalysed[4].

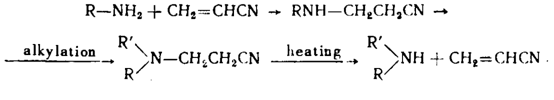
This review covers all the methods of cyanoethylation with reagents other than acrylonitrile, as well as decyanoethylation and transcyanoethylation. This last reaction can hardly be discussed separately, since it consists in simultaneous cyanoethylation and decyanoethylation:

$$R{-}CH_2CH_2CN + R'{-}H \rightarrow R'{-}CH_2CH_2CN + R{-}H.$$

In addition to acrylonitrile, β-halopropionitriles, ethylene cyanohydrins, β-alkoxypropionitriles, cyanoethyl esters, β-aminopropionitrile and its *N*-substituted derivatives, and certain other compounds can also be used as cyanoethylating agents. In cases where cyanoethylation with acrylonitrile yields polymers, by using some of the above agents the reaction can be carried out under milder conditions and arrested at the monomer stage. These agents are also known to give positive results in cases where acrylonitrile failed to react or gave too low yields of the product. Certain cyanoethyl compounds can only be obtained by transcyanoethylation.

The course of decyanoethylation and transcyanoethylation provides the evidence that the bond attaching β-cyanoethyl groups to oxygen, sulphur, nitrogen, carbon, *etc.*, is, as a rule, more labile than the bonds between alkyl radicals or other groups with these atoms. The mobility of the β-cyanoethyl group is clearly demonstrated by the decyanoethylation of certain cyanoethyl derivatives on distillation.

Decyanoethylation and transcyanoethylation are interesting both from the theoretical and preparative viewpoints. For instance, β-cyanoethyl group can be used for protecting an amino-group[5,6]:



$$R{-}NH_2 + CH_2{=}CHCN \rightarrow RNH{-}CH_2CH_2CN \rightarrow$$
$$\xrightarrow{\text{alkylation}} \begin{matrix}R'\\R\end{matrix}\!\!>N{-}CH_2CH_2CN \xrightarrow{\text{heating}} \begin{matrix}R'\\R\end{matrix}\!\!>NH + CH_2{=}CHCN.$$

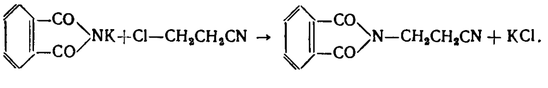
1. β-HALOPROPIONITRILES AS CYANOETHYLATING AGENTS

(a) Cyanoethylation with β-chloropropionitrile. The β-halopropionitrile most widely used in cyanoethylations is β-chloropropionitrile.

The reaction of β-chloropropionitrile with acid sodium sulphide[7], sodium sulphide[8], potassium sulphide[9], ammonium thiocyanate[10], sodioacetoacetic ester[11] and potassium phthalimide[12] yields cyanoethylation products. For example:

$$K_2S + 2\ Cl{-}CH_2CH_2CN \rightarrow S(CH_2CH_2CN)_2 + 2\ KCl,$$

$$NH_4SCN + Cl{-}CH_2CH_2CN \rightarrow NCS{-}CH_2CH_2CN + NH_4Cl,$$



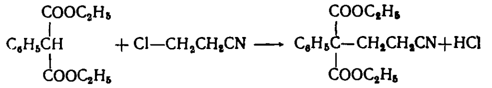
β-Chloropropionitrile has been used for the cyanoethylation of ethanol[13].

The reduction of β-chloropropionitrile by Vyshnegradskii's method yields γ-alkoxypropylamines[14]:

$$Cl{-}CH_2CH_2CN \xrightarrow[KOH]{Na} RO{-}CH_2CH_2CH_2NH_2\,.$$

The reaction of β-chloropropionitrile with ketones[15,16] can be more easily stopped at the stage of monocyanoethylation, and the yields of products are, as a rule, higher than in the case of acrylonitrile.

Phenylmalonyl diethyl ester reacts with β-chloropropionitrile forming 32% cyanoethylation product[17]:

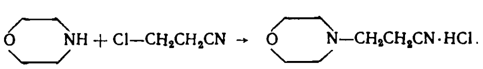


$$C_6H_5\overset{COOC_2H_5}{\underset{COOC_2H_5}{CH}} + Cl{-}CH_2CH_2CN \longrightarrow C_6H_5\overset{COOC_2H_5}{\underset{COOC_2H_5}{C}}{-}CH_2CH_2CN + HCl$$

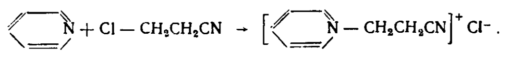
Heininger[10,18] showed that in the reaction of β-chloropropionitrile with amines, different products are obtained depending on the nature of the amine. Certain amines (trimethylamine, triethylamine, quinoline, quinaldine, α-picoline, acridine, *etc.*) react with β-chloropropionitrile forming amine hydrochlorides and acrylonitrile, for instance:

$$(CH_3)_3N + Cl{-}CH_2CH_2CN \rightarrow (CH_3)_3N{\cdot}HCl + CH_2{=}CHCN\,.$$

On the other hand amines like n-butylamine, pyrrolidine, and morpholine yield in this case the hydrochlorides of *N*-substituted β-aminopropionitriles:



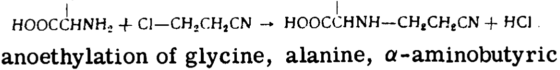
Still another group of amines (pyridine, isoquinoline, β- and γ-picolines) form the quaternary ammonium salts, for example:



According to Heininger[18] the reaction of β-chloropropionitrile with aniline in absolute ethanol yields aniline hydrochloride and acrylonitrile. Butkus and Denis[19] showed, however, that in aqueous solution these two compounds react forming *N*-(β-cyanoethyl) aniline in good yield:

$$C_6H_5NH_2 + Cl{-}CH_2CH_2CN \rightarrow C_6H_5NH{-}CH_2CH_2CN + HCl\,.$$

The cyanoethylation of α-amino-acids with β-chloropropionitrile[20,21] is accompanied by heat evolution and proceeds according to the following scheme:



$$HOOC\overset{R}{C}HNH_2 + Cl{-}CH_2CH_2CN \rightarrow HOOC\overset{R}{C}HNH{-}CH_2CH_2CN + HCl\,.$$

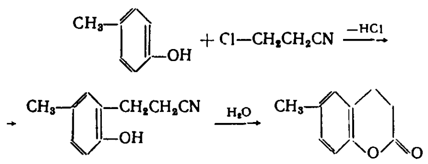
Cyanoethylation of glycine, alanine, α-aminobutyric acid, cystine, β-phenyl-α-alanine, and tyrosine, in 70–96% yields, has also been reported.

β-Chloropropionitrile was also used to obtain the *N*-cyanoethylation products of β-phenyl-β-alanine[22], γ-aminobutyric acid, δ-aminovaleric acid, ε-aminohexanoic acid, and taurine[23].

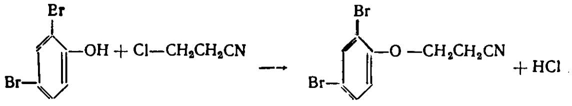
Tsukervanik and Grebenyuk[24–26] showed that direct cyanoethylation of benzene and chlorobenzene with acrylonitrile by the Friedel–Craft–Gustavson method proceeded with difficulty and gave low yields. This reaction proceeds more readily and with better yields if hydrogen chloride is added to acrylonitrile. In that case, presumably, it is not acrylonitrile, but β-chloropropionitrile which takes part in the reaction. The reaction proceeds equally readily with β-chloropropionitrile:

$$C_6H_6 + Cl{-}CH_2CH_2CN \xrightarrow{AlCl_3} C_6H_5{-}CH_2CH_2CN + HCl\,.$$

Probably the nuclear cyanoethylation of phenols by acrylonitrile and hydrogen chloride in the presence of zinc or aluminium chloride also proceeds via an intermediate formation of β-chloropropionitrile[27–34]. Cyanoethylation of the nucleus in the presence of the Friedel–Crafts–Gustavson catalyst proceeds only with great difficulty. β-Chloropropionitrile, on the other hand, may be used to obtain the products of cyanoethylation in the nucleus of many mono- and polyhydric phenols[32–34], for example:



If phenols are treated with β-chloropropionitrile in the presence of caustic alkali, cyanoethylation takes place at the hydroxyl group[35], as for example:



β-Chloropropionitrile has also been used to cyanoethylate ammonia[18,36–38], diethylamine[39], glycylglycine[21], hexitylamines[40], anthranilic acids[41,42], piperidine[43], 1-benzyl-5-aminotetrazole[44], peptones and proteins[23], cellulose[45] and other compounds[6,39,46–52].

In certain cases the cyanoethylation seems to proceed not by the direct substitution of the halogen but via the formation of acrylonitrile as an intermediate[15,41]. This assumption is favoured by the fact that acrylonitrile is formed from β-chloropropionitrile by the action of potash, caustic alkali or tertiary amines, *i.e.* compounds which react with hydrogen chloride[18,20,21,41,53]. This reaction may be of preparative importance, since the yield of acrylonitrile may reach 75–80%. Other cases of the formation of acrylonitrile from β-chloropropionitrile have also been reported[54].

(b) Use of other β-halopropionitriles in cyanoethylation. β-Bromopropionitrile was used for the cyanoethylation of diethylamine, aniline, piperidine, glycine, α-alanine, α-aminobutyric acid, cystine, α-aminophenylacetic acid, tyrosine, β-phenyl-α-alanine, β-phenyl-β-alanine, taurine, δ-aminovaleric acid, ε-aminohexanoic acid[55], hexitylamines[40], 5-aminotetrazole, 1-benzyl-5-aminotetrazole[44], certain compounds containing a mobile hydrogen atom attached to carbon[56,57], and other compounds[58,59]. Caustic alkali and tertiary amines react with β-bromopropionitrile forming acrylonitrile[55].

β-Iodopropionitrile has also been used in cyanoethylation[46].

There are no data in the literature on the use of β-fluoropropionitrile for this purpose.

2. INTRODUCTION OF THE CYANOETHYL GROUP BY MEANS OF ETHYLENE CYANOHYDRIN

The reaction of ethylene cyanohydrin with aqueous solution of potassium cyanide results in low yields of succinic dinitrile[60].

In the course of the reduction of ethylene cyanohydrin with sodium in a series of alcohols, *e.g.* ethyl, isopropyl, n-butyl, and isopentyl, the alcohol undergoes cyanoethylation, which is followed by the reduction of the nitrile group[14]:

$$\mathrm{HO{-}CH_2CH_2CN \xrightarrow[ROH]{Na} RO{-}CH_2CH_2CH_2NH_2}.$$

In no case was it possible to isolate γ-propanolamine from the reaction mixture.

Ethylene cyanohydrin reacts with benzyl alcohol in the presence of sodium forming β-benzyloxypropionitrile[61]:

$$\mathrm{C_6H_5CH_2OH + HO{-}CH_2CH_2CN \rightarrow C_6H_5CH_2O{-}CH_2CH_2CN + H_2O}.$$

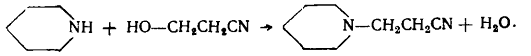
The reaction of ethylene cyanohydrin with triphenylchloromethane in the presence of pyridine yields β-(triphenylmethoxy)propionitrile[62]:

$$\mathrm{(C_6H_5)_3CCl + HO{-}CH_2CH_2CN \rightarrow (C_6H_5)_3CO{-}CH_2CH_2CN + HCl}.$$

Heated with ammonia, ethylene cyanohydrin forms β-alanine[63]. When a mixture of an amine with ethylene cyanohydrin at 300° is passed over finely powdered aluminium good yields of *N*-substituted β-aminopropionitriles are obtained[64].

In the reaction with aniline ethylene cyanohydrin yields only traces of β-(phenylamino)propionitrile[19].

The cyanoethylation of piperidine with ethylene cyanohydrin yields β-(*N*-piperidyl)propionitrile[65,66]:



The yield of the product is 22%. If powdered tin is added to the reaction mixture, as in the preparation of acrylonitrile, the cyanoethyl derivatives of piperidine is obtained in 52.5% yield.

In the presence of tin powder at 150°–170°, anabasine and ethylene cyanohydrin form the corresponding *N*-cyanoethyl derivative in 60% yield[67].

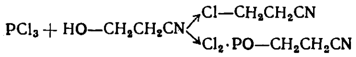
Chelintsev and his associates[68–70] showed that ethylene cyanohydrin reacted with esters of carboxylic acids in the presence of equimolar amount of sodium alcoholate forming β-alkoxypropionitriles:

$$\mathrm{HCOOC_2H_5 + HO - CH_2CH_2CN + C_2H_5ONa \rightarrow HCOONa + C_2H_5O{-}CH_2CH_2CN + C_2H_5OH}.$$

The authors regard this reaction as an unusual alkylation of ethylene cyanohydrin by carboxylic esters.

The reaction of ethylene cyanohydrin with acids, acid anhydrides and acid chlorides, as well as with isocyanates, yields the cyanoethyl esters of the corresponding acids[1,3,71–84].

In the reaction with phosphorus trichloride, ethylene cyanohydrin yields β-cyanoethyldichlorophosphite in addition to β-chloropropionitrile[85]:



$$\mathrm{PCl_3 + HO{-}CH_2CH_2CN} \begin{array}{l} \nearrow \mathrm{Cl{-}CH_2CH_2CN} \\ \searrow \mathrm{Cl_2 \cdot PO{-}CH_2CH_2CN} \end{array}$$

There are data on the use of ethylene cyanohydrin in cyanoethylations of hexitylamines[40], aldehydes and ketones[86], resorcinol (in the nucleus)[32], phenylhydrazine[52], indole[87], and other compounds[33,88,89]. Attempts to cyanoethylate α-amino-acids[20,90] and proteins[23] with ethylene cyanohydrin were unsuccessful, although under the same conditions these substances reacted with acylonitrile and β-halopropionitriles.

Ethylene cyanohydrin react with certain ethers, replacing an alkyl group by cyanoethyl group[91,92], for example:

$$\mathrm{(CH_3)_2CHOCH{=}CH_2 + HO{-}CH_2CH_2CN \rightarrow CH_2{=}CHO{-}CH_2CH_2CN + (CH_3)_2CHOH}.$$

The reaction can proceed similarly with esters[93].

3. MOBILITY OF THE CYANOETHYL GROUP BOUND TO OXYGEN

(a) β-Alkoxypropionitriles. The existence of a dynamic equilibrium and the reversibility of cyanoethylation is especially noticeable in the reaction of acrylonitrile with alcohols. Only the β-alkoxypropionitriles obtained by cyanoethylating lower primary or secondary alcohols (up to C_7) can be isolated from the reaction mixture by simple distillation. On further increase of the molecular weight, the boiling point of the resulting β-alkoxypropionitrile is so high that on distillation the reverse reaction can occur[1,94,95]. Yields obtained in cyanoethylations of secondary alcohols are lower than those from primary alcohols. The reaction of tertiary alcohols with acrylonitrile is even more difficult. Certain tertiary alcohols, *e.g.* t-butanol, can be used as solvents in cyanoethylations. On heating to 60°–80° t-butanol reacts with acrylonitrile, but the resulting ether readily decomposes into the starting components[1–3].

An exchange of the alkyl radicals takes place on heating (50°–60°) β-alkoxypropionitriles with aliphatic or aliphatic-aromatic alcohols in the presence of alkali or alcoholates[61,96]:

$$\mathrm{RO{-}CH_2CH_2CN + R'{-}OH \rightleftarrows R'O{-}CH_2CH_2CN + ROH}.$$

The yield of transcyanoethylation products is 75–80%.

Kost and Yashunskii[14] observed that if in the Vyshnegradskii reduction the alkoxy groups in β-alkoxypropionitrile and in the alcohol used as solvent are identical, the normal reaction product is obtained, the amine corresponding to the nitrile taking part in the reaction (*e.g.* β-ethoxypropionitrile in ethanol yields γ-ethoxypropylamine). If they are not identical, the γ-alkoxypropylamine formed contains the alkoxy group from the alcohol used as solvent. For instance, the reductions of both β-methoxypropionitrile and β-(β′-hydroxyethoxy)propionitrile in n-butanol yield only γ-butoxypropylamine. Similar observations were made by Seeger[97].

It may be noted that in the Vyshnegradskii reaction α- and γ-alkoxynitriles undergo normal reduction, without the exchange of alkoxy groups.

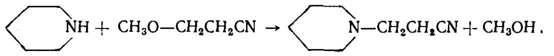
The cleavage of the cyanoethyl–oxygen bond occurs in the reduction of β-alkoxypropionitriles with lithium aluminium hydride[98,99], or with Raney nickel catalyst [100-102]. The yields of alcohols in reductions by lithium aluminium hydride are 80–90%.

Attempts to hydrate the β-cyanoethyl ether derived from dimethyl vinyl ethynyl carbinol in aqueous methanol solution resulted in the splitting off of one molecule of acrylonitrile, followed by the isomerisation of the remaining dimethyl vinyl ethynyl carbinol into β,β-dimethyldivinyl ketone; under the reaction conditions used the latter compound united with methanol forming 1-methoxy-5-methyl-4-hexen-3-ol[103]. The saponification of β-cyanoethyl ethers to the corresponding acids has to be carried out with concentrated hydrochloric acid, since heating with alkalis catalyses the reversal of cyanoethylation. The alkaline hydrolysis of β-cyanoethyl ethers derived from acetylenic alcohols in 50% aqueous methanol yields β-methoxypropionic acid[106]. Heating β-alkoxypropionitriles with aqueous ammonia yields β-alanine[107,108].

Decyanoethylation occurs on pyrolysis of β-alkoxypropionitriles[109]. Heating β-methoxypropionitrile at 300°–350° yields 80–90% acrylonitrile. Acrylonitrile is obtained in the same yield from β-ethoxypropionitrile. Other cases of the cleavage of the bond between the cyanoethyl group and oxygen in acid[109,110] or alkaline media[1-3,14,95,110] are also known.

Certain β-alkoxypropionitriles can be used as cyanoethylating agents. For instance, β-methoxypropionitrile was used to cyanoethylate ammonia[107,111], dimethylamine[112], dibutylamine[112,113], piperidine[113], morpholine and other amines[112]. In all cases the products of transcyanoethylation were isolated, namely β-aminopropionitrile and its *N*-substituted derivatives:

$$(CH_3)_2NH + CH_3O{-}CH_2CH_2CN \rightarrow (CH_3)_2N{-}CH_2CH_2CN + CH_3OH,$$



In the reaction with β-ethoxypropionitrile, malonic ester gave its mono- and di-cyanoethyl derivatives[113]. This alkoxynitrile was used in the preparation of *N*-(β-cyanoethyl)indole[87]. Cyanoethylation of diethylamine and malonic ester was also carried out by means of β-butoxypropionitrile[114].

Heating β-alkoxypropionitriles with aromatic amines[19,115] in aqueous solution at 100° results in transcyanoethylation according to the following scheme:

$$C_6H_5NH_2 + RO{-}CH_2CH_2CN \rightarrow C_6H_5NH{-}CH_2CH_2CN + ROH .$$

Alkoxypropionitriles were obtained by cyanoethylating methyl, ethyl, propyl, butyl, isobutyl, s-butyl, pentyl, and isopentyl alcohols. The reaction proceeds in the presence of very small amounts of caustic alkali or triethylamine.

Instead of acrylonitrile, certain β-alkoxypropionitriles were reacted with phenylhydrazine to form 3-amino-1-phenylpyrazoline[52].

(b) β,β′-Dicyanodiethyl ether. Kost and Yashunskii[14] showed that the Vyshnegradskii reduction of β,β′-dicyanodiethyl ether proceeded in an anomalous manner, giving rise to γ-alkoxypropylamines, in which the alkoxy radical was that of the alcohol used as solvent:

$$O(CH_2CH_2CN)_2 \xrightarrow[C_4H_9OH]{Na} C_4H_9O{-}CH_2CH_2CH_2NH_2$$

The linear diamine could not be isolated.

Reduction of β,β′-dicyanodiethyl ether in the presence of Raney nickel (15–150 atm, 80°–125°) yielded a mixture of products, from which γ,γ′-diaminodipropyl ether, γ-aminopropanol, and propylamine were isolated[116]:

$$O(CH_2CH_2CN)_2 \begin{array}{l} \nearrow O(CH_2CH_2CH_2NH_2)_2 \\ \searrow HOCH_2CH_2CH_2NH_2 + CH_3CH_2CH_2NH_2 \end{array}$$

Use of β,β′-dicyanodiethyl ether for cyanoethylating hydrogen sulphide[117], mercaptans and thiophenols[118], and ketones[119], has been described in patents.

Heating β,β′-dicyanodiethyl ether with aqueous aniline in the presence of small amounts of caustic alkali or triethylamine gave the transcyanoethylation product, *viz.* β-(phenylamino) propionitrile[19].

Heating β,β′-dicyanodiethyl ether at 195°–210° in the presence of sodium formate resulted in 94% acrylonitrile[120]. Acrylonitrile utilised in the side-reaction for the formation of β,β′-dicyanodiethyl ether during the cyanoethylation of cellulose fibres, can in this way be recovered[121]. Decyanoethylation occurs upon saponification[122] and pyrolysis[109] of β,β′-dicyanodiethyl ether, or upon its heating with aqueous ammonia[108].

(c) Products of the cyanoethylation of monohydric alcohols and carbohydrates. Dicyanoethyl derivatives of ethylene glycol and propane-1,2-diol and the tricyanoethyl derivative of glycerol react in aqueous solution at 100° with aromatic amines forming β-arylaminopropionitriles[115]. In contrast to β-alkoxypropionitriles, the glycol di-β-cyanoethyl ether does not require an alkaline catalyst.

Heating diethylene glycol with its dicyanoethyl derivative in the presence of caustic alkali yields the corresponding monocyanoethyl derivative[123].

Attempts to cyclise the dicyanoethyl derivative of 1,10-decanediol by the Ziegler method into the corresponding imine were unsuccessful. In this reaction decanediol was recovered in 90% yield[124]:

$$NCCH_2CH_2{-}O(CH_2)_{10}O{-}CH_2CH_2CN \rightarrow HO(CH_2)_{10}OH + 2\ CH_2{=}CHCN.$$

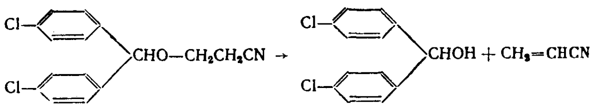
Yashunskaya *et al.*[125] made a study of the conditions for the preparation of carboxyethylcellulose *via* the cyanoethylation with acrylonitrile. They established that the rate of cyanoethylation increased with increasing concentration of sodium hydroxide up to 8%. Further increase of alkali concentration caused a lowering of the number of cyanoethyl groups in the reaction product. Other conditions being equal, raising the reaction temperature to 45° causes a considerable drop in the extent of cyanoethylation. However, the authors explain this by the concentration of acrylonitrile being reduced due to hydrolysis. On treatment with a solution of caustic soda, or on repeated washing with soap or soda solution, the nitrogen content of the cyanoethyl derivative is lowered[121]. This was also considered to be due to the saponification of cyanoethyl groups. The authors neglected the possible reverse reaction in the presence of alkali, namely of the removal of acrylonitrile from the cyanoethyl derivative of cellulose, or of acrylic acid from its carboxyethyl derivative. Such cleavage of the bond between the cyanoethyl group and oxygen is known to take place in the products of cyanoethylation of polyvinyl alcohol[126,127] and certain polysaccharides[128]. Further evidence was provided by the work of Danilov and Lopatenok[129], who showed that with sodium in liquid ammonia cyanoethylcellulose underwent partial deoxidation, the principal reaction under these conditions being the direct removal of acrylonitrile. Polyacrylonitrile and acrylic acid were also observed among the reaction products. No carboxyethylcellulose was observed under these conditions.

(d) Products of the cyanoethylation of alicyclic, aromatic, and heterocyclic alcohols. Boiling β-cyclohexyloxypropionitrile, 1-phenyl-, 2-phenyl-2-propyl-, and 2-phenyl-2-benzyl-1-(β-cyanoethoxy)cyclohexane with chloroacetyl chloride in chloroform or ether, or with bromopropionyl bromide in the presence of potash, results in the formation of the corresponding cyclohexylchloroacetates or cyclohexylbromopropionates[130].

The reaction of β-cyclohexyloxypropionitrile with aniline consists in transcyanoethylation, the product being β-(phenylamino)propionitrile[115].

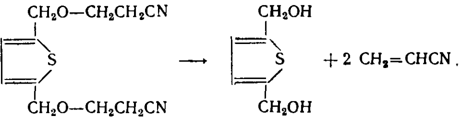
The reaction product from benzaldehyde and acrylonitrile eliminates acrylonitrile in alkaline media[131].

97% decyanoethylation occurs on hydrolysis of the cyanoethyl derivative of *p,p'*-dichlorodiphenylcarbinol with 15–25% alkali solution[132]:



The bond between the cyanoethyl group and oxygen in β-benzyloxypropionitrile undergoes cleavage in the presence of Raney nickel catalyst[100].

Decyanoethylation is also observed during the reduction of the cyanoethyl derivatives of certain heterocyclic alcohols in the presence of Raney cobalt[133]:

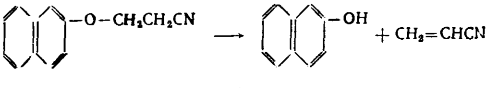


(e) β-Aryloxypropionitriles. The reaction of β-aryloxypropionitriles with aromatic amines in aqueous solution at 100° consists of transcyanoethylation[19,115]:

$$ArO—CH_2CH_2CN + Ar'NH_2 \rightarrow Ar'NH—CH_2CH_2CN + ArOH.$$

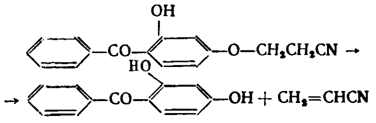
This reaction proceeds more readily than in the case of β-alkoxypropionitriles, and no alkali is required. In addition to the product of transcyanoethylation, that of decyanoethylation could often be isolated. It may be noted that under similar conditions the reaction of aromatic amines with β-aryloxypropionic acids did not form the products of dealkylation or transalkylation.

Decyanoethylation occurs on heating β-phenoxypropionitrile, the β-cyanoethyl ethers derived from α- and β-naphthols, as well as the dicyanoethyl ethers derived from pyrocatechol, resorcinol, and hydroquinone, with 5% alkali solution[115]. Decyanoethylation yields the corresponding phenols, for instance:



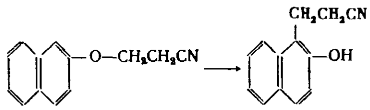
The yield of β-naphthol is 87%.

Certain β-cyanoethyl ethers derived from 2- and 4-aroylphenols behave similarly[134]. For instance, 4-benzoylresorcinol monocyanoethyl ether forms 2,4-dihydroxybenzophenone on heating for five minutes with 10% sodium hydroxide:

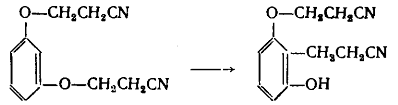


It follows from the foregoing that the β-cyanoethyl ethers derived from phenols cannot be saponified to corresponding β-carboxyethyl ethers using alkali. Mineral acids should be used instead. If the cyanoethyl group is not attached to oxygen, but to carbon [*e.g.* in 1-(β-cyanoethyl)-2-naphthol] the saponification proceeds readily in the presence of alkali hydroxides. In that case neither the higher concentration of alkaline solutions nor longer heating can give rise to decyanoethylation[135].

On heating 2-naphthyl β-cyanoethyl ether in benzene solution in the presence of alkali, the cyanoethyl group is transferred from oxygen to carbon, 1-(β-cyanoethyl)-2-naphthol being formed in the process[115]:



Similar reaction takes place on heating a methanol solution of resorcinol dicyanoethyl ether in the presence of sodium alcoholate:

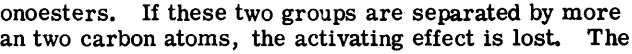


Possibly, the reported *C*-cyanoethylation of 2,6-di-t-butylphenol[136], β-naphthol[135], 9-fluorenol[137], and resorcinol[138] with acrylonitrile in the presence of alkali also proceeds via *O*-cyanoethylation.

The cleavage of the bond between the cyanoethyl group and oxygen is also observed on reduction of β-aryloxypropionitriles with lithium aluminium hydroxide[98] or on pyrolysis[109].

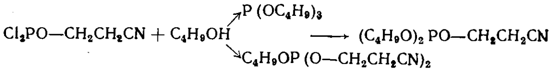
(f) β-Cyanoethyl esters. The preparation of acrylonitrile from ethylene cyanohydrin is sometimes effected by the esterification of the latter compound with acid anhydrides or chlorides followed by thermal or catalytic removal of acrylonitrile[1,78-84], for instance:

$$CH_3COO—CH_2CH_2CN \rightarrow CH_3COOH + CH_2{=}CHCN,$$



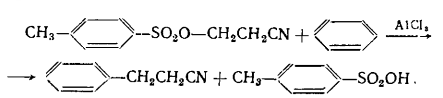
A nitrile group in the β-position to a $-OPO_3H_2$ group acts as an activator of the hydrolysis of these phosphate monoesters. If these two groups are separated by more than two carbon atoms, the activating effect is lost. The effect of the nitrile group in activating hydrolysis is stronger than that of a carboxyl or ester group[139,140]. The β-cyanoethyl group in mixed esters of phosphoric acid is more readily removed by hydrolysis than other groups[141].

Tributylphosphate, dibutyl β-cyanoethyl phosphite, and butyl di-(β-cyanoethyl) phosphite were isolated from the mixture of products obtained in the reaction of β-cyanoethyl dichlorophosphite with butanol[142]:



$$Cl_2PO—CH_2CH_2CN + C_4H_9OH \longrightarrow \begin{cases} P(OC_4H_9)_3 \\ (C_4H_9O)_2PO—CH_2CH_2CN \\ C_4H_9OP(O—CH_2CH_2CN)_2 \end{cases}$$

The reaction of p-toluenesulphonyl cyanoethyl ester with benzene in the presence of aluminium chloride gave 72% β-phenylpropionitrile[78]:



With pyrrolepotassium this ester yields *N*-(β-cyanoethyl)-pyrrole[143].

Cyanoethyl esters have also been used for cyanoethylating piperidine[144] and resorcinol (in the nucleus)[33].

4. THE BOND BETWEEN A CYANOETHYL GROUP AND SULPHUR

Decyanoethylation is observed during the reaction of β-alkylmercaptopropionitriles with organomagnesium compounds[145].

Transcyanoethylation occurs in the reaction of β-cyanodiethyl sulphide with aniline[19] in aqueous solution at 100°:

$$C_2H_5S—CH_2CH_2CN + C_6H_5NH_2 \rightarrow C_6H_5NH—CH_2CH_2CN + C_2H_5SH.$$

The yield of β-(phenylamino)propionitrile is very small. Certain *S*-cyanoethyl compounds react with heterocyclic bases forming quaternary ammonium salts[10].

The reduction of dicyanodiethyl sulphide by the Vyshnegradskii method yields β-alkoxypropylamines[14]:

$$S(CH_2CH_2CN)_2 \xrightarrow[C_4H_9OH]{Na} C_4H_9O—CH_2CH_2CH_2NH_2.$$

This reaction seems to proceed through the intermediate formation of acrylonitrile. An attempt to obtain the linear diamine was unsuccessful. Under these conditions other *S*-cyanoethyl compounds also fail to give the normal reduction products[146].

In 1956, in their study of the action of acrylonitrile on the aqueous solution of sodium sulphinates, Achmatowicz and Michalski[147] showed that an equilibrium was established in the system, containing only small amounts of sulphones. To obtain the latter compounds they added reagents which bind sodium hydroxide. The resulting sulphones (where the cyanoethyl group was one of the radicals) are unstable in alkaline solution, and decomposes even at room temperature yielding acrylonitrile.

$$R\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—CH_2CH_2CN \rightarrow RSO_2H + CH_2{=}CHCN.$$

5. THE BOND BETWEEN A CYANOETHYL GROUP AND NITROGEN

(a) Cyanoethylation products from ammonia and hydrazine. Terent'ev *et al.*[148] studied the reaction of acrylonitrile with aqueous ammonia: the proportion of the resulting mono-, di-, and tri-cyanoethyl derivatives depends on the reaction conditions and the ratio of the starting components. At all stages of the reaction there existed a dynamic equilibrium between the participants:

$$CH_2{=}CHCN \underset{-NH_3}{\overset{+NH_3}{\rightleftarrows}} NH_2—CH_2CH_2CN \underset{+NH_3}{\overset{-NH_3}{\rightleftarrows}} NH(CH_2CH_2CN)_2 \underset{+NH_3}{\overset{-NH_3}{\rightleftarrows}} N(CH_2CH_2CN)_3.$$

Other research workers have also observed the dynamic equilibrium in the cyanoethylation of ammonia[3,58,65,116,149–152]. Using only a small excess of ammonia the main reaction product is β,β'-dicyanodiethylamine (88%). Increased ammonia concentration causes an increase of the yield of β-aminopropionitrile. Raising the reaction temperature also has a favourable effect on the formation of the mono-cyanoethyl derivative. If the reaction is carried out rapidly (1–5 min), at high temperature (105°–110°), and using considerable excess of ammonia, the yield of β--aminopropionitrile may reach 80–92%.

Moist β-aminopropionitrile decomposes on storage, and pressure builds up in the container even at room temperature[153].

Whitmore and his collaborators considered that the polymer formed during the storage of β-aminopropionitrile consisted of polyacrylonitrile, formed as a result of the liberation of ammonia[58]. Other authors, however, refuted this assumption[148,151].

On catalytic reduction of β-aminopropionitrile, trimethylenediamine, di-(γ-aminopropyl)amine, and tri-(γ--aminopropyl)amine are obtained[58,116]. The same mixture was obtained by the reduction of β,β'-dicyanodiethylamine.

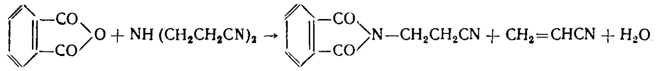
During the storage of pure β,β'-dicyanodiethylamine, ammonia is liberated, leaving the crystalline tricyanoethyl product. If the sample is kept in a closed container, part of the liberated ammonia re-enters the reaction, and β--aminopropionitrile separates on distillation.

Heated to 200°–250° or higher, β,β'-dicyanodiethylamine decomposes into acrylonitrile and β-aminopropionitrile[3,148,154]:

$$NH(CH_2CH_2CN)_2 \rightarrow NH_2—CH_2CH_2CN + CH_2{=}CHCN.$$

This reaction proceeds more readily *in vacuo* in the presence of a catalyst, *e.g.* disodium phosphate. The yield of β-aminopropionitrile in that case may reach 85%. Ammonia reacts with β,β'-dicyanodiethylamine forming β-aminopropionitrile[148,149] or β-alanine[155].

β,β'-Dicyanodiethylamine reacts with acetic anhydride and phthalic anhydride forming, respectively, *N*-(β--cyanoethyl)acetamide[150] and the cyanoethyl derivative of phthalimide (at 200°, by elimination of acrylonitrile)[156]:



Heating β,β'-dicyanodiethylamine at 230° with the anhydride of perylene-3,4,9,10-tetracarboxylic acid, yields the dicyanoethyl derivative of the corresponding diimide[157,158].

Efforts to synthesise β,β'dicyanodiethyl(triphenylmethyl)amine from β,β'-dicyanodiethylamine and triphenylchloromethane failed owing to the elimination of one molecule of acrylonitrile during the reaction[62]:

$$(C_6H_5)_3CCl + NH(CH_2CH_2CN)_2 \rightarrow (C_6H_5)_3CNH—CH_2CH_2CN + CH_2{=}CHCN + HCl.$$

β-Cyanoethyl(triphenylmethyl)amine was obtained in 78% yield.

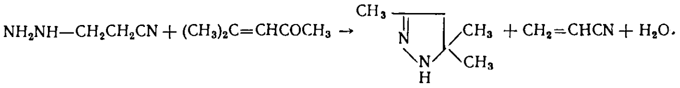
In the presence of equimolar amounts of hydrochloric acid, the mono-, di-, and tri-cyanoethyl derivatives of ammonia react with aniline in aqueous solution yielding β-(phenylamine)propionitrile[19].

Hydrazine hydrate reacts vigorously with acrylonitrile, adding up to four molecules of the latter. However, the tetracyanoethyl derivative of hydrazine loses two molecules of acrylonitrile on distillation in a high vacuum giving a mixture of the isomeric dicyanodiethyl derivatives of hydrazine[3].

Benzoyl chloride reacts with unsymmetrical di-(β-cyanoethyl)hydrazine forming β-cyanoethyldibenzoylhydrazine[159]:

$$NH_2N(CH_2CH_2CN)_2 + 2\ C_6H_5COCl \rightarrow C_6H_5CONHN\begin{matrix} CH_2CH_2CN \\ COC_6H_5 \end{matrix} + CH_2{=}CHCN + 2HCl.$$

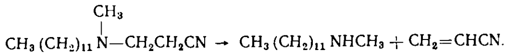
Kost and his associates[160] found that heating β-cyanoethylhydrazine with mesityl oxide in neutral solution yields 3, 5, 5-trimethylpyrazoline:



N-(β-Cyanoethyl)pyrazoline could not be obtained under these conditions. The authors consider that the reaction proceeds by the intermediate removal of β-cyanoethylhydrazine, forming unsubstituted hydrazine. The assumption that the N-(β-cyanoethyl)pyrazoline already formed splits off the cyanoethyl group is not probable, since this compound is stable under the given condition.

(b) β-Alkylaminopropionitriles. The instability of the bond between the cyanoethyl group and nitrogen is illustrated by the decyanoethylation of certain β-alkylaminopropionitriles on distillation. Thus, the addition products from acrylonitrile and ethanolamine or diethanolamine decompose completely on vacuum distillation into the starting components[58,161]. The vacuum distillation of higher β-dialkylaminopropionitriles has to be carried out rapidly and at the lowest possible residual pressure, in order to avoid an appreciable dissociation into starting compounds[58].

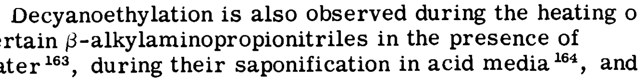
On heating for many hours at 250°–275° the cyanoethyl derivative of methyldodecylamine decomposes practically quantitatively into the initial amine and acrylonitrile[5,6]:



$$CH_3(CH_2)_{11}\overset{\overset{CH_3}{|}}{N}{-}CH_2CH_2CN \rightarrow CH_3(CH_2)_{11}NHCH_3 + CH_2{=}CHCN.$$

β-(Cyanoethyl)methyldodecylamine is usually obtained by cyanoethylation of dodecylamine followed by methylation. The foregoing reaction thus represents a method for preparing unsymmetrical secondary amines, the cyanoethyl group serving to protect the amino radical.

On heating dicyanoethylethylenedinitramine with aqueous alkali the starting nitramine is recovered in 82% yield[162]:



$$\begin{matrix} O_2N \\ NCCH_2CH_2 \end{matrix}NCH_2CH_2N\begin{matrix} NO_2 \\ CH_2CH_2CN \end{matrix} \rightarrow O_2NNHCH_2CH_2NHNO_2 + 2\ CH_2{=}CHCN$$

Decyanoethylation is also observed during the heating of certain β-alkylaminopropionitriles in the presence of water[163], during their saponification in acid media[164], and in some other cases[165].

Heating β-cyanoethyl(triphenylmethyl)amine with an excess of ethylene glycol at 160°–170° for 4–5 hours yields the decyanoethylated product[166]:

$$(C_6H_5)_3CNH{-}CH_2CH_2CN \rightarrow (C_6H_5)_3CNH_2 + CH_2{=}CHCN.$$

The yield of triphenylethylamine is 90%. Decyanoethylation does not proceed with the same ease in the case of β-(dimethylamino) and β-(diethylamino)propionitriles.

β-(Diethylamino)propionitrile hydrochloride decomposes on heating into diethylamine hydrochloride and acrylonitrile[167,168].

Acrylonitrile is readily removed by pyrolysis of the quaternary ammonium salts prepared from β-dialkylaminopropionitriles[53]. In the presence of alkali this proceeds even at 100°, and the yield of acrylonitrile may reach 88%.

During the alkylation of the cyanoethyl derivative of 2-amino-2-methyl-1-propanol with ethyl iodide, acrylonitrile is split off and the hydroiodide of the N-ethylated amino alcohol is obtained[169]:

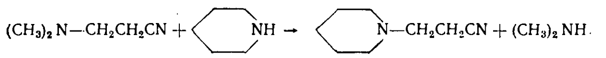
$$HOCH_2C(CH_3)_2NH - CH_2CH_2CN + C_2H_5I \rightarrow HOCH_2C(CH_3)_2NHC_2H_5{\cdot}HI + CH_2{=}CHCN.$$

Allyl bromide reacts similarly.

Methylation of β-(benzylamino)propionitrile by formaldehyde and formic acid yields 38% benzyldimethylamine[170]:

$$C_6H_5CH_2NH{-}CH_2CH_2CN + 2\ CH_2O + 2\ HCOOH \rightarrow$$
$$\rightarrow C_6H_5CH_2N(CH_3)_2 + CH_2{=}CHCN + 2\ CO_2 + 2\ H_2O.$$

A great deal of work has been devoted to the study of β-aminopropionitriles as cyanoethylating agents. By heating β-dimethylaminopropionitrile with piperidine at 150°–160° for 10 h, Terent'ev *et al.*[113] succeeded in obtaining 30% β-(N-piperidyl) propionitrile:



They carried out the cyanoethylation of dibutylamine in the same manner.

By heating methanol and butanol with the quaternary methosulphate of β-(dimethylamino)propionitrile, the above authors obtained β-methoxypropionitrile and β-butoxypropionitrile, respectively. For example:

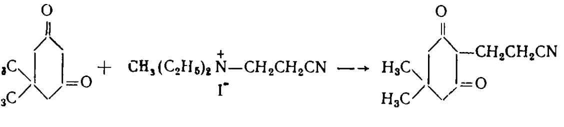
$$(CH_3)_3N{-}CH_2CH_2CN{\cdot}(CH_3)SO_4^- + CH_3OH \rightarrow CH_3O{-}CH_2CH_2CN + (CH_3)_3N + CH_3HSO_4.$$

Heated with indole in alkaline solution, β-(dimethylamino)propionitrile forms β-(N-indolyl)propionic acid[87].

Methyl and butyl alcohols react with the quaternary salts derived from β-dialkylaminopropionitriles yielding the corresponding β-alkoxypropionitriles[53]. β-Butoxypropionitrile was obtained in 74% yield.

β-(Diethylamino)propionitrile and β-(ethylbenzylamino)propionitrile methiodides react with potassium cyanide forming succinic dinitrile[60]. β-(Diethylamino)propionitrile methiodide reacts with the aqueous solution of potassium cyanide forming succinic acid[53]. β-(Diethylamino)propionitrile methiodide has also been used for the cyanoethylation of morpholine and malonic ester[114].

Bradford and his collaborators[171] failed in their attempt to cyanoethylate dimedone with acrylonitrile. They succeeded, however, in cyanoethylating the sodium salt of dimedone with β-(diethylamino)propionitrile methiodide:



Nazarov and Zav'yalov[172] showed later that in the presence of aqueous caustic soda at 100° dimedone reacts readily and completely with acrylonitrile forming mono- and di-cyanoethyl derivatives. These authors dispute the reaction mechanism suggested by English research workers, whereby the possible intermediate formation of acrylonitrile is excluded.

Heated with triethylphosphite, β-(dimethylamino)propionitrile methiodide forms the diethyl ester of β-cyanoethylphosphinic acid[173].

In the reaction of acrylonitrile with 9, 10-dihydrophenanthridine Bates and Cymerman-Craig[174] observed that the latter compound underwent dehydrogenation. The cyanoethyl derivative of 9, 10-dehydrophenanthridine was obtained using β-(diethylamino)propionitrile.

By heating β-(diethylamino)propionitrile with the salts of aromatic amines, Bekhli[167,168] obtained the monocyanoethyl derivatives of the latter compounds, and thus discovered a new method for the preparation of β-arylaminopropionitriles. The author regards this reaction as one of alkyl–aryl transamination. β-(Diethylamino)propionitrile reacts similarly with anthranilic acids[41].

Cyanoethylation of aromatic amines with β-(diethylamino)propionitrile has also been studied by a number of other research workers[19,60,175-177].

Besides β-(diethylamino)propionitrile, the monocyanoethyl derivatives of methylamine, dimethylamine, butylamine, benzylamine[19] and ethylbenzylamine[60], and the dicyanoethyl derivatives of methylamine, ethylamine, and butylamine, have also been used for cyanoethylating aromatic amines[19].

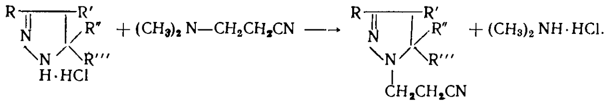
Since it requires only one mole of acid, cyanoethylation is usually carried out with the salts of aromatic amines (hydrochlorides, acetates, sulphonates, *etc.*), or the salts of β-alkylaminopropionitriles. If two moles of acid are present, as for instance in the reaction of the hydrochloride of an aromatic amine with β-alkylaminopropionitrile hydrochloride, transcyanoethylation does not take place. The yield of β-arylpropionitrile increases with the basicity of the aromatic amine. The presence of *O*- or *N*-substituents in aromatic amine has an adverse effect on the yield of cyanoethylation products. The presence of a methyl radical in the cyanoethyl group lowers the capacity of this compound to take part in such reactions. β-(Diethylamino)-α-dimethylpropionitrile (where elimination of the unsaturated compound is not possible) does not react with *p*-anisidine. Nevertheless, the problem of the reaction mechanism remains uncertain.

Bekhli[167,168] considers that the cyanoethylation of aromatic amines by β-(diethylamino)propionitrile proceeds *via* the formation of acrylonitrile, followed by the addition of the latter to the amine. The experimentally established elimination of acrylonitrile in 47% yield under the conditions used in this reaction, and in 77% yield on heating β-(diethylamino)propionitrile hydrochloride in the absence of arylamine, may be taken as evidence supporting this mechanism.

According to Cymerman-Craig and his associates[177] this reaction proceeds by a substitution mechanism. They showed that in the cyanoethylation of arylamine salts by the deuterated diethylaminopropionitrile, $(C_2H_5)_2N-CH_2CHDCN$, the $-CH_2CHDCN$ group remains unchanged throughout the reaction.

A method has been described for the cyanoethylation of aromatic amines[178,179] (in the form of hydrochlorides or benzenesulphonates) and of anthranilic acid[41], by means of acrylonitrile and diethylamine. It is possible that here the reaction proceeds through the intermediate formation of diethylaminopropionitrile, namely that it is in fact a transcyanoethylation.

The cyanoethyl derivatives of dimethylamine and diethylamine rather than acrylonitrile itself were reacted with phenylhydrazine in the synthesis of 3-amino-1-phenylpyrazoline[52]. β-(Dimethylamino)propionitrile and *p*-tolylhydrazine similarly gave 3-amino-1-*p*-tolylpyrazoline[180]. The reaction of acrylonitrile with pyrazolines in anhydrous media results not in cyanoethylation, but in a vigorous polymerisation of acrylonitrile. The cyanoethylation of pyrazolines was carried out with β-(dimethylamino)propionitrile[181]:



The reaction proceeds at 170° in the presence of one equivalent of hydrogen chloride (either pyrazoline hydrochloride or aminonitrile hydrochloride are used). The yields of the cyanoethylated pyrazolines are 30–50%.

(c) *N*-Cyanoethyl derivatives of acid amides. On vacuum distillation (150°, 1.9 mm) the dicyanoethyl derivative of acrylamide yields the monocyanoethyl derivative[182]:

$$CH_2{=}CHCON(CH_2CH_2CN)_2 \rightarrow CH_2{=}CHCONH{-}CH_2CH_2CN + CH_2{=}CHCN.$$

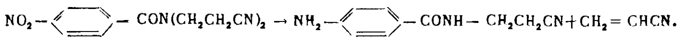
On heating the dicyanoethyl derivatives of a series of amides of carboxylic and sulphonic acids (acetamide, benzamide, *p*-nitrobenzamide, *p*-chlorobenzenesulphonamide, *etc.*) in absolute ethanol, or benzene in the presence of sodium alcoholate or potassium hydroxide for 2–5 h, the *N*-monocyanoethyl derivatives of the corresponding acid amides are formed in good yields[183]:

$$RCON(CH_2CH_2CN)_2 \rightarrow RCONH{-}CH_2CH_2CN + CH_2{=}CHCN\ ,$$
$$RSO_2N(CH_2CH_2CN)_2 \rightarrow RSO_2NH{-}CH_2CH_2CN + CH_2{=}CHCN.$$

β-Ethoxypropionitrile may be found among the reaction products. In the presence of even very small amounts of water the nitrile group is partly hydrolysed[183,184].

The elimination of one cyanoethyl group is observed on heating certain dicyanoethyl derivatives of thiourea in the presence of alkoxides[185].

One cyanoethyl group is also eliminated during the reduction of the nitro-group in *N*,*N*-di-(β-cyanoethyl)-*p*-nitrobenzamide, under the conditions leaving the nitrile group intact[183]:

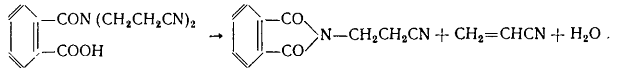


When acetamide is heated with its dicyanoethyl derivative in the presence of alkali the monocyanoethyl derivative is obtained in 62% yield[3]:

$$CH_3CON(CH_2CH_2CN)_2 + CH_3CONH_2 \rightarrow 2\ CH_3CONH{-}CH_2CH_2CN.$$

p-Toluenesulphonamide and its dicyanoethyl derivative similarly form the monocyanoethyl compound[186]. In fact, the disproportionation of dicyanoethyl compounds in the presence of alkali is the best method for preparing the monocyanoethyl derivatives of arylsulphonamides[187].

Heating dicyanoethyl monoamides of dibasic acids yields the corresponding *N*-cyanoethyl imides[156,188], for instance:



Alkaline hydrolysis of *N,N*-dicyanoethyl derivatives of a series of sulphonamides (toluene sulphonamide, *p*-chlorobenzenesulphonamide, β-naphthalenesulphonamide, *etc.*) yields the corresponding carboxylethyl derivatives[184,189–191]:

$$RSO_2N(CH_2CH_2CN)_2 \rightarrow RSO_2NH-CH_2CH_2COOH.$$

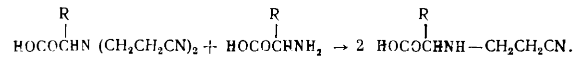
The hydrolysis of *N,N*-dicyanoethyl sulphonamides into dicarboxyethyl sulphonamides is carried out in the presence of hydrochloric acid[192] or a concentrated solution of potassium hydroxide in isopentyl alcohol[187].

(d) Cyanoethylation of amino-acids and their derivatives. The mobility of β-cyanoethyl group in mono- and di-cyanoethyl amino-acids and their derivatives has lately been given much attention. Butskus and Denis[193] established that one of the two cyanoethyl groups attached to nitrogen in amino-acids is easily removed on heating in water in the presence of tertiary amines or caustic alkali:

$$HOCO\overset{R}{C}HN(CH_2CH_2CN)_2 \rightarrow HOCO\overset{R}{C}HNH-CH_2CH_2CN + CH_2{=}CHCN.$$

In certain cases this reaction proceeds on simply heating the aqueous solution, or by pyrolysis.

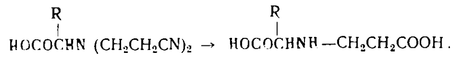
On heating α-amino-acids with their dicyanoethyl derivatives in the presence of caustic alkali, a redistribution of cyanoethyl groups takes place:



$$HOCO\overset{R}{C}HN(CH_2CH_2CN)_2 + HOCO\overset{R}{C}HNH_2 \rightarrow 2\ HOCO\overset{R}{C}HNH-CH_2CH_2CN.$$

In their study of the *N,N*-dicyanoethyl derivatives of α-amino-acids, McKinney and his collaborators[194–196] observed the instability of one cyanoethyl group to heat, alkali, and acids. On heating *N,N*-di-(β-cyanoethyl)-α-alanine above its melting point, it solidifies and then melts again at the melting point of *N*-monocyanoethyl-α-alanine.

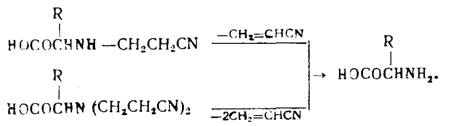
During the hydrolysis of dicyanoethyl derivatives of α-amino-acids one cyanoethyl group is eliminated giving rise to the formation of monocarboxyethyl derivatives of amino-acids:



$$HOCO\overset{R}{C}HN(CH_2CH_2CN)_2 \rightarrow HOCO\overset{R}{C}HNH-CH_2CH_2COOH.$$

There is no formation of dicarboxyethyl derivatives in this reaction.

By selecting suitable reaction conditions, complete removal of cyanoethyl groups in mono- and di-cyanoethyl derivatives of α-amino-acids can be effected[193]:



$$\left.\begin{array}{l} HOCO\overset{R}{C}HNH-CH_2CH_2CN \xrightarrow{-CH_2=CHCN} \\ HOCO\overset{R}{C}HN(CH_2CH_2CN)_2 \xrightarrow{-2CH_2=CHCN} \end{array}\right] \rightarrow HOCO\overset{R}{C}HNH_2.$$

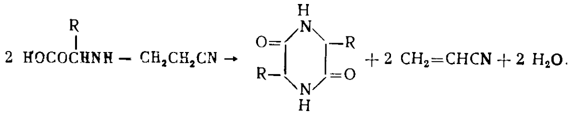
The yields of the products of complete decyanoethylation may reach 80%. The compound to undergo decyanoethylation is heated at 100° in aqueous solution of ammonia, hydrazine, dimethylamine, diethylamine, or piperidine. Other amines, *e.g.* methylamine, ethylene diamine, *etc.* can also be used. Good results are obtained using 2–10% aqueous ammonia. By increasing the ammonia concentration to 25% the yield of the decyanoethylation product is lowered. Use of gaseous or alcoholic ammonia does not give positive results.

The decyanoethylation of esters, amides, or hydrazides of cyanoethyl derivatives of α-amino-acids by 10% aqueous ammonia is accompanied by hydrolysis of the ester, amide, and hydrazide function to carboxylic acid[193,197]. It is remarkable that the presence of water favours both the introduction of cyanoethyl groups into the esters of α-amino-acids[198], and their removal[20,193].

N-Mono- and *N,N*-di-(β-cyanoethyl)glycylglycine readily undergo decyanoethylation in the presence of 2–5% aqueous ammonia, namely under the conditions which do not affect the peptide bond[193]. It is thus possible to use the β-cyanoethyl group for the protection of the amino-group in the synthesis of peptides.

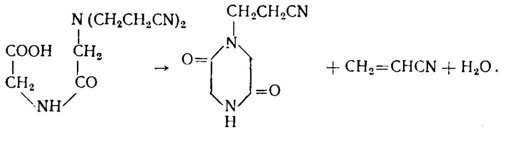
Heating mono- and di-cyanoethyl derivatives of β-amino acids[22], ε-aminohexanoic acid, and taurine[23] with an aqueous solution of ammonia and hydrazine, results in the formation of the corresponding unsubstituted amino-acids. This reaction proceeds less readily with the cyanoethyl derivatives of δ-aminovaleric acid.

On heating α-amino-acids in glycol solution diketopiperazines are formed. Butskus[199] showed, however, that on heating the monocyanoethyl derivatives of α-amino-acids (glycine, alanine, α-aminobutyric acid and valine) in ethylene glycol at 160°–170° the expected 1,4-di-(β-cyanoethyl)-2,5-diketopiperazines are not formed, but their decyanoethylation products, namely 2,5-diketopiperazines:



Dicyanoethyl derivatives of α-amino-acids behave likewise.

Heating *N,N*-di-(β-cyanoethyl)glycylglycine in ethylene glycol removes one cyanoethyl group and causes simultaneous cyclisation into 1-(β-cyanoethyl)-2,5-diketopiperazine:



1-(β-Cyanoethyl)-2,5-diketopiperazine is obtained by cyclisation of *N*-(β-cyanoethyl)glycylglycine, *viz.* the reaction proceeds without the elimination of the cyanoethyl group.

The conversion of the cyanoethyl derivatives of α-amino-acids to 2,5-diketopiperazines seems, therefore, to proceed *via* decyanoethylation, followed by the cyclisation of the resulting α-amino-acids. The fact that the reaction can be stopped at a stage where compounds present give a positive ninhydrin reaction, contain an amino-group which may be determined by the Van Slyke method, and give a negative picric acid reaction, may be taken as evidence in favour of this mechanism[199]. Besides, heating the cyanoethyl derivatives of amino-acids incapable of forming cyclic derivatives (α-aminophenylacetic acid, phenylalanine, and tyrosine) in glycol yields entirely the decyanoethylation products[166]. On the other hand 1,4-di-(β-cyanoethyl)-2,5-diketopiperazine remains unchanged under the above reaction conditions[199].

Mono- and di-cyanoethyl derivatives of taurine also undergo decyanoethylation on being heated in ethylene glycol[166]. Decyanoethylation is observed on heating *N*-(β-cyanoethyl)tyrosine in 1,2-propanediol, glycerol, and erythritol[166], as well as on pyrolysis of *N*-(β-cyanoethyl)-glycylglycine[200]. The products of the decomposition of *N*-(β-cyanoethyl)alanylglycine in the presence of alkali seem to contain the decyanoethylated derivatives[201].

Butskus and others[23,197,202,203] studied the reaction of cyanoethyl products from amino-acids and their derivatives, with aromatic amines. Amines such as aniline, *p*-nitroaniline, *p*-toluidine, and β-naphthylamine react with mono- and di-cyanoethyl derivatives of α-, β, γ-, δ-, and ε-amino-acids forming their decyanoethylated products, namely α-, β-, γ-, δ-, and ε-amino-acids, as well as the corresponding products of transcyanoethylation, *viz.* β-arylaminopropionitriles. This reaction, studied in a number of cases, proceeds according to the following scheme:

$$\mathrm{HOCO\,(CH_2)_x\,NH{-}CH_2CH_2CN + ArNH_2 \rightarrow HOCO\,(CH_2)_x\,NH_2 + ArNH{-}CH_2CH_2CN},$$

$$\mathrm{HOCO\,(CH_2)_x\,N\,(CH_2CH_2CN)_2 + 2\ ArNH_2 \rightarrow HOCO\,(CH_2)_x\,NH_2 + 2\ ArNH{-}CH_2CH_2CN}.$$

The yields of amino-acids range from 36 to 92%. The reaction of aromatic amines with the cyanoethyl derivatives of taurine, glycylglycine and alanylglycine proceeds likewise. In the reaction of aromatic amines with the esters, amides, and hydrazides of the cyanoethyl amino-acids hydrolysis of the ester, amide, or hydrazide function to carboxylic group occurs simultaneously with transcyanoethylation.

The cyanoethyl derivatives of proteins and peptides react with aromatic amines forming β-arylaminopropionitriles[23].

All the above reactions are carried out by heating aqueous solution at 100°. Heated at 130°–140° with aromatic amines without the solvent the dicyanoethyl derivatives of α-amino-acids split off one cyanoethyl group forming the monocyanoethyl derivatives. At higher temperatures (180°) the second cyanoethyl group is also eliminated. Nevertheless, in this case the reaction proceeds less readily than in water solution, and there is considerable resinification.

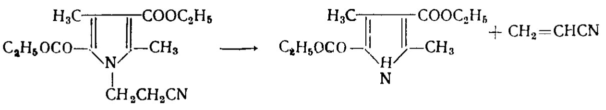
When heated under the above conditions in aqueous ammonia or aniline, or in glycol solution *N*-(β-cyanoethyl)-aceturic acid, *N*-(β-cyanoethyl)hippuric acid and *N*,*N*′-di-(β-cyanoethyl)-2,5-diketopiperazine do not undergo decyanoethylation. This is evidence that the bond of the cyanoethyl group with an amide nitrogen atom is stronger than that with an amine nitrogen.

If heated for many hours with aromatic amines either without a catalyst or in the presence of acids or alkalis, the *N*-carboxyethyl derivatives of α-amino-acids also fail to undergo dealkylation or transalkylation.

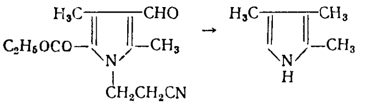
(e) β-(Cyclohexylamine)propionitrile. The cleavage of the bond between the cyanoethyl group and nitrogen in β-(cyclohexylamino)propionitrile has been reported[165,204].

(f) β-Arylaminopropionitriles. The bond between the cyanoethyl group and nitrogen is stronger in β-arylaminopropionitriles than in β-alkylaminopropionitriles. β-Arylaminopropionitriles and *N*-(β-cyanoethyl)-anthranilic acid do not undergo decyanoethylation on being heated in ethylene glycol[166]. Some authors[205], however, report that the removal of the cyanoethyl group from dicyanoethyl derivatives of aromatic amines may occur during their cyclisation. Bekhli[206] pointed out that in acid or alkaline media β-arylaminopropionitriles undergo not only saponification, but also decompose forming an arylamine. This process is minimised by lowering the reaction temperature. Products of the decomposition in acid media of β-(methylphenylamino)propionitrile[207], β-(ethylphenylamino)propionitrile[208], and *N*-(β-cyanoethyl)-anthranilic acid[41,209] also contain decyanoethylated derivatives.

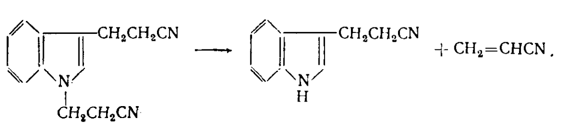
(g) Cyanoethylation of heterocyclic compounds containing nitrogen in the nucleus. Certain derivatives of *N*-(β-cyanoethyl)pyrrole lose a cyanoethyl group on being heated at 150° with sodium ethoxide in absolute ethanol, forming the corresponding pyrroles[210]. For example:



In the reduction of β-(2,4-dimethyl-3-formyl-5-ethoxycarbonylpyrryl-1)propionitrile by the Kishner method, 2,3,4-trimethylpyrrole is obtained:



The *N*,β-dicyanoethyl derivative of indole splits off acrylonitrile on heating *in vacuo* to 250°, forming quantitatively β-cyanoethylindole, which is stable under these conditions[87]:

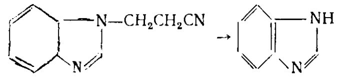


Heated with concentrated potassium hydroxide *N*-(β-cyanoethyl)indole undergoes hydrolysis to the corresponding acid, and yields at the same time indole (10%), the product of decyanoethylation. Under similar conditions certain derivatives of *N*-(β-cyanoethyl)indole yield the corresponding indole derivatives[211].

The cyanoethyl group attached to nitrogen in indole, or the more stable one in the β-position can thus both be eliminated. The migration of the cyanoethyl group from the nitrogen atom to the β-position in indole has not been effected[212].

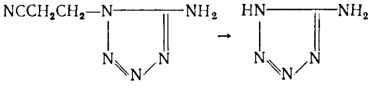
It seems that the hydrolysis of *N*-(β-cyanoethyl)gramine to the corresponding amino-acid is accompanied by decomposition[213]. Under specified conditions *N*-(β-cyanoethyl)-indoline may yield indoline and acrylonitrile[214,215].

Heated with aqueous solutions of acids or alkalis the cyanoethyl derivative of benzimidazole undergoes decyanoethylation to benzimidazole[216]:



The cyanoethyl group, however, could not be eliminated from the cyanoethyl derivative of 2-methylbenzimidazole.

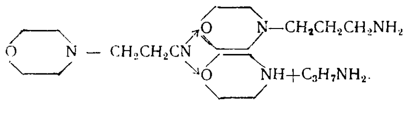
Hydrolysis of 1-(β-cyanoethyl)-5-aminotetrazole with aqueous barium hydroxide is accompanied by decyanoethylation[44]:



Pyrolysis of 1-(β-cyanoethyl)-6-methyl-2-pyridone yields 6-methyl-2-pyridone and acrylonitrile[217].

The cyanoethyl derivative of piperidine must be distilled rapidly *in vacuo*, since slow distillation results in partial decyanoethylation[65]. Decyanoethylation is also observed on heating β-(N-piperidyl)propionitrile in ethylene glycol[166].

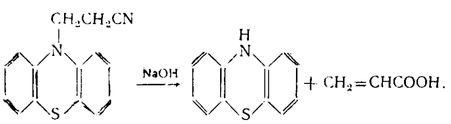
On reduction β-(N-cyanoethyl)morpholine forms, in addition to other products, morpholine and propylamine[58]:



Decyanoethylation occurs during the oxidation of N-(β-cyanoethyl)anabasine by means of potassium permanganate. This reaction is taken as evidence of the structure of anabasine[67].

Attempts to remove the cyanoethyl group from 1-(β-cyanoethyl)-4-keto-1, 2, 3, 4-tetrahydroquinoline using alkali have failed. In the presence of a mixture of concentrated hydrochloric acid and excess acetic anhydride, however, 1-acetyl-4-keto-1, 2, 3, 4-tetrahydroquinoline was isolated[205].

Smith[218] made an effort to hydrolyse the cyanoethyl derivative of phenothiazine by heating it with sodium hydroxide in aqueous ethylene glycol. Instead of the carboxyethyl derivative, however, he isolated phenothiazine and acrylic acid (the latter, in the author's opinion, being formed by dehydration of β-hydroxypropionic acid):



Smith obtained the carboxyethylphenothiazine by hydrolysis of the corresponding cyanoethyl derivative with alkali in aqueous methanol. It was later shown, however, that under these conditions considerable decyanoethylation takes place[219]. Smith himself[220] observed this in the case of the oxidation product from N-(β-cyanoethyl)phenothiazine.

Alkaline hydrolysis of β-cyanoethyl phenoselenazine yields the carboxyethyl derivative, while by acid hydrolysis the product of decyanoethylation is formed[221].

Decyanoethylation takes place during the hydrolysis of the cyanoethylphenoxazine with caustic soda in ethanol[222]. Under these conditions N-(β-cyanoethyl)benzophenothiazine simultaneously undergoes hydrolysis and decyanoethylation.

Certain cyanoethyl derivatives of heterocyclic nitrogen bases were used for introducing the cyanoethyl group into other compounds. Thus, N-(β-cyanoethyl)pyrrolidine and N-(β-cyanoethyl)morpholine methiodides with potassium cyanide formed succinic dinitrile[60]. Cyanoethylation of aromatic amines has been effected by means of N-(β-cyanoethyl)pyrrolidine[60], N-(β-cyanoethyl)piperidine[19], and N-(β-cyanoethyl)morpholine[60]. However, the transcyanoethylation does not take place during the reaction of aniline with 1, 4-di-(β-cyanoethyl)-2, 5-diketopiperazine. Only by adding small amounts of an alkali hydroxide or triethylamine was it possible to isolate traces of β-(phenylamino)propionitrile[202,223].

The reversibility of the reaction of N-(α-cycloalkenyl)-pyrrolidines with acrylonitrile has been reported[224].

6. THE BOND BETWEEN A CYANOETHYL GROUP AND PHOSPHORUS

The bond between a cyanoethyl group and phosphorus has been studied in the case of the mono-, di-, and tri-cyanoethyl phosphines as well as of their P-substituted derivatives. Although Rauhut and his associates[225] were unsuccessful in their attempts to remove the cyanoethyl group from these compounds, other American workers[226] showed that decyanoethylation and transcyanoethylation are possible in case of P-cyanoethyl compounds.

7. THE BOND BETWEEN A CYANOETHYL GROUP AND CARBON

If during cyanoethylation the cyanoethyl group becomes attached to a carbon atom, it can only be removed with difficulty.

Chloroform reacts with acrylonitrile in the presence of alkali at 0°—5°, yielding not more than 12% cyanoethylated derivative. The low yield is taken to indicate the reversibility of this reaction[1,227,228]:

$$CHCl_3 + CH_2{=}CHCN \rightleftarrows Cl_3C{-}CH_2CH_2CN.$$

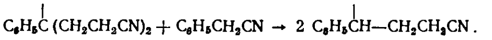
Under similar conditions bromoform yields only 5% of cyanoethyl derivative.

Acrylonitrile reacts with compounds containing mobile hydrogen atoms in methylene or methyl groups, yielding mainly the di- and tri-cyanoethyl derivatives. Even in the presence of an excess of the substance undergoing cyanoethylation, the yield of monocyanoethyl derivative is usually small. However, under certain conditions (high temperature, small amounts of sodium cyanide and water), the reaction can be arrested at the monocyanoethylation stage[229-231]. The monocyanoethylation of a series of ketones with acrylonitrile has been carried out in the presence of amines, amino-alcohols, and Schiff's bases[232-234], in 80—95% yields. It should be noted that the C-monocyanoethyl compounds are obtained either under very mild conditions or, as above, under more vigorous conditions than the corresponding di- and tri-cyanoethyl derivatives. In the latter case the high temperature and other conditions seem to favour the reverse process, *viz.* decyanoethylation. If a compound easy to cyanoethylate, *e.g.* an amine, is added to the reaction mixture, transcyanoethylation may also take place.

It is most interesting that if during the monocyanoethylation of diisopropyl ketone with acrylonitrile the reaction mixture is treated with small amounts of the reaction product, *viz.* the monocyanoethyl diisopropyl ketone, the yield of the latter compound is increased from 33 to 70%.[235]

In the reaction of acrylonitrile with phenyl benzyl sulphone, in dioxane at 80°, and in the presence of alcoholic sodium ethoxide, the methylene group only forms the monocyanoethyl derivative, since the dicyanoethyl compound is unstable under these conditions[1,3].

On hydrogenation of 1, 2, 3, 6-tetramethyl-3-cyanoethyl-4-piperidone at 100°–120° in the presence of Raney nickel a considerable amount of a compound, which has been assigned the structure of 1, 2, 3, 6-tetramethylpiperidine, is obtained[236]. On hydrogenation over copper chromite, the dicyanoethyl derivative of phenylacetonitrile (220°, 175 atm) forms β-phenylpiperidine[237]. Heated 3 h with phenylacetonitrile at 225° in the presence of a small amount of sodium cyanide, the same compound yields the corresponding monocyanoethyl derivative[231]:



$$C_6H_5\overset{\overset{CN}{|}}{C}(CH_2CH_2CN)_2 + C_6H_5CH_2CN \rightarrow 2\ C_6H_5\overset{\overset{CN}{|}}{C}H{-}CH_2CH_2CN.$$

Under the same conditions acetophenone reacts with its tricyanoethyl derivative forming mono- and di-cyanoethylated products:

$$C_6H_5COC(CH_2CH_2CN)_3 + C_6H_5COCH_3 \rightarrow$$
$$\rightarrow C_6H_5COCH_2{-}CH_2CH_2CN + C_6H_5COCH(CH_2CH_2CN)_2.$$

Under certain conditions succinic dinitrile (the cyanoethylation product from hydrocyanic acid) decomposes into hydrocyanic acid and acrylonitrile (94%):[3,238–240]

$$NC{-}CH_2CH_2CN \rightarrow HCN + CH_2 = CHCN.$$

On alkaline hydrolysis the tricyanoethyl derivative of nitromethane splits off one molecule of acrylonitrile forming γ-ketopimelic acid[3]:

$$O_2NC(CH_2CH\ CN)_3 \rightarrow OC(CH_2CH_2COOH)_2.$$

Although in tricyanoethylacetone all cyanoethyl groups are attached to the same carbon atom, the compound has withstood all efforts at decyanoethylation or transcyanoethylation. Heating 1, 1, 1-tri-(β-cyanoethyl)acetone to 150° with acetone in the presence of potassium hydrazide, or to 200° in the presence of sodium methoxide or diethylamine, gave only the starting compounds and small amounts of resin[113].

Attempts to obtain the monocyanoethyl derivative of ethyl methyl acetone from ethyl methyl ketone and its dicyanoethyl derivative have also failed[241].

It was shown above that the reaction of aromatic amines with β-alkoxy-, β-aryloxy-, β-alkylmercapto-, and β-alkylamino-propionitriles yields β-arylaminopropionitriles. Transcyanoethylation does not occur, however, when aniline is made to react with compounds containing cyanoethyl groups attached to a carbon atom, *e.g.* 1, 1, 1-tri(β-cyanoethyl)acetone, 2, 2, 6, 6-tetra-(β-cyanoethyl)-cyclohexanone, *etc.*[19].

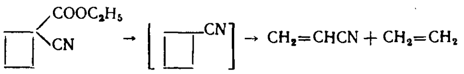
Although the thermal decomposition of polystyrene, rubber, polymethylmethacrylate, and certain other polymers involves the formation of the corresponding monomers, no depolymerisation occurs in the case of polyacrylonitrile. Polyacrylonitrile is very resistant to heat, and remains unchanged up to 300°. It decomposes at higher temperatures, without forming acrylonitrile[242].

8. MISCELLANEOUS CASES OF TRANSCYANOETHYLATION, DECYANOETHYLATION, AND THE FORMATION OF ACRYLONITRILE

The reaction product from acrylonitrile or ethylene cyanohydrin and furfural, furfurylideneacryl amide, may act as a cyanoethylating agent in the reaction with compounds containing a mobile hydrogen atom[243].

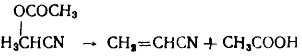
On heating, the Diels–Alder reaction between tetraphenylcyclopentadienone and acrylonitrile is reversed[244].

Pyrolysis of 1-cyano-1-ethoxycarbonylcyclobutane at 520° yields 56% of acrylonitrile[245]:



Acrylonitrile was also observed among the pyrolysis products from 1-cyano-2, 2-dimethyl-3-methylenecyclobutane[246].

Passing the vapours of β-alkoxypropionamide over silica gel at 350°–500° results in the formation of acrylonitrile[247]. Acrylonitrile was also obtained in 40% yield by the pyrolysis of β-methoxypropionamide[248], and during the pyrolysis of α-chloro-, α-hydroxy-, and α-acetoxy-propionitriles[1]. In the presence of catalysts at 620° the last compound yields 90% or more of acrylonitrile[249]:



$$CH_3\overset{\overset{OCOCH_3}{|}}{C}HCN \rightarrow CH_2{=}CHCN + CH_3COOH$$

There are no data in the literature on the cleavage of the bond between the β-cyanoethyl group and silicon. It was recently shown, on the contrary, that the *Si*–cyanoethyl compounds are resistant to high temperatures, alkalis, and acids, and that they do not lend themselves to decyanoethylation or transcyanoethylation reactions[250,251].

SUMMARY

The bond of the β-cyanoethyl group with oxygen, sulphur, nitrogen, carbon, *etc.* is as a rule more labile than the bonds between other alkyl radicals and these atoms. The β-cyanoethyl group is more mobile than other groups or alkyl radicals. To a certain extent this can be explained by the considerable tendency of acrylonitrile and its derivatives to form systems with conjugated multiple bonds. The conversion of the cyanoethyl compounds to corresponding amides, alkoxycarbonyl and carboxyethyl compounds lowers reactivity, *e.g.* in dealkylation and transalkylation. This difference is more prominent in compounds which are unable to form systems of conjugated multiple bonds.

The conversion of the cyanoethyl compounds to corresponding amides, alkoxycarbonyl and carboxyethyl compounds lowers reactivity, *e.g.* in dealkylation and transalkylation. This difference is more prominent in compounds which are unable to form systems of conjugated multiple bonds.

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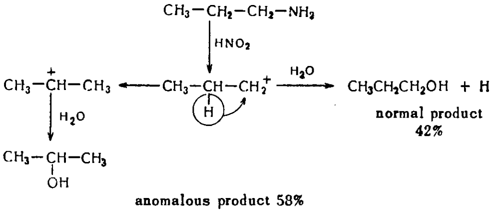
NEW DATA ON HYDRIDE-TRANSFER REACTIONS

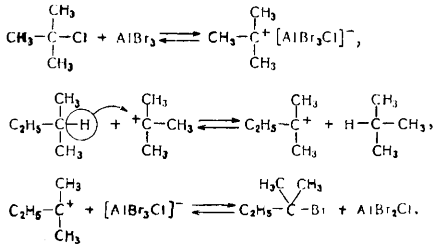
D. N. Kursanov and Z. N. Parnes

There are many organic reactions involving intermolecular transfer of hydrogen in the form of a proton. Such processes, which are fairly well understood, do not however constitute the only possible pathway for hydrogen transfer: in particular, a hydrogen nucleus associated with a pair of electrons may be transferred from one molecule to another. Processes of this sort are known as hydride-transfer reactions[1,2]. The present review is not concerned with the problem of the form and extent of association between a hydrogen nucleus and an electron pair in these reactions. However, the fairly high affinity of a hydrogen atom for an electron, 17.5 kcal mole^{-1}, suggests that such association may exist in hydride transfers[3].

As far as we know, the concept of intramolecular hydride transfer was first introduced in 1932 by Whitmore[4] to explain the anomalous course of reactions which may involve the formation of carbonium ions as intermediates. According to Whitmore, the latter isomerise through intramolecular hydride transfers. For example, Whitmore gives the following explanation of the formation of isopropanol, in addition to n-propanol, when nitrous acid reacts with n-propylamine:



The concept of intermolecular hydride transfer was introduced by Bartlett *et al.*[5] in 1944. They studied the reaction of isopentane with t-butyl chloride in the presence of aluminium bromide. Using an ingenious technique and apparatus, they shortened the time of contact of the components to 0.001 sec and obtained isopropyl bromide and isobutane. The reaction appears to involve intermolecular hydride transfer:

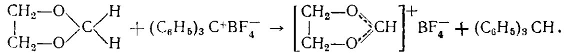


In recent years the concept of intermolecular and intramolecular hydride transfer has been widely employed to interpret the mechanism of complex reactions, and also to some extent in the search for new synthetic methods. Hydride transfers have been included in many mechanisms proposed for a large number of important organic reactions: the mechanism of the Meerwein–Ponndorf–Verley reaction proposed by Woodward *et al.*[6]; the mechanism of the Cannizzaro reaction proposed by Hammett[7]; the mechanism of the Tishchenko reaction proposed by Pfeil[8]; the mechanism of the Leuckart reaction proposed by Pollard and Young[9], and by Titov[10]; the mechanisms of aluminium chloride catalysed reactions of saturated hydrocarbons, proposed by Nenitzescu[2]; the mechanism of the isotopic hydrogen exchange in saturated hydrocarbons under the action of sulphuric acid, proposed by Otvos *et al.*[11], and a similar mechanism propsed by Kursanov and Setkina[12]; and many others.

In general, hydride transfer involves the transfer of a hydrogen nucleus with an electron pair, H: (subsequently to be called a hydride ion), from a donor to an acceptor. The acceptors are very often carbonium ions; the donors can belong to many different classes. When the migrating hydrogen atom is initially bound to a carbon atom, hydride transfer results in the formation of a new carbonium ion. Obviously the activity of a given substance as a hydride donor increases with increase in the stability of the corresponding carbonium ion.

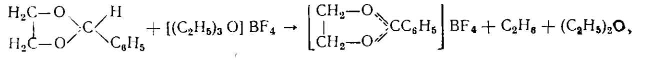
A characteristic feature of the mechanisms quoted above and of many of the mechanisms discussed in a recent review by Deno *et al.*[13] is the fact that hydride transfer is effected through as powerful a hydride acceptor as the carbonium ion. This in fact frequently results in a certain arbitrariness of the proposed mechanisms, since in many cases the existence of the intermediate carbonium ions is difficult to demonstrate, particularly of those which are the most active and consequently the least stable. The most self evident and convincing hydride-transfer reactions are those in which the carbonium ion formed as a result of the transfer is stable.

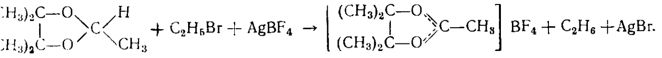
In this connection much interest attaches to the recently published paper by Meerwein *et al.*[14], who employed triphenylmethyl fluoroborate as the hydride acceptor, which is converted in the reaction to triphenylmethane. The hydride donor used was 1,3-dioxolane which, as a result of the transfer, is converted into a carboxonium (dioxolenium) ion:



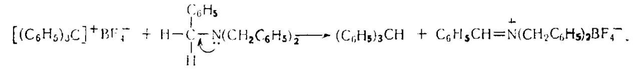
Dioxolenium salts are stable[15]. 2-Methyl-1,3-dioxolane, 2-phenyl-1,3-dioxolane, and 2,4,4,5,5-pentamethyl-1,3-dioxolane react similarly. The yields of triphenylmethane in all these reactions vary from 58 to 84% and those of the dioxolenium salts from 64 to 100%.

Since ethylfluoroborate is unstable, in order to demonstrate the ability of an ethyl cation to remove a hydride ion, the authors allowed 1,3-dioxolanes to react with a mixture of ethyl bromide and dry silver fluoroborate or triethyloxonium fluoroborate. In all cases, 1,3-dioxolenium fluoroborates and ethane were formed:

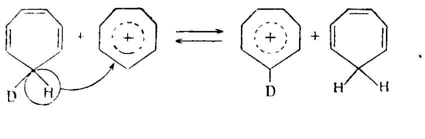




Aliphatic-aromatic tertiary amines may also be employed as hydride donors. Thus in the reaction between triphenylmethyl fluoroborate and tribenzylamine (in acetonitrile solution) triphenylmethane is formed in 89% yield and benzylidenedibenzylammonium fluoroborate in 94% yield:



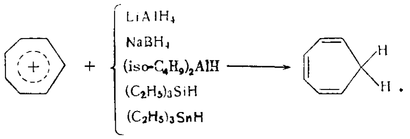
Parnes *et al.*[16,17] employed cycloheptatriene as a hydride donor and a stable carbonium ion — tropylium — as an acceptor. The formation of tropylium in reactions with cycloheptatriene and of cycloheptatriene in reactions with tropylium is clear and unambiguous evidence of the existence of hydride transfers. The first such reaction studied was that between tropylium bromide and cycloheptatriene. In order to be able to follow this reaction, the cycloheptatriene was monodeuterated:



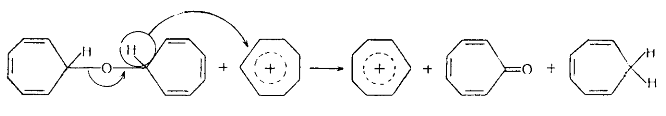
After a few hours at room temperature the deuterium is uniformly distributed among all the hydrogen atoms of the cycloheptatriene and the tropylium, *i.e.* equilibrium has been attained. The reaction takes place in various solvents: acetic acid, methanol, ethanol, nitromethane, etc. Second-order rate constants [$K_{10} = 1.04 \times 10^{-3}$, $K_{15} = 1.41 \times 10^{-3}$, $K_{20} = 2.16 \times 10^{-3}$, and $K_{30} = 4.3 \times 10^{-3}$] and the activation energy, $E = 12$ kcal, have been determined for this reaction in acetic acid solution[18].

It had been shown earlier that the tropylium ion does not enter into hydrogen exchange even with such powerful proton (deuteron) donors as sulphuric acid and hydrogen bromide in the presence of aluminium bromide[19]. It is evident that the exchange between cycloheptatriene and tropylium is a reversible hydrogen transfer. The fact that the reaction will occur in acid media, *i.e.* in the presence of protons, shows that free hydride ions are not formed and that the hydride transfer is effected in an activated complex. It is very probable that the energy of the activated complex in the hydride-transfer reaction is reduced because of the low energy of the system of two electrons in the field of three nuclei. The absence of free hydride ions in organic hydride-transfer reactions has also been noted by other authors (see, for example, the work of Nenitzescu[2]). Since cycloheptatriene on releasing a hydride ion is converted into the stable tropylium ion, it follows that the former must be an active hydride donor. Conversely, it is to be expected that the tropylium ion will prove to be a relatively weak hydride acceptor. In order that the stable tropylium ion should remove a hydride ion from the molecule of another substance, it is necessary that the latter should be a powerful hydride donor, *i.e.* that following hydride transfer it should yield a species no less stable than the tropylium ion.

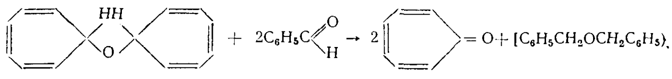
It has been shown that tropylium is vigorously reduced, in quantitative yield, to cycloheptatriene under the action of such powerful hydride donors as sodium borohydride, lithium aluminium hydride, and diisobutylaluminium hydride. Tropylium can remove a hydride ion from triethylsilane and triethylstanane with the formation of cycloheptatriene in ~70% yield:



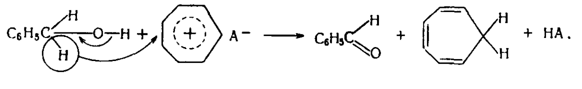
Tropylium can remove a hydride ion from cycloheptatrienyl ether[20-22] which results in a chain reaction: tropylium is converted into cycloheptatriene on reaction with the hydride ion and one half of the ether molecule is converted to tropone and the remainder to tropylium, which can again remove a hydride ion from another cycloheptatrienyl ether molecule. Thus each molecule of the ether finally yields one molecule of tropone and one molecule of cycloheptatriene:



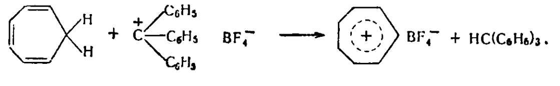
Both cycloheptatrienyl residues can be converted to tropone when benzaldehyde is used as the hydride acceptor:



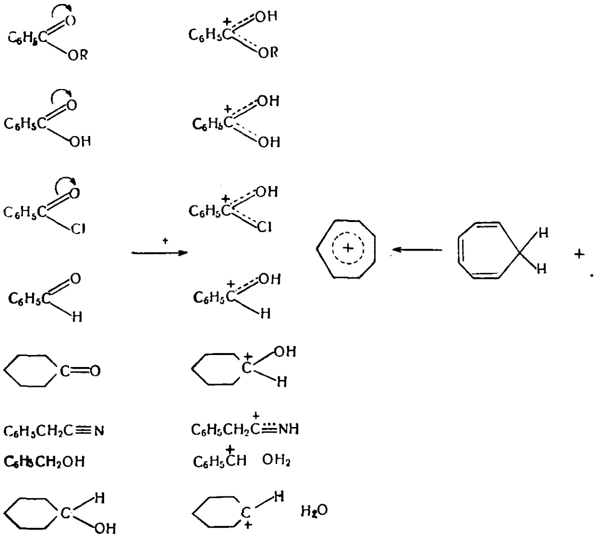
The tropylium ion can react with benzyl alcohol to yield benzaldehyde and cycloheptatriene. In acetic acid solution this reaction is practically quantitative. It has been shown that reaction between tropylium bromide and D-benzyl alcohol (C_6H_5CHDOH) results in the formation of deuterated cycloheptatriene. The kinetic isotopic effect, as in other cases of hydride transfer, proved to be small and equal to 2.1:



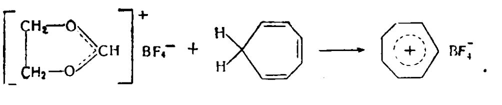
It follows from the above data that the tropylium ion can remove a hydride ion from a wide variety of substances. However, tropylium cannot be reduced to cycloheptatriene either by benzaldehyde, or by acetic acid, or even by formic acid, *i.e.* it is a relatively weak hydride acceptor. Conversely, cycloheptatriene must be a strong hydride donor. The available methods for the preparation of tropylium are based on the fact that cycloheptatriene readily gives up a hydride ion when acted upon by Lewis acids, PCl_5, concentrated H_2SO_4,[23] and the triphenylmethyl carbonium ion[24]:



In phosphoric acid, cycloheptatriene is converted to the tropylium ion under the action of benzoic acid esters, benzoyl chloride, benzaldehyde, cyclohexanone, benzyl cyanide, benzyl alcohol, and cyclohexanol. It is interesting that the reaction does not occur in acetic acid. Probably in phosphoric acid all the above compounds form carbonium (carboxonium, carbammonium) ions which can remove a hydride ion from cycloheptatriene:



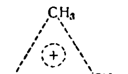
Meerwein's 1,3-dioxolenium ion[15] can also remove a hydride ion from cycloheptatriene with the formation of tropylium:



The formation of the tropylium ion in reactions is very easy to detect since it forms an insoluble chloroplatinate $(C_7H_7)_2PtCl_6$, and with acetylacetone it yields a cycloheptatrienyl derivative, $CH_3COCH(C_7H_7)COCH_3$ (m.p. 123°–124° after recrystallisation from petroleum ether)[25].

In view of the ready transfer of hydride from cycloheptatriene to carbonium (carboxonium, carbammonium) ions and the ease with which this reaction can be controlled, application of cycloheptatriene may help in elucidating the mechanism of many reactions involving hydride transfer.

Recently, apart from studies on hydride transfers involving stable carbonium ions, further advances have been made in the investigation of hydride-transfer reactions with the participation of unstable carbonium ions. Tracer-atom techniques have revealed reactions based on the isomerisation of the propyl cation. For example, Roberts and Halmann[26] found that when nitrous acid acts on [$^{14}C_{(1)}$]propylamine, $\underset{(3)}{CH_3}\underset{(2)}{CH_2}{}^{14}\underset{(1)}{CH_2}NH_2$, a rearrangement takes place as a result of which some of the ^{14}C is displaced from position 1. The authors thought that the rearrangement was of the pinacol type and that ^{14}C moves to position 2. To explain this, Roberts and Halmann suggested that the reaction involves the formation of a non-classical carbonium ion as an intermediate:



Recently Reutov and Shatkina[27] re-examined the reaction of [$^{14}C_{(1)}$]propylamine with nitrous acid. They isolated both n-propanol and isopropanol from the reaction mixture. To establish the location of ^{14}C in propanol, they determined the ^{14}C content of the molecule as a whole and then oxidised the alcohol to acetic acid. They then determined the ^{14}C content in the acid and subjected it to the Schmidt degradation, which results in the formation of methylamine. The ^{14}C content in the methylamine proved to be the same as in the acetic acid. Thus in n-propanol ^{14}C is present in either position 1 or 3 but not in 2. The authors explain the isomerisation of the propyl cation by the migration of a hydride ion, either in one stage from $C_{(3)}$ to $C_{(1)}$:

$$\underset{(3)}{CH_3}-\underset{(2)}{CH_2}-\underset{(1)}{{}^{14}\overset{+}{C}H_2}\rightleftarrows\underset{(3)}{\overset{+}{C}H_2}-\underset{(2)}{CH_2}-\underset{(1)}{{}^{14}CH_3};$$

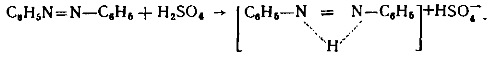
or in two stages:

$$CH_3-CH_2-{}^{14}\overset{+}{C}H_2\rightleftarrows CH_3-\overset{+}{C}H-{}^{14}CH_3\rightleftarrows\overset{+}{C}H_2-CH_2-{}^{14}CH_3.$$

The second of the above mechanisms is analogous to that proposed by Whitmore[4] for the isomerisation of carbonium ions, and to the mechanism of the isomerisation of the carbonium ions prepared from hydrocarbons by the action of sulphuric acid[11] or aluminium chloride[28].

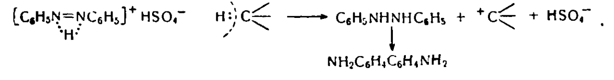
In all the above examples the hydride acceptor was a carbonium ion or at least a molecule containing a carbon atom with a partial positive charge.

Nesmeyanov and Golovnya[29] recently found that protonated azobenzene, formed by the action of strong acids on azobenzene[30], is a good hydride acceptor:



$$C_6H_5N{=}N{-}C_6H_5+H_2SO_4\rightarrow\left[C_6H_5{-}\underset{\cdot\cdot H\cdot\cdot}{N{=}N}{-}C_6H_5\right]^+HSO_4^-.$$

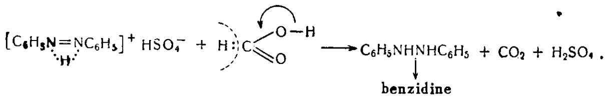
On combination with a hydride ion, it is converted to hydrazobenzene, which in the presence of acid undergoes the usual rearrangement to benzidine:



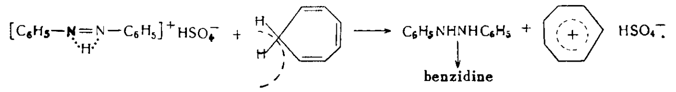
$$[C_6H_5\underset{\cdot\cdot H\cdot\cdot}{N{=}N}C_6H_5]^+HSO_4^-\quad H{:}C\lessgtr\longrightarrow\underset{\displaystyle\downarrow\atop NH_2C_6H_4C_6H_4NH_2}{C_6H_5NHNHC_6H_5}+{}^+C\lessgtr+HSO_4^-.$$

The authors found that protonated azobenzene can remove a hydride ion from a wide variety of organic compounds, itself undergoing conversion to benzidine. In many cases the hydride-transfer reaction was established only from the formation of benzidine. In the majority of cases the other reaction products are unstable carbonium ions, which later undergo many more or less complicated reactions resulting in the formation of stable compounds. In particular, carbonium ions can be frequently stabilised by the removal of a proton and the formation of unsaturated compounds. The latter polymerise in the presence of sulphuric acid forming resinous products of unknown constitution. Hydride transfers have been established in this way in reactions with acetone, cyclohexanone, acetic acid, succinic acid, benzaldehyde, butyl ether, benzene, thiophen, nitrobenzene, cyclohexane, and n-hexane.

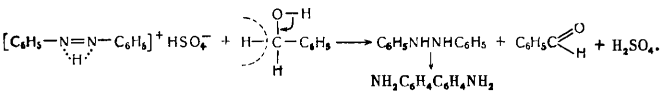
In many cases Nesmeyanov and Golovnya were able to identify both reaction products. Thus in the reaction between protonated azobenzene and formic acid carbon dioxide was found in addition to benzidine:



In the reaction with cycloheptatriene a good yield of a tropylium salt was obtained in addition to benzidine:



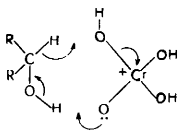
Reaction with benzyl alcohol results in the formation of benzaldehyde as the second product:



These products are fully consistent with the suggested mechanism and serve as its confirmation.

It is noteworthy that protonated azobenzene as a hydride acceptor is comparable in effectiveness with carbonium ions, and possibly even superior to them. It removes a hydride ion not only from all the compounds which undergo hydride transfer with carbonium ions, but also from benzene, nitrobenzene, and thiophen, which do not react with carbonium ions. Dehydroaromatic compounds are probably formed initially and then undergo further changes.

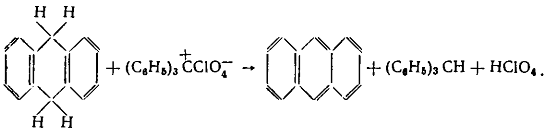
Reactions are known in which the hydride ion is transferred to atoms other than carbon or nitrogen. Much work has been done on the chromic acid oxidation of hydrocarbons containing a tertiary carbon atom[31], alcohols[32-36], and aldehydes[37]. Roček[34,37] showed that hydride transfer is the rate-determining stage in the oxidation of alcohols and aldehydes. To explain the mechanism of the alcohol oxidation, Roček and Krupička proposed the following cyclic scheme:



in which hydride transfer to the chromic acid oxygen is the slowest stage. To demonstrate the correctness of his scheme, Roček[34] studied the kinetics of the oxidation of a large number of primary alkyl and aralkyl alcohols containing various substituents and having the general formula RCH_2OH. The inductive effect of the substituents was examined. Following the application of the Hammett–Taft equation, Roček found that for the majority of substituents† the relation between log$K$ and σ^* is linear. Thus the oxidation of primary alcohols by chromic acid obeys the Taft equation: $\log(K/K_0) = \rho^*\sigma^*$. This equation describes the same relationship for the aliphatic series as had been found by Hammett for aromatic compounds. K_0 is the rate constant for the unsubstituted compound, K the rate constant for the substituted compound, σ^* a function of the substituent, and ρ^* a function of the reaction.

The following substituents were employed: Cl_3C, Cl_2CH, $(CH_3)_3\overset{+}{N}$, $CNCH_2$, $ClCH_2C_6H_4$, $HOCH_2$, CH_3OCH_2, H, $C_6H_5CH_2$, $C_6H_5CH_2CH_2$, CH_3, C_2H_5, n-C_3H_7, cyclohexyl, iso-C_3H_7, neopentyl, and n-C_5H_{11}. Since the oxidation of of neopentyl, and trochloroethyl alcohols also obeys the Taft equation, steric effects do not have much influence on the reaction. $\rho^* = -1.06 \pm 0.06$. The negative value indicates that a decrease in the electronegativity of the substituent leads to an increase in the reaction rate. This is consistent with the postulate that hydride transfer is the rate-determining stage. If Westheimer's mechanism[38] were correct, *i.e.* if the rate-determining stage were proton transfer in the initially formed ester, ρ^* would have to be positive since increase in electronegativity of the substituent enhances proton mobility. Roček's scheme for the oxidation of aldehydes is analogous to that for the alcohols, the rate-determining stage being hydride transfer from the aldehyde to the chromic acid oxygen.

It might be useful to interpret the mechanism of the action of many oxidising agents in terms of hydride transfers, since removal and addition of hydride ions constitute some of the simplest oxidation and reduction reactions respectively. Braude and Linstead[39] dehydrogenated dihydroaromatic compounds under the action of quinones, and explained the reaction in terms of hydride transfer. Bonthrone and Reid[40] found that when dihydroanthracene, tetrahydropyrone, and other similar compounds are allowed to react with triphenylcarbonium perchlorate, aromatic compounds are obtained. For example:



There is reason to believe that in future considerable progress will be made in the elucidation of the role of hydride transfer in oxidation–reduction processes.

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† Except methyl alcohol (R = H), benzyl alcohol (R = C_6H_5), and choline perchlorate [R = $(CH_3)_3\overset{+}{N}CH_2$].

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PRINCIPAL FACTORS IN THE FREE-RADICAL CHLORINATION OF ALKANES

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CONTENTS

I. INTRODUCTION

The utilisation of natural and petroleum gases for the heavy organic chemical industry is an important task for the national economy. The huge reserves of gas and petroleum provide the chief raw material for the chemical industry. Saturated hydrocarbons, or alkanes, constitute the bulk of the natural and accompanying gases and a considerable proportion of petroleum, so that the employment of alkanes for organic synthesis is of particular interest. Among the varied processes for their chemical treatment (chlorination, chlorosulphonation, dehydrogenation, oxidation, sulphonation, nitration, etc.) one of the most important is chlorination. This reaction can take place by three different mechanisms depending on the way in which the bond between the atoms in the chlorine molecule is broken.

In the symmetrical, homolytic rupture of the Cl–Cl bond, chlorination subsequently proceeds by a free-radical chain mechanism independently of the method by which the free chlorine atoms were produced (photochemically, thermally, chemically, by means of radiation, etc.)[1-6].

$$\begin{gathered} \mathrm{Cl_2 \rightarrow Cl\cdot + Cl\cdot} \\ \mathrm{Cl\cdot + RH \rightarrow R\cdot + HCl} \\ \mathrm{R\cdot + Cl_2 \rightarrow RCl + Cl\cdot} \text{ etc.} \end{gathered} \tag{I}$$

Chlorination can take place by an ionic mechanism, the chlorine molecule undergoing heterolytic fission, in the presence of chlorides of metals which are able to form complex ions[7], *e.g.* the chlorides of Fe, Cu, Sb, Sn, Bi, Ti, Al, As, etc.

$$\begin{gathered} \mathrm{FeCl_3 + Cl - Cl \rightarrow Cl^+ [FeCl_4]^-} \\ \mathrm{Cl^+ [FeCl_4]^- + RH \rightarrow [RHCl]^+ [FeCl_1]^-} \\ \mathrm{[RHCl]^+ [FeCl_4]^- \rightarrow RCl + HCl + FeCl_3} \text{ etc.} \end{gathered} \tag{II}$$

Chlorides of S, I, P, and some other non-metals act in a similar way.

Finally, in the third case

$$Cl_2 + RH \rightarrow RCl + HCl, \qquad \textbf{(III)}$$

chlorination takes place by a bimolecular mechanism, without the formation of free radicals or ions. This mechanism plays an appreciable role at high temperatures (above 400°), when both chlorine and alkane molecules are activated. The weakening of the bonds between the atoms in the molecules makes it possible for the latter to interact directly.

The present paper examines the effects of a number of factors on the chlorination of alkanes by the free-radical chain mechanism.

II. ROLE OF THE MOLECULAR STRUCTURE OF THE ALKANES AND ALKYL CHLORIDES

Molecular structure has a considerable effect on the course of chlorination processes. The optimum conditions for chlorination, and the composition and structure of the resulting products, depend to a large extent on the polarity of the C–H bonds, and to a lesser extent on steric factors. Those hydrogen atoms which are less "protonised" (or more "electronised") in the alkane and alkyl chloride molecules will be more rapidly replaced by chlorine. The state of these H atoms will depend on the strength and character of the effect which the rest of the molecule has on the C–H bond. In the chlorination of alkanes, substitution of the hydrogen atoms depends on the nature of the carbon atom to which they are linked, in the following sequence: tertiary > > secondary > primary[8]. In the gas phase at 300° the relative rates of substitution (or, what is the same thing, the relative reactivities) of these hydrogen atoms are 4.43 : 3.25 : 1.0. The difference in the relative reactivities of hydrogen atoms attached to the three different types of carbon atoms in alkanes results from the different intensities of the positive inductive effect (+*I* effect) exerted by neighbouring alkyl groups on the corresponding C–H bonds[9,10].

As the alkane chain increases in length, the secondary hydrogen atoms increase in number relative to the primary, and this increases both the reactivity of the alkanes towards chlorination and the relative quantities of secondary chlorides and of polychlorides formed. Thus it is clear from Fig. 1 that, at a given temperature, a greater proportion of the chlorine reacts in the thermal chlorination of heptane than in that of hexane or of pentane[11]. The chlorination of methane, ethane, propane, and butane supports this rule[12,13]. Table 1 gives the proportions of primary and secondary chlorides formed in the chlorination, under conditions which avoid polychlorination or pyrolysis, of n-alkanes containing different numbers of carbon atoms[14].

The relative reactivity of hydrogen atoms linked to primary, secondary, and tertiary carbon atoms in an alkane is not constant but is greatly affected by the chlorination temperature and the nature of the solvent. The presence of moisture, charcoal, catalysts, or light, however, has no great effect[8].

The relative reactivities of the hydrogen atoms change markedly during the polychlorination of alkanes, owing to the inductive effect of the chlorine atoms which have entered the molecule.

Thus a study of the liquid-phase chlorination of 1-chlorobutane, 1,1-dichlorobutane, and 1,1,1-trichlorobutane has shown that the chlorine which has entered the molecule deactivates the C–H bonds of its immediate neighbours, and this effect is intensified by increasing the number of chlorine atoms in position 1 in the alkane molecule. Table 2 shows that even the presence of one chlorine atom deactivates position 2, while having little effect on position 3. The presence of two or more chlorine atoms in position 1 is sufficient to deactivate position 3 as well[15].

In the chlorination of 1-chlorobutane the relative reactivity of the hydrogen atoms in position 2 is found to be half the value for position 3 (3.2 and 6.7 respectively). In the 1,1-dichlorobutane molecule the relative reactivity of hydrogen in position 2 is one-quarter of that for position 3 and one-half of that for hydrogen in position 4 (the respective values being 3.0, 12.3, and 6.2).

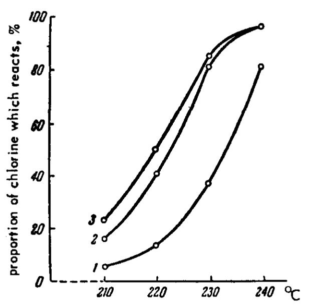


Fig. 1. Effect of chain length on relative rates of thermal chlorination of alkanes:
1) n-pentane; 2) n-hexane; 3) n-heptane.

TABLE 1. Effect of chain length of alkanes on composition of monochlorides.

No. of C atoms in molecule	Primary chlorides, %	Secondary chlorides, %	No. of C atoms in molecule	Primary chlorides, %	Secondary chlorides, %
3	50.0	50.0	12	8.5	91.5
4	33.0	67.0	20	4.9	95.1
5	23.5	76.5	25	3.9	96.1
6	18.7	81.3	30	3.2	96.8
10	10.3	89.7			

TABLE 2. Effect of chlorine atoms on reactivity of hydrogen atoms in n-butane.

Position of Cl atom	$\underset{4}{C}$ –	$\underset{3}{C}$ –	$\underset{2}{C}$ –	$\underset{1}{C}$ –	X
% substituted on chlorination	27	47	22	7	Cl (1-chloro)
Relative reactivity of H atom	2,6	6,7	3.2	1	
% substituted on chlorination	37	49	12	2	Cl_2 (1,1-dichloro)
Relative reactivity of H atom	6.2	12.3	3.0	1	
% substituted on chlorination	51	49	0	0	Cl_3 (1,1,1-trichloro)
Relative reactivity of H atom	1	1.4	0	0	

The deactivation of the C−H bonds is a result of the negative inductive (*-I*) effect of the chlorine atom which has already replaced one of the hydrogen atoms (a particular case of the "vicinal effect"[16-19]).

In the presence of a chlorine atom not located on a terminal carbon atom the greatest relative reactivity is shown by the hydrogen atoms which are farthest removed from the negative substituent (chlorine) and are under the influence of the *+I* effect of the alkyl groups. The *-I* effect of the chlorine atom is much greater in magnitude than the *+I* effect of the alkyl groups. Therefore the reactivity of hydrogen atoms is numerically much smaller in alkyl chlorides than in alkanes, and it decreases still further as chlorine atoms accumulate in the molecule. Thus the reactivities of the hydrogen atoms in butyl chloride, methylene chloride, and chloroform are 12%, 1.1%, and 0.5% of the reactivity of a methyl hydrogen atom in n-heptane. The reactivity of the hydrogen atom in chloroform is 0.12% of that of a hydrogen atom in position 2 in 2,3-dimethylbutane[20].

Owing to the deactivation of the hydrogen atoms in alkyl chlorides, the latter undergo chlorination less readily than do the alkanes. Methane is an exception to this rule, as it is more difficult to chlorinate than is methyl chloride[21].

TABLE 3. Effect of solvents on the observed relative reactivity of a hydrogen atom attached to a tertiary carbon atom in 2,3-dimethylbutane.

Non-aromatic solvents (concn. 4 M)	Relative activity at 55°	Aromatic solvents (concn. 4 M)	Relative activity at 55°
2,3-Dimethylbutane	3.7	Nitrobenzene	4.9
Nitromethane	3.3	9-n-Butylanthracene (2 M)	5.0
Chloroform	3.5	Benzoyl chloride	6.4
Cyclohexene	3.6	Trifluoromethylbenzene	6.9
Trichloroethylene	3.6	Methyl benzoate	10.2
Silicon tetrachloride	3.7	Chlorobenzene	10.2
Propionitrile	4.0	Fluorobenzene	10.3
Butyric acid	4.1	Thiophen	13.3
Methyl acetate	4.3	Benzene	14.6
Butyl alcohol	4.8	*o*-Xylene	15.0
Dioxan	5.6	Toluene	15.4
Butyl ether	7.2	Ethylbenzene	16.3
Thionyl chloride	7.3	Anisole	18.4
NN-Dimethylformamide	9.1	*p*-Xylene	18.6
Sulphur monochloride	14.0	Cumene	20.3
Carbon disulphide	33.0 (25°)	*m*-Xylene	22.4
Butyl iodide	390	Butylbenzene	24.0
Ethyl iodide	600	Mesitylene	25.0
		2-Isobutylnaphthalene	30.0
		Iodobenzene	31.0
		1-Chloronaphthalene	33.0

III. EFFECT OF SOLVENTS

It is usually considered that solvents have a negligible effect on the velocity and course of competing free-radical chain reactions, in particular on chlorination[22,23]. Recent research[20,24,25] has shown, however, that the solvent does not act merely as a reaction medium. Solvents can change the direction of the process and the composition of the chlorination products. Thus at 25° the photochemical chlorination of pure 2,3-dimethylbutane gives 60% of 1-chloro-2,3-dimethylbutane and 40% of 2-chloro-2,3-dimethylbutane. In the presence of 12 M carbon disulphide, however, the 2-chloro compound constitutes 97.4% of the total yield of chloro-2,3-dimethylbutanes[20]. The observed relative reactivity of the methylidyne hydrogen atom has thus increased from 4 to 225. When n-heptane is chlorinated under the same conditions, the relative reactivity of a methylene hydrogen atom is observed to increase from 3.7 to 29.0. The effect of solvents has been most fully studied in the photochlorination of 2,3-dimethylbutane[20,24] (see Table 3).

It is seen from Table 3 that aromatic solvents generally exert a fairly strong influence on the observed relative reactivities of the hydrogen atoms. Most non-aromatic solvents have only a feeble effect in this case. The difference is evidently associated with the differing abilities of these types of solvents to solvate the highly electrophilic chlorine atom to form complex compounds of different reactivity[20,24]. The more stable the resulting complexes, and hence the lower their reactivity, the greater is the selectivity of the chlorine atom combined in the complex. From the electronic point of view, this is a result of the decrease in the electrophilic character of the coordinated chlorine atom, the effect becoming more marked as the stability of the complexes increases. This diminution in electrophilic properties and the associated lower activity of the chlorine atom in the complex makes it difficult or impossible to remove the more "protonised" hydrogen atom of the alkane. Fig. 2 illustrates the effect of complex-forming solvents on the chlorination of alkanes[25]. The energy relationships of reactions involving free chlorine atoms have been calculated from data on the gas-phase reactions and the known bond dissociation energies. The energetics of reactions involving chlorine atoms combined in complexes are more sketchy, but they do show both the origin of the greater selectivity and the greater effect of temperature. Investigation of the kinetics of the chlorination of 2,3-dimethylbutane in the presence of solvents has shown[20] the presence of a dynamic equilibrium between free and coordinated chlorine atoms, the relative proportions being 1 : 10.4 with 8 M benzene as solvent at 25°. The free chlorine atom replaces hydrogen atoms attached to a primary as well as those attached to a tertiary or a secondary carbon atom. Thus the composition of the chlorination products of an alkane and the observed relative reactivity of the hydrogen atoms depend on the relative proportions of chlorine atoms which are free and which are coordinated with the solvent.

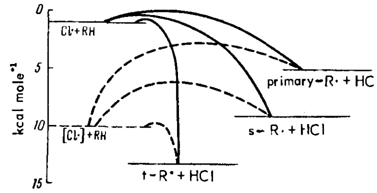


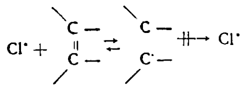
Fig. 2. Energetics of reactions of coordinated and free chlorine atoms with alkanes.

When aromatic solvents are involved, the highly electrophilic chlorine atom forms complex compounds by association with the π electrons of a double bond in the aromatic nucleus. Aromatic solvents containing electronegative substituents (nitrobenzene, chlorobenzene, fluorobenzene, trifluoromethylbenzene) have only a slight effect.

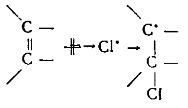
In contrast, those containing electron-donor substituents (butylbenzene, mesitylene, cumene, *m*-xylene) exert a considerable influence on the observed relative reactivity towards chlorination of the hydrogen atoms in alkanes.

The polarisability of the substituent is of immense importance. When it is high, complexes of great selectivity are formed. It is seen from Table 3 that solvents containing the readily polarisable sulphur and iodine atoms (sulphur monochloride, carbon disulphide, butyl iodide, ethyl iodide, iodobenzene) have a very marked effect on the composition of the chlorination products obtained from alkanes. However, it is undesirable to employ solvents having an unnecessarily high capacity for solvating electrophilic molecules, owing to the formation of unreactive complexes. Thus compounds containing an ethylenic bond (cyclohexene, trichloroethylene) and anthracene compounds (9-n-butylanthracene) have no appreciable effect on the observed relative reactivities of the hydrogen atoms in the chlorination of 2,3-dimethylbutane.

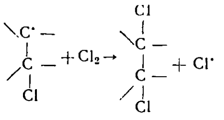
The π complexes formed in this case,



are rapidly converted into σ complexes,



with the ultimate formation of products in which the chlorine has been added to a double bond in the solvent molecule:



In this case the hydrogen atoms in the alkane are split off only by a free chlorine atom, so that there is no effect of the solvent on the observed relative reactivities of the hydrogen atoms towards chlorination.

The equilibrium between free and coordinated chlorine atoms, and hence the observed relative reactivities of the hydrogen atoms, are considerably affected by the temperature and especially the concentration of the solvent. Fig. 3 shows[25] that, with a carbon disulphide concentration of 11.1 M, an increase in the chlorination temperature from 0° to 68° reduces the observed relative reactivity of a methylidyne hydrogen atom in 2,3-dimethylbutane from 93.2 to 34.0, *i.e.* by a factor of 2.7. The same rise in temperature in the absence of the solvent results in a fall in relative reactivity from 4.9 to 4.0, *i.e.* by a factor of only 1.2. The chlorination of n-butane follows a similar pattern, chlorination under the same conditions showing a decrease in relative reactivity of a hydrogen atom attached to a secondary carbon atom by a factor of 2.0 in the presence of solvent, compared with 1.1 without a solvent[25]. The concentration of the solvent has a still greater effect, Fig. 4 showing that an increase in the carbon disulphide concentration from 2 M to 12 M involves an increase in the observed relative reactivity of a methylidyne hydrogen atom at 2,3-dimethylbutane from 15.0 to 225.0.[20]

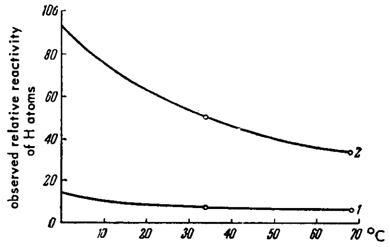


Fig. 3. Effect of temperature on observed reactivity of hydrogen atoms (relative to those attached to primary carbon atoms in the same compound) in the presence of 11.1 M carbon disulphide:
1) activity of hydrogen atoms attached to secondary carbon atom in n-butane;
2) activity of hydrogen atoms attached to tertiary carbon atom in 2,3-dimethylbutane.

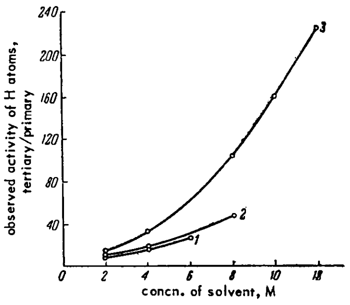


Fig. 4. Effect of concentration of different solvents on observed relative activity of hydrogen atom in 2,3-dimethylbutane at 25°:
1) chlorobenzene; 2) benzene; 3) carbon disulphide.

Up till now we have been concerned mainly with the effect of the reactivity of the coordinated chlorine atom on the composition of the chlorination products. In the chlorination of alkyl chlorides, however, solvents which readily solvate electrophilic molecules have also a direct effect on the reactivity of the hydrogen atoms of C–H bonds. Thus the reactivity of a hydrogen atom in methylene chloride towards photochlorination in the absence of solvent is 0.3% of the reactivity of a methylene hydrogen in n-pentane, whereas in the presence of 12 M carbon disulphide the corresponding figure is 1.2%, a fourfold increase[20]. When chloroform is chlorinated under analogous conditions, the reactivity of the hydrogen atom increases nearly sevenfold from 0.12% to 0.8% of the reactivity of a hydrogen atom attached to a tertiary carbon atom in 2,3-dimethylbutane[20].

The increased reactivity of hydrogen atoms attached to carbon atoms in these and similar cases is evidently a result of solvation, not only of the free chlorine atom, but also of the molecule of alkyl chloride undergoing chlorination. Solvation of the latter by electron-donor solvents decreases the *-I* effect of the chlorine atom, and hence increases the reactivity of the hydrogen atoms during chlorination[20,26].

IV. EFFECT OF TEMPERATURE

The chlorination of the lower alkanes has been investigated at temperatures up to 1000° and above[8,12,27-30].

Methane, ethane, propane, and the butanes yield considerable amounts of chloro-derivatives even at 300°. As already noted, temperature exerts a marked effect on the process and on the composition of the products. As the temperature rises, the relative reactivities of the different hydrogen atoms become increasingly similar.

Thus the vapour-phase photochlorination of propane at 80° yields 61.5% of 2-chloropropane and 38.5% of 1-chloropropane. When the reaction temperature is raised to 600° the corresponding yields are 42.2% and 57.8% respectively. The relative reactivity of the methylene hydrogen atom has fallen[8] from 4.7 to 2.2.

The chlorination of isobutane under similar conditions shows a decrease in the yield of 2-chloro-2-methylpropane from 45.3% to 23.5% of the total quantity of monochlorides obtained. The reactivity of hydrogen attached to a tertiary carbon atom relative to that of a primary hydrogen falls in this case[8] from 7.4 to 2.8. The relative reactivities of the hydrogen atoms are more sensitive to a change in temperature in liquid-phase than in gas-phase chlorination. Thus, in the liquid-phase photochemical chlorination of propane, a rise in temperature of 90° (from -60° to +30° in CCl_4 medium) is accompanied by a diminution in the relative reactivity of a methylene hydrogen atom from 8.3 to 3.2, *i.e.* by a factor of 2.6, whereas in the gas-phase thermal chlorination an increase in temperature of 300° (from +300° to +600°) entails a fall in relative reactivity from 3.2 to 2.2, *i.e.* only by a factor of 1.4.

Given relative reactivities of the hydrogen atoms in alkanes are reached at considerably lower temperatures in liquid-phase than in gas-phase chlorination. Thus it can be seen from the preceding example that a relative reactivity of 3.2 for a methylene hydrogen atom in propane is reached at +30° in the case of liquid-phase chlorination, whereas a temperature of +300° is necessary with gas-phase chlorination. The chlorination of isobutane shows a similar pattern[8].

The effect of temperature on the relative reactivities of hydrogen atoms in the chlorination of alkanes, the general picture of which is illustrated in Fig. 5, is apparently explained by the different stabilities of the alkyl chlorides[8]. The stability falls in the sequence primary > > secondary > tertiary, which leads to a corresponding change in relative rates of substitution of the hydrogen atoms, and hence in their relative reactivities, when the temperature is raised. Steric factors probably play an important part at low temperatures, especially in liquid-phase chlorination. Owing to the decrease in kinetic energy in the liquid phase when the temperature drops, the vibrations of the C–C links in the alkane chains also diminish. The alkane molecules take up the energetically most favourable form, which is less bent and more extended. The screening of some of the C–H bonds involving secondary or tertiary carbon atoms by other parts of the molecule decreases. This leads to an increase in the observed relative reactivity of the hydrogen atoms attached to secondary or tertiary carbon atoms[31-35].

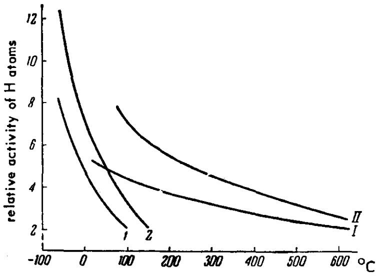


Fig. 5. Effect of temperature on relative activities of hydrogen atoms attached to different carbon atoms in alkanes:
1) secondary C/primary C } in liquid phase
2) tertiary C/primary C
I) secondary C/primary C } in vapour phase
II) tertiary C/primary C

It follows from Fig. 5 that the maximum yield of primary chlorides is achieved at high temperatures, and the maximum yield of secondary or tertiary chlorides at low temperatures. This makes it possible to control the chlorination and to obtain preferential formation of either primary or secondary and tertiary alkyl chlorides. Table 4 shows that, in the vapour-phase thermal chlorination of the C_6–C_{10} alkanes, the temperature for preferential formation of primary monochlorides is 120°–160° above that for preferential formation of secondary monochlorides[36,37]. 1-Chlorohexane (at 197°) and 2-chlorohexane (at 77°) can be obtained in yields of 71% and 75% of theoretical. Polychlorination increases as the hydrocarbon chain becomes longer, which entails some decrease in the yield of monochlorides, and raises the optimum temperature for obtaining the latter.

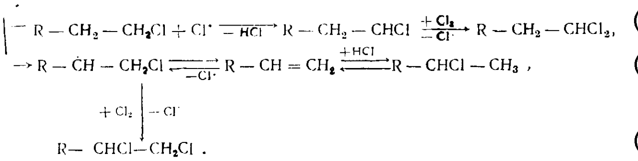
Vigorous formation of polychlorides begins above 500°, and is due not so much to further chlorination of monochlorides as to the chlorination of pyrolysis products. However, the formation of polychlorides can be reduced to a minimum by the use of high bulk rates of flow, which shorten the time during which the reaction products and the initial alkanes remain in the high-temperature zone[8].

TABLE 4. Yield of isomeric monochlorides at the optimum temperatures for chlorination and at an alkane : chlorine molar ratio of 10 : 1.

Normal alkane	Primary alkyl chlorides predominant		Secondary alkyl chlorides predominant	
	optimum temp., °C	yield of primary monochloride, % of alkane chlorinated	optimum temp., °C	yield of secondary monochloride, % of alkane chlorinated
Hexane	197	71.0	77	75.0
Heptane	257	67.0	137	73.7
Octane	277	60.3	177	69.2
Nonane	317	58.3	187	64.7
Decane	357	55.0	197	61.2

As the temperature rises above 300° the rate of 1,1 and 1,1,1 chlorination increases, while that of chlorination in the 1,2 position falls. Thus although chlorination of ethane at 320° yields 1,1-dichloroethane and 1,2-dichloroethane in the proportions 4 : 1 with no 1,1,1-trichloroethane, at 415° the relative proportions of these three products are [8,12] 18.5 : 1.0 : 2.4. The distortion of the orienting influence of the chlorine is due to the free-radical character of thermal chlorination. Among the possible chlorination products, the one derived from the intermediate hydrocarbon radical which is the most stable at the given temperature is formed preferentially.

The stabilities of hydrocarbon radicals decrease in the sequence tertiary > secondary > primary[38]. When, therefore, the temperature of chlorination is increased beyond a certain limit (which is quite definite for any given alkane), the composition of the reaction products is displaced towards the formation of 1,1- and 1,1,1-chloro-derivatives. The unstable free radical of the type $\cdot CHR.CH_2Cl$ which is formed exhibits a tendency to stabilise itself by splitting off the chlorine atom to form an olefine. The chlorination of alkyl chlorides can be represented by the following general equations[15]:



$$\begin{aligned} & R-CH_2-CH_2Cl + Cl^{\cdot} \xrightarrow{-HCl} R-CH_2-CHCl \xrightarrow[-Cl^{\cdot}]{+Cl_2} R-CH_2-CHCl_2, && (a)\\ & \rightarrow R-\dot{C}H-CH_2Cl \underset{-Cl^{\cdot}}{\rightleftarrows} R-CH=CH_2 \overset{+HCl}{\rightleftarrows} R-CHCl-CH_3\ , && (b)\\ & \qquad \big\downarrow {\scriptstyle +Cl_2\ \mid\ -Cl^{\cdot}} && \\ & R-\ CHCl-CH_2Cl\ . && (c) \end{aligned}$$

When chlorination takes place below this temperature limit (*e.g.* in the liquid phase) equilibrium (*b*) is displaced to the left, and the free radical $\cdot CHR.CH_2Cl$ reacts with molecular chlorine to form the 1,2-dichloride.

In view of the pyrolysis and isomerisation reactions which take place at high temperatures, special interest attaches to photochemical and also catalysed chlorination, which makes it possible to carry out the process under milder temperature conditions. The use of catalysts to accelerate chlorination by an ionic mechanism has a similar effect.

Liquid alkanes are usually chlorinated photochemically, but this method has not yet been widely used for the industrial chlorination of the lower, gaseous alkanes owing to the difficulty of designing suitable equipment. Nevertheless, even in this case photochemical chlorination can be more efficient than the thermal process. Thus the photochemical chlorination of ethane takes place in the gas phase at quite low temperatures (125°–150°) and nearly stoichiometric proportions of chlorine and ethane. The product of the reaction consists of ethyl chloride and dichloroethane in the proportions 6.4 : 1.0. The amount of chlorine which reacts reaches 98.5%. By increasing the relative amounts of ethane it is possible to achieve almost complete conversion of the ethane into ethyl chloride. Use of a solvent which is inert towards chlorine (*e.g.* CCl_4) allows the reaction to be carried out at room temperature[39]. Even the chlorination of methane to carbon tetrachloride has proved possible by photochemical means. The reaction medium is 31.2 M CCl_4 with the reactants in the molar proportion $Cl_2 : CH_4 = 4 : 1$ at +11°. The chlorine was supplied at a rate of 1.4 mole h^{-1}, and the methane at 0.35 mole h^{-1}.

Owing to the poor solubility of methane and the great solubility of chlorine in CCl_4 (and in other solvents), the two reactants are introduced separately in this case, the methane being highly dispersed and the point where it is introduced into a current of chlorine dissolved in carbon tetrachloride being strongly illuminated. In this method the chlorination evidently takes place mainly at the interface between the two phases. The proportion of methane converted into chlorinated products[40] can be as high as 90.8%.

Initiated chlorination is free from the disadvantages of the thermal and the photochemical methods, but little work has been done on it. A few papers dealing with this method will be considered in the section on the effect of impurities.

V. EFFECT OF IMPURITIES

The chlorination of alkanes is very sensitive to various impurities. The inhibiting and the inducing effects of impurities have been most thoroughly investigated.

1. Impurities which Inhibit Free-Radical Chain Processes of Chlorination

Effect of oxygen. Free-radical chain processes of chlorination are greatly retarded in the presence of even small amounts of oxygen. Thus in the thermal chlorination of methane (mixture containing 60% of CH_4 + + 40% of Cl_2), 30% of the chlorine has reacted after 5 min. In the presence of 5% of oxygen, however, practically no chlorination takes place[27]. The retarding effect of oxygen is explained by its interaction with the hydrocarbon radicals which are formed:

$$\begin{gathered} Cl^{\cdot} + RH \rightarrow R^{\cdot} + HCl \\ R^{\cdot} + O_2 \rightarrow ROO^{\cdot}. \end{gathered}$$

This reaction is 5000 times as rapid as the reaction of the radicals with molecular chlorine, so that the chain chlorination is inhibited. The peroxy-radical $ROO\cdot$ undergoes further change with the formation of various oxygen-containing compounds, depending on the temperature[14,41,42].

The retarding effect of oxygen is not constant but depends mainly on the composition of the gaseous mixture and the temperature. Thus the reaction velocity in the photochemical chlorination of methane in the presence of oxygen is represented by the equation[43]

$$\frac{d\,[CH_3Cl]}{dt} = \frac{k\,[Cl_2]^2 \cdot [CH_4]}{[O_2] \cdot (k\,[CH_4] + [Cl_2])}\ .$$

Hence it follows that the higher the chlorine content of the mixture the smaller is the inhibiting effect of the oxygen. At higher temperature the peroxy-radical $ROO\cdot$ is less stable, and above 300° it is no longer formed, so that oxygen then no longer exerts an inhibiting effect on the chlorination of alkanes[41,42]. Thus, although at 300° the retarding effect of 5% of oxygen on the thermal chlorination of methane is still considerable, at 375° this quantity of oxygen no longer produces any effect[27].

The peroxide radicals formed in the chlorination of alkyl chlorides are thermally less stable than the $AlkOO\cdot$ radicals. Therefore the inhibiting effect of oxygen in the chlorination of alkyl chlorides disappears at lower temperatures than in that of alkanes. Thus, oxygen inhibits the chlorination of chloroform only at or below 200°.[42]

Effect of nitrogen trichloride. Technical chlorine always contains nitrogen trichloride which, in spite of its minute concentration (of the order of 0.001%), undoubtedly has an appreciable effect on the chlorination of alkanes at moderate temperatures. The effect of nitrogen trichloride is due to the reaction[41]

$$Cl^{\cdot} + NCl_3 \rightarrow NCl_2 + Cl_2.$$

The energy of the N−Cl bond is about 20 kcal smaller than that of Cl−Cl, and as a result the regeneration of chlorine atoms by the reaction

$$NCl_2 + Cl_2 \rightarrow NCl_3 + Cl^{\cdot} - 20\ \text{kcal},$$

is extremely slow at room temperature. The destruction of the active chlorine atoms leads to inhibition of the chain process.

A study of the photochemical chlorination of hydrogen has shown that a given retardation can be produced by a concentration of nitrogen trichloride which is only 10^{-5} of the oxygen concentration required. At high temperatures, on the other hand, nitrogen trichloride accelerates the chlorination owing to its decomposition to form free chlorine atoms

$$2NCl_3 \rightarrow N_2 + 6Cl^{\cdot}.$$

Effect of catalysts which act as chlorine carriers. Among these we are concerned most often with the effect of iron salts, which under the conditions of purely chain (*e.g.* photochemical) processes of chlorination retard the reaction[44]. The inhibiting effect of iron salts is evidently a result of interaction between the alkyl radicals which are formed and ferric ions, with reduction of the latter to the ferrous state[45]

$$R^{\cdot} + Fe^{3+} + Cl^{-} \rightarrow RCl + Fe^{2+},$$

$$Cl_2 + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2Cl^{-},\ \text{etc.}$$

The harmful effects of iron salts can be eliminated by adding 0.1−1% of a phosphoric ester or of some other organic compound of phosphorus which will convert iron salts into complex compounds. The presence of water has a similar though less marked effect, as it deactivates the salts by hydrating them[46]. Under certain conditions, however, iron salts can initiate free-radical chain processes. Thus in the absence of light and initiators, $FeCl_3$ is able to catalyse the chlorosulphonation of alkanes[47], which, in contrast to chlorination processes, takes place only by a free-radical mechanism[48]:

$$Cl^{\cdot} + RH \rightarrow R^{\cdot} + HCl,$$

$$R^{\cdot} + SO_2 \rightarrow RSO_2^{\cdot};\quad RSO_2^{\cdot} + Cl_2 \rightarrow RSO_2Cl + Cl^{\cdot},\text{etc.}$$

The activation of free-radical chain processes by ferric chloride is evidently due to the exothermic nature of the ionic chlorination of alkanes which occurs under its influence. The energy evolved in this process is partly dissipated as heat and partly used up in the dissociation of a chlorine molecule to form free atoms:

$$RCl^{*} + Cl_2 \rightarrow RCl + Cl^{\cdot} + Cl^{\cdot}.$$

The free chlorine atoms which are formed now enable chlorination and chlorosulphonation to take place as chain reactions[14,49]. Other catalysts which are chlorine carriers have an effect analogous to that of ferric chloride. Like the latter, they are able under certain conditions to inhibit or to catalyse free-radical chain reactions. A study of the chlorosulphonation of n-heptane and of isooctane at 35°−40° in the absence of light and initiators has shown that the catalysts used could be arranged in the following sequence of decreasing activity[14]:

$$S > PCl_5 > SbCl_5 > I_2.$$

When n-heptane is chlorosulphonated in the presence of sulphur the yield of heptanesulphonyl chlorides is 17% of theoretical, compared with 45.3% in the photochemical process. The formation of one mole of monochlorides of heptane is accompanied by the formation of 2.5 moles of heptanemonosulphonyl chlorides. The chlorosulphonation of isooctane under the same conditions yields 21.1% of monosulphonyl chlorides compared with 21.2% in the photochemical process, the formation of one mole of monochlorides of isooctane being accompanied by that of 1.55 moles of isooctanemonosulphonyl chlorides[14].

The fact that in the presence of these catalysts the yield of sulphonyl chlorides is proportional to the amount of chlorides formed is a direct indication that the free-radical chain reactions occurring under these conditions are dependent on processes of ionic chlorination.

2. Impurities which Induce Free-Radical Chain Processes of Chlorination

Effects of SO_2 and NO_2. Sulphur dioxide and nitrogen dioxide have an appreciable effect on chain processes. Both thermal and photochemical chlorination of alkanes are considerably accelerated in the presence of SO_2, as well as in the presence of initiators for chain reactions[30]. The chlorination of alkanes in also considerably accelerated in the presence of NO_2. Thus with n-butane and an addition of 2% of NO_2 at 150° the amount of chlorine consumed is 44%, whereas in the absence of NO_2 there is practically no reaction at this temperature[50]. Very little work has been done on this phenomenon, which is apparently explained by SO_2 and NO_2 acting as intermediate links in the chain reaction. This reduces to a minimum the processes by which chains, once started, are terminated, and lengthens their life. The following is a possible example of a chain reaction involving SO_2:

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2,$$

$$Cl^{\cdot} + RH \rightarrow R^{\cdot} + HCl,$$

$$R^{\cdot} + SO_2Cl_2 \rightarrow RCl + SO_2Cl^{\cdot},$$

$$SO_2Cl^{\cdot} \rightarrow SO_2 + Cl^{\cdot},\ \text{etc.}$$

When NO_2 is used, direct initiation of the chain reaction may also occur, the nitrogen dioxide displaying its latent radical character[41,51]

$$NO_2 + RH \rightarrow R^{\cdot} + HNO_2,$$

$$R^{\cdot} + Cl_2 \rightarrow RCl + Cl;$$

$$Cl^{\cdot} + RH \rightarrow R^{\cdot} + HCl,\ \text{etc.}$$

Effect of olefines. The catalytic action of small amounts of olefines on the chlorination of alkanes is of great practical interest. Thus it has been shown that, in the absence of light and other impurities, the chlorination of propane, butane, and pentane is greatly accelerated in the presence of ethylene[52,53]. When liquid n-butane is chlorinated in the presence of but-2-ene, the formation of one mole of 2,3-dichlorobutane is accompanied by the substitution of chlorine for hydrogen in ten moles of the n-butane[52]. It follows from this that the additive chlorination of olefines can induce the chlorination of alkanes. In the presence of traces of some metal salts, the former takes place by an ionic mechanism. The energy evolved in the chlorination of, for example, ethylene

$$Cl_2 + C_2H_4 \rightarrow C_2H_4Cl_2 + 58 \text{ kcal mole}^{-1},$$

as in the case of the inducing effect of catalysts which are chlorine carriers, causes the molecular chlorine to dissociate into free atoms:

$$C_2H_4Cl_2^{*} + Cl_2 \rightarrow C_2H_4Cl_2 + Cl^{\cdot} + Cl^{\cdot}.$$

The free-radical chain processes involved in the chlorination of alkanes then proceed in the usual way. The above mechanism for the inducing effect of olefines is confirmed by the ability of olefines to catalyse free-radical chain processes in the chlorosulphonation of alkanes. Thus the chlorosulphonation of n-heptane in the presence of ethylene and in the absence of light and other impurities goes very smoothly at 45° with a yield of heptanemonosulphonyl chlorides which is ~45% of theoretical[14]. An unnecessarily high content (20% or more) of olefines in the hydrocarbon mixture and the use of too low reaction temperatures (which are quite definite with each particular olefine) are undesirable, since the additive chlorination then becomes the main consumer of the chlorine, and the chlorination of the alkanes is retarded[54]. The presence of oxygen has a detrimental effect on the olefine-induced chlorination of alkanes, which is readily understood from the chain character of chlorination and chlorosulphonation processes.

Effect of initiators. Chain initiation is the most difficult step in the chlorination chain reaction, although the energy of rupture of the C–H bond in different alkanes and especially in alkyl chlorides is of some significance. Dissociation of the original molecules into two free radicals or atoms is the simplest way in which the initial radicals can be formed. Comparing the energy of the Cl–Cl bond (57.2 kcal mole^{-1}) with those of C–H and C–C in alkanes (85–101 and 60–83 kcal mole^{-1} respectively) we see that, in the alkane–molecular chlorine system, the latter dissociates the more readily to form active species. However, even the dissociation of molecular chlorine requires quite severe treatment, such as temperatures of 300° and above, light quanta, exposure to radioactive materials, or X-rays[41,55]. Therefore, the presence of initiators, whose molecules dissociate into free atoms and radicals more readily than molecular chlorine, is of great importance in free-radical chain chlorination processes. Among such substances are other halogens, alkali metals, organometallic compounds, organic peroxides and hydroperoxides, azo and diazo compounds, tetrazens, disulphides, arylethanes, etc. However, the effectiveness of initiators is determined not only by the readiness with which they decompose but also by the reactivity of the resulting free atoms or radicals. In other words, an initiator will be highly effective only if the low energy required for its decomposition into free radicals or atoms is complemented by a fairly high energy of bonding of the latter in the reaction products. Thus the energy of dissociation of molecular iodine into free atoms is 35.5 kcal mole^{-1}, compared with 57.2 kcal mole^{-1} for molecular chlorine[41]. However, the free atoms of iodine formed by the dissociation of I_2 are not very active, and are unable to split off a hydrogen atom from an alkane molecule, since the energy of the H–I bond is less than that of C–H (70.5 and 85–101 kcal × × mole^{-1} respectively). The reaction

$$I^{\cdot} + Cl_2 \rightarrow ICl + Cl^{\cdot},$$

is also energetically unfavourable, since the energy of the I–Cl bond is less than that of Cl–Cl (49.8 and 57.2 kcal × × mole^{-1} respectively).

Furthermore, in the presence of I_2 free chlorine atoms which have been formed in some other way react, not with the alkane, but with molecular iodine,

$$Cl^{\cdot} + I_2 \rightarrow ClI + I^{\cdot},$$

since the I–I bond is considerably weaker than C–H: *i.e.* under certain conditions I_2 can act as an inhibitor of chain chlorinations. Such very active initiators as fluorine, alkali metals, and organometallic compounds of the alkali and alkaline-earth metals are seldom employed because their great chemical reactivity makes their practical application difficult. Fluorine occupies a special position among all other initiators because the relatively high energy of the F–F bond (37.6 kcal mole^{-1}) cannot be reconciled with the exceptionally large effect of fluorine at low temperatures on the basis of dissociation into free atoms. Chlorination of ethane in the presence of fluorine at room temperature and below gives a 90–100% yield of ethyl chloride and dichloroethane, with the whole of the chlorine reacting[56].

The action of fluorine on chlorination processes apparently consists in the formation of free radicals by reaction with the alkane:

$$F_2 + RH \rightarrow R^{\cdot} + F^{\cdot} + HF.$$

The unusual behaviour of fluorine is due to the fact that the resulting H–F bonds are very stable compared with the F–F bonds (bond energies 134 and 37.6 kcal mole^{-1} respectively). Owing to this, the reaction of fluorine with an alkane is characterised by a negligible activation energy (a few kilocalories per mole), and involves practically no consumption of energy: *i.e.* it is either thermoneutral (with methane) or exothermic (with other alkanes and with alkyl chlorides). The extraordinarily great activity of fluorine in reactions with other organic compounds is due to the above factors, as has been suggested[41].

The initiating action of alkali metals has been most fully investigated in the chlorination of hydrogen[41]. Addition of sodium vapour (energy of Na–Na bond 17.5 kcal × × mole^{-1}) to a mixture of chlorine and hydrogen enables the dark reaction to occur even at 100°, whereas in the absence of sodium this reaction takes place only at 300°.

$$Na_2 \rightarrow Na^{\cdot} + Na^{\cdot},$$
$$Na^{\cdot} + Cl_2 \rightarrow NaCl + Cl^{\cdot},$$
$$Cl^{\cdot} + H_2 \rightarrow HCl + H^{\cdot},$$
$$H^{\cdot} + Cl_2 \rightarrow HCl + Cl^{\cdot}, \text{ etc.}$$

As a result, 1000 HCl molecules are formed for every Na atom which has reacted. The effect of a number of other initiators on the chlorination of the lower alkanes has been investigated. Thus in the presence of tetraethyllead, chlorination of ethane with 95% consumption of the chlorine takes place even at 132°, whereas the thermal chlorination starts[12] only at 280°; the composition of the chlorination products is the same in the two cases.

Tetraethyl-lead is highly effective even at extremely low concentrations in the reactant mixture (~0.002 vol.%). Good results have also been obtained in the chlorination of propane, n-pentane, and other alkanes. That of propane takes place at 136°–140° with more than 95% of the chlorine reacting. Chlorination of liquid n-pentane in the presence of $Pb(C_2H_5)_4$ is quantitative.

The initiating action of $Pb(C_2H_5)_4$ at temperatures below 150° (at which thermal decomposition starts) is explained by the formation not of ethyl radicals

$$Pb(C_2H_5)_4 \rightarrow Pb + 4C_2H_5^{\cdot},$$

but of active chlorine atoms, resulting from the reactions

$$Pb(C_2H_5)_4 + 4Cl_2 \rightarrow PbCl_4 + 4C_2H_5Cl \text{ and } PbCl_4 \rightarrow PbCl_2 + 2Cl^{\cdot}.$$

Lead tetrachloride is unstable even at room temperature, and, in contrast to other metal chlorides, is readily decomposed with the formation of chlorine atoms instead of ions[14].

Tetraphenylethane and azomethane have been used for the dark chlorination of alkanes[12,57], but they are less active than metal alkyls as initiators for the vapour-phase chlorination. Thus in the presence of azomethane at 144°, the chlorination of n-butane uses up 5.5–6% of chlorine, whereas in the absence of azomethane no reaction takes place at this temperature[57].

In the chlorination of liquid alkanes the greatest practical use has been made of various organic peroxides (*e.g.* benzoyl, lauroyl, and phthaloyl peroxides) and azo compounds (*e.g.* azodiisobutyronitrile), added in amounts of 0.01–1% to the alkane. In the presence of these initiators chlorination takes place readily and rapidly at temperatures of about 70°–120°.[58,59]

The use of a solvent which is inert towards chlorine as the reaction medium makes it possible to employ the above initiators for the chlorination of gaseous alkanes as well. Thus ethane can be chlorinated at 65°–70° in CCl_4 containing 1% of azodiisobutyronitrile, benzoyl peroxide, or dimethyl percarbonate, 60% of the ethane being converted into chlorinated derivatives[60].

VI. EFFECT OF SURFACE

The surface of the reaction vessel and of its packing material substantially affects chlorination processes, causing both initiation and termination of chains. Under steady-state conditions the effect of the surface is apparently due to its acquisition of semiconducting properties by forming a firmly adsorbed film of the components of the reaction mixture (adsorption being effected by valency or coordinate bonds)[1,41,61].

The thermal chlorination of 2,2,4-trimethylpentane, 2,3-dimethylbutane, n-pentane, n-hexane, and n-heptane in a Pyrex glass reaction vessel is preceded by an induction period of 30–60 min depending on the alkane[11]. The existence of the induction period has been shown to be associated with the absorption of hydrocarbon radicals by the surface of the vessel. The hydrophobic film which is formed has the composition $\rangle\!\!-Si-O-R$, and is removed by washing the reaction vessel with concentrated alcoholic potash or by oxidation in a current of oxygen at 300°. The maximum rate of chlorination is reached when this film is formed. If the surface is contaminated with highly chlorinated reaction products, for example when the process is prolonged, the rate of chlorination gradually falls, which suggests that the $\rangle\!\!-Si-O-R$ film plays an active part in the catalysis of chain processes[28]. The presence of the semiconducting layer causes the appearance of free valences on the surface, which arise under the influence of thermal motion and possess the properties of a free radical. A chlorine molecule from the gas phase incident on a point of the surface having a free valence V, reacts with the latter

$$Cl_2 + V \rightarrow VCl + Cl^{\cdot}, \qquad \text{(I)}$$

to yield an active chlorine atom in the reaction zone. As with all free-radical reactions, the activation barrier to such a reaction is low, which explains the ease with which the surface generates free chlorine atoms. The energy of the $V-Cl$ bond is, of course, considerably greater than that of Cl–Cl. Chain termination during chlorination is mainly due to chemisorption of the free chlorine atom. On collision with the active surface, the Cl· is first held by comparatively weak forces, a one-electron bond apparently being formed. From this weakly bound state the Cl· can either escape back into the reaction space or surmount the activation barrier and become firmly chemisorbed by forming the surface compound VCl:

$$V_2 + Cl^{\cdot} \rightarrow VCl + V, \qquad \text{(II)}$$

where V_2 is an element of surface which can form two free valences by dissociation:

$$V_2 \rightarrow V + V - U \text{ kcal}. \qquad \text{(III)}$$

The presence of a considerable activation barrier in reaction (II) as compared with (I) is responsible for the change in character of the surface effect with change in temperature. Surface activation of the chain process occurs mainly at comparatively low temperatures, close to those at which chlorination of the alkane starts. At higher temperatures the surface begins to exert a retarding effect on the reaction. The energetic non-uniformity of the surface, which derives from its physical non-uniformity, results in chain initiation and chain termination taking place simultaneously on the surface. At relatively low temperatures, however, the rate of initiation predominates over that of termination, so that an increase in the surface : volume ($S:V$) ratio in this case tends to accelerate the chlorination. With rise in temperature the rate of chain termination on the surface exceeds that of surface initiation. As a result, the surface has the opposite effect: *i.e.* at higher temperatures an increase in the $S:V$ ratio tends to retard the chlorination. Thus Fig. 6 shows that in the thermal chlorination of n-butane the packing (short lengths of glass tubing) accelerates the process[50] up to about 250°. Above this temperature the packing starts to retard chlorination, and at

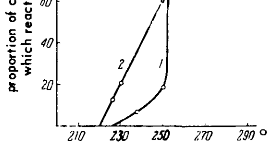


Fig. 6. Temperature variation of proportion of chlorine which reacts in the thermal chlorination of n-butane:
1) without packing; 2) with packing.

300° it no longer has any effect. This is apparently explained by the predominance of bulk chain initiation due to the dissociation of molecular chlorine into free atoms. The activation and inhibition of free-radical chain reactions by the surface undoubtedly depends on the chemical composition of the latter and also on the presence and composition of inclusions. This aspect of the surface effect has unfortunately been little investigated, and existing data are not very accurate because it is difficult to produce surfaces of comparable characteristics. A number of investigations have shown, however, that the type of packing employed has a marked effect both on the reduction in temperature and on the composition of the products. Thus the optimum temperature for the thermal chorination of n-butane is lowered from 300° to 200° in the presence of active aluminium oxide, and to 170° in the presence of silica gel. With a space velocity of $\sim 300\ h^{-1}$ for the process and an n-butane: chlorine molar ratio of 4.5 : 1, the whole of the chlorine is consumed in all cases[50]. The effects of different packings on chlorination processes can be estimated from the activation energy (see Table 5)[50].

TABLE 5. Activation energies for the chlorination of n-butane using different packings.

Packing	Apparent activation energy, cal mole^{-1}
No packing	39 000
Pieces of glass tubing	17 000
Active aluminium oxide	14 700
Silica gel	8 200

The use of highly porous packings usually results in an increased yield of di- and poly-chlorides. This is primarily explained by the fact that chlorine and alkyl chlorides are considerably more readily adsorbed than are the lower alkanes, resulting in a more thorough chlorination.

In the chlorination of n-butane on active aluminium oxide and silica gel, 50% of dichlorobutanes are formed, whereas in the purely thermal gas-phase chlorination (at 300° and with the same proportions of the components in the reaction mixture) monochlorobutanes are formed practically exclusively. This effect is most clearly exhibited in the chlorination of methane on activated charcoal, carbon tetrachloride being the main product at both low and high temperatures[62].

Further investigation of the chlorination of alkanes is needed to clarify the laws governing the reaction and its mechanism. This should lead to a better control of the chlorination process and yield new derivatives from natural gas and from petroleum of the greatest value to the national economy.

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SORPTION AND CHROMATOGRAPHY OF MACROMOLECULAR SUBSTANCES

G. V. Samsonov

CONTENTS

I. INTRODUCTION

The considerable successes recently achieved by sorption and chromatographic methods for the separation, isolation, and purification of substances of low molecular weight have given rise to a series of papers on the fractionation of macromolecular compounds using these methods, and also on the application of chromatographic methods to the analysis of polymer mixtures. Advances in sorption and chromatographic methods as applied to polymers have been due on the one hand to the development of a theory and a laboratory technique of chromatography whereby mixtures of very similar substances can be separated, and on the other to the synthesis of specific polymeric sorbents, mainly ion-exchange resins, the structure of which can be controlled during their preparation. The preparation of cross-linked polymeric sorbents, possessing great intramolecular porosity and capable of absorbing large quantities of macromolecular ions, has been especially important in this connection.

Nevertheless, the development of sorption and chromatographic methods for separating and analysing polymers has encountered a number of difficulties which were of no significance in work with substances of low molecular weight. The first important obstacle was the low rate at which sorption equilibrium is established. Although, in the absorption of substances of low molecular weight, decreasing the grain size of the sorbent and creating conditions under which the boundaries of the chromatographic zones were sharpened enabled the spreading of the bands in the sorption column to be successfully overcome, with macromolecular substances it proved considerably more difficult to sharpen the boundaries of the chromatographic bands. A second circumstance impeding the development of sorption methods in this field is the complicated dependence of the sorption capacity on the molecular weight of the absorbed substances. The capacity increases with increasing molecular weight in a series of homologous polymers of comparatively low molecular weight, and decreases with polymers of relatively high molecular weight[1-5]: on the one hand the usual increase in sorption capacity in conformity with Traube's rule, and on the other a decrease due to the fact that large molecules cannot penetrate the pores of the sorbent. This latter phenomenon, of course, can prove useful in a number of cases for the separation of polymers according to their molecular weights, on the molecular sieve principle.

The dependence of the sorption capacity of polymers on the composition of the solvent in contact with the sorbent has been studied with several materials[4,6,7]. Thus more polystyrene is sorbed by activated charcoal from the comparatively "poor" solvent ethyl methyl ketone than from the "better" toluene[7]. Addition of the very "poor" solvent methanol to ethyl methyl ketone improves the sorption of polystyrene[4]. This phenomenon can be compared with the analogous influence of solubility on the sorption capacity of a substance observed earlier by Tiselius[8].

The rate of sorption of polymers is greatly dependent on their molecular weight. A series of investigations by Yurzhenko *et al.*[9,10] has shown that polyisopropylene, polystyrene, and butadiene–styrene rubber of low molecular weight are sorbed on carbon black much more rapidly than are samples of the same polymers having high molecular weights. The sorption of an unfractionated polymer is accompanied by an increase in the intrinsic viscosity of the solution surrounding the sorbent, indicating selective absorption of the low-molecular-weight fraction[9,10]. The low rate of sorption on carbon black of the high-molecular-weight fraction of butadiene–styrene rubber produces the very interesting phenomenon that, after a certain time,

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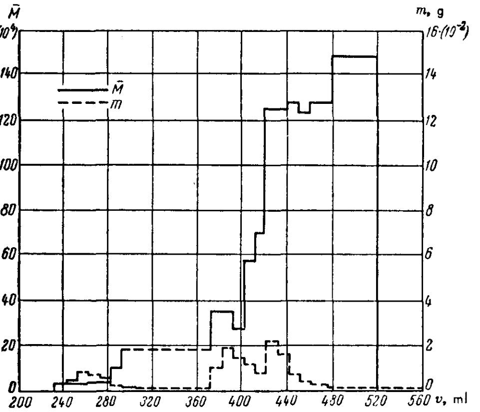

Fig. 1. Chromatographic fractionation of polystyrene on an activated charcoal column. Eluent solution consists of mixtures of toluene and tetralin (3 : 1, 1 : 1, and 1 : 3). $\bar{M}$ = mean molecular weight of polymer in the fraction; m = quantity (in grammes) of polymer in the fraction; v = volume (in ml) of effluent.

II. ELUTION CHROMATOGRAPHY

The most widespread variant of the chromatographic method is elution chromatography, which consists in sorbing a mixture of substances in the upper part of a column and eluting them with a definite solvent or solution. In such a process each component moves along the column by being repeatedly sorbed and desorbed. The rate at which the substance moves depends on its adsorbability, and is inversely proportional to the adsorption coefficient[12]. As a result of this displacement, the components of the mixture are separated and leave the column in the form of pure fractions of the individual substances or mixed fractions, still incompletely resolved. If the process is carried out with dilute solutions, the concentration in each of the bands falls in direct proportion to the square root of the time, and the band width (the length of column occupied by each band) increases according to the same law. The degree of blurring of the bands depends on the rate of establishment of the sorption equilibrium. With the low rates of sorption observed for polymers a considerable blurring is to be expected.

Nevertheless, in a number of cases, beginning with the work of Mark and Saito[13], it has proved possible to effect the chromatographic separation of polymers according to their molecular weights. Polystyrene of low molecular weight ($M = 10^4$) could be eluted with toluene from a column of activated charcoal mixed with celite[7]. Tetralin, however, elutes both the polystyrene fraction of low molecular weight, which leaves the column at the start of the process, and that of high molecular weight ($M = 10^6$). Fractionation was most successfully accomplished by the successive application of a series of eluent mixtures of toluene and tetralin containing these solvents in the proportions 3 : 1, 1 : 1, and 1 : 3 (Fig. 1). The increase in molecular weight observed on passing up the column, both here and in other investigations[14-16], contradicts the fall in sorption capacity with increase in molecular weight[3,4] predicted by the theory of chromatography[12], according to which components which are sorbed to a smaller extent are the first to move along the column. These contradictory results can be ascribed to different laws for the sorption of polymers, to the fact that in different experiments sorption capacity is determined at different stages in the establishment of sorption equilibrium[16], or even, finally, to the effect of additional factors in the chromatographic process, such as precipitation of the polymer in the column[7].

Different types of polymer sorbed on a column may be completely separated by elution with a solvent. This has been achieved in the case of poly(vinyl chloride) and poly(vinyl acetate) on an activated charcoal column[17]. When isobutyl ketone is employed as eluent, poly(vinyl chloride) is the first to emerge from the column, and only after a considerable time does the acetate appear.

In order to separate rubbers by another variant of the chromatographic method, paper chromatography, the filter paper must be specially treated with a 5% solution of methyltrichlorosiloxane in benzene[18]. The hydrophobic paper obtained in this way retained benzene in its pores instead of the usual solvent – water – employed in paper chromatography. Cyclohexanone was used as the mobile solvent. Guayule and synthetic butadiene–styrene rubbers were separated by this means, the latter rubber being displaced at the greater rate. This method has been used also to investigate the changes in properties undergone by rubbers on milling. Paper-chromatographic fractionation of poly(vinyl chloride) and poly(vinyl acetate) has been accomplished in the usual way without hydrophobic treatment [17], using isobutyl ketone as the mobile phase. While the poly(vinyl chloride) moves with the solvent front in this system, the poly(vinyl acetate) spot remains stationary. The sorption of polymers on paper may be the controlling factor in this process.

The fractionation of stereoisomers of low molecular weight by chromatographic methods is based on the use of optically active sorbents. On an analogous principle, Natta *et al.*[19] used insoluble isotactic polypropylene sorbents of high molecular weight in order to separate soluble polypropylene into fractions of different degrees of stereoregularity. It was established in these experiments that molecules possessing great stereospecificity and forming highly crystalline polymers are linked firmly to such a sorbent. Components of a low degree of crystallinity are comparatively easily eluted with isopropyl ether. Samples of crystallinity varying from 2.5% to 30% were obtained in these experiments from a stereoblock polypropylene of 22% crystallinity. On such a sorbent, fractionation takes place predominantly according to the degree of stereoregularity, and to a lesser extent according to molecular weight. The chromatographic analysis is most conveniently carried out on a column containing silica gel on which the polypropylene of high molecular weight has been deposited.

III. FRONTAL CHROMATOGRAPHY

In view of the difficulties involved in the desorption of sorbed polymers, Claesson developed a frontal chromatographic method for determining the molecular-weight distribution of polymers[2]. The frontal method which he worked out together with Tiselius[20,21], is a process of continuous filtration of a multicomponent solution through a sorbent column. As a result of the different adsorbabilities of the components, each of them appears at the outlet of the column at a quite definite time, after a certain volume of solution has passed through the column. This latter quantity is an important characteristic defining the dynamic sorption properties of a particular component, and when it relates to a column containing 1 g of sorbent it is termed the retention volume. For dilute solutions this quantity is constant for a given component and a given sorbent.

The rate of movement of the chromatographic zone boundary for a substance in a column can be easily calculated from the mass continuity equation for the substance[12]

$$\frac{\partial c}{\partial x} + \alpha\frac{\partial c}{\partial v} + \frac{\partial m}{\partial v} = 0, \tag{1}$$

where c is the concentration of the substance at a given cross-section of the column, x the distance from the top of the column, v the volume of solution which has run through the column, α the volume of the pores in a column of height 1 cm and cross-section 1 cm^2, and m the amount of substance absorbed by the sorbent at the given cross-section of the column calculated for the quantity of sorbent occupying unit height of the column.

From Eqn. (1) the rate of displacement along the column of a point corresponding to a constant concentration of the substance is defined by the equation

$$\left(\frac{\partial x}{\partial v}\right)_c = \frac{1}{\alpha + \frac{\partial m}{\partial c}}, \tag{2}$$

provided that the substance has a definite sorption isotherm

$$m = f(c). \tag{3}$$

The theory of chromatography shows that, in the case of a sorption isotherm concave to the concentration axis (Langmuir and Freundlich types), a sharp leading edge is formed when a solution of the substance is filtered through a column. In other words, the instant the substance appears at the outlet from the column, its concentration increases abruptly to that in the initial solution. It can be shown from Eqn. (1) that the rate of displacement of the sharpened leading edge is given by the equation

$$\left.\frac{\partial x}{\partial v}\right|_{\mathrm{fr}} = \frac{1}{\alpha + m/c}. \tag{4}$$

All these relationships, which hold for a one-component system, become more complicated with solutions which contain several substances. In the presence of polymer homologues in the solution, the laws of motion of the components along the column are defined by a set of equations of type (1)

$$\frac{\partial f_\omega}{\partial x} + \alpha\frac{\partial f_\omega}{\partial v} + \frac{\partial m_\omega}{\partial v} = 0, \tag{5}$$

for all polymer homologues having molecular weights lying between M and $M \pm dM$, where $f_\omega(M)dM$ is the concentration of each polymer homologue. The Langmuir sorption isotherm equation for each such component is of the form

$$m_\omega(M) = \frac{k(M) f_\omega(M)}{1 + \int\limits_0^\infty l(M)\, f_\omega(M)\, dM}, \tag{6}$$

where k and l are constants depending on the properties of the polymer and sorbent molecules.

It is difficult to find a general solution for the movement of a system of polymer homologues along the column. With dilute solutions, however, the equation of the sorption isotherm is simplified and becomes linear

$$m_\omega(M) = k(M) f_\omega(M). \tag{7}$$

In this case, since the amount of each polymer homologue sorbed depends only on its concentration, it is possible to solve each material balance Eqn. (5) separately, as has been demonstrated in a number of cases[12]. For linear adsorption isotherms the front edge and the point of constant concentration then move with the same velocity

$$\left.\frac{\partial x}{\partial v}\right|_{\mathrm{fr}} = \left(\frac{\partial x}{\partial v}\right)_c = \frac{1}{\alpha + m_\omega(M)/f_\omega(M)}. \tag{8}$$

Thus all polymer homologues move along the column at a rate depending only on the properties of the given polymer fraction and those of the sorbent, independently of their concentration and of the total concentration of polymer in the solution. Under these conditions the concentration of each component increases in the column from zero to a limiting value equal to the concentration of these substances in the initial solution.

Thus when a volume v of solution is run through the column, all components for which the retention volume v_0 is less than v appear in the filtrate; at any given instant the mixture arriving at the outlet from the column contains all the components eluted from the column at a concentration equal to their concentration in the original solution. This means that an extremely simple relation exists between the molecular-weight distribution of the polymer and the elution curve for frontal analysis.

With polymers containing no fractions of low molecular weight, the adsorbability should fall with increase in molecular weight[2,3]. The theory of fractionation can also be applied to substances showing an inverse relation between sorption capacity and molecular weight. In conformity with Eqn. (8) the velocity of the front should thus be greater the higher the molecular weight, and therefore an inverse relation should exist between the retention volume v_0 of the polymer homologue and its molecular weight

$$M = \gamma(v_0). \tag{9}$$

The equation to the elution curve for the frontal process can be written

$$\frac{C}{C_0} = \psi(v_0), \tag{10}$$

where C and C_0 are the concentrations of the polymer at the outlet from the column and in the initial solution respectively.

From the above considerations it follows that $\psi(v_0)$ is the weight fraction of substances of molecular weight exceeding

M (a single-valued function of v_0). Consequently there exists a function

$$F(M) = 1 - \psi(v_0) = 1 - \frac{C}{C_0}, \qquad (11)$$

which represents the weight fraction of all polymer homologues of molecular weight equal to or less than M.

In order to study the molecular-weight distribution, it is thus necessary to determine the form of the frontal elution curve $\psi(v_0)$ and to plot the graph of $f_\omega = \partial F(M)/\partial v$ against v_0. Since the above arguments hold only for dilute solutions, the elution curves obtained experimentally must be extrapolated to zero concentration. On Claesson's suggestion this is effected by extrapolating along straight lines intersecting the elution curves in characteristic points. The intercepts on each such straight line are then extrapolated to zero concentration. On this basis Claesson obtained a series of curves representing the molecular-weight distributions in polymers. Three curves of this type for different samples of poly(methyl methacrylate) are shown in Fig. 2. The dependence of f_ω on v_0 along these curves is quite definite, whereas the relation between v_0 and M is extremely rough, since the scale factor of the horizontal axis in terms of molecular weight must be determined in independent experiments on fractionated samples (dependence of v_0 on M). Nevertheless, the curves obtained, even without a knowledge of the v_0–M relation, give valuable information of the presence of maxima on the molecular-weight distribution curve (owing to the inverse character of the above relation), and are also useful for the comparison of polymers of the same type. A more important defect of the proposed method is evidently the requirement of equilibrium, common to all relations deriving from the theory of chromatography. The low rate of sorption of substances of high molecular weight can greatly distort the pattern of sorption and lead to an erroneous analysis of the data. A low rate of filtration of the solution through the column is absolutely essential in such experiments.

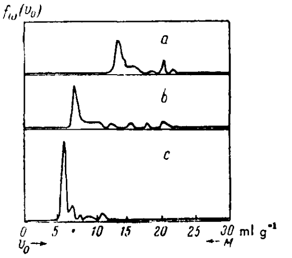

Fig. 2. Determination of molecular weight distribution in poly(methyl methacrylate) by frontal sorption analysis:
a) polymer prepared with benzoyl peroxide; *b*) and *c*) commercial specimens; v_0 = volume of effluent (retention volume); M = molecular weight; $f_\omega(v_0)$ = molecular weight distribution function.

IV. NEW CHROMATOGRAPHIC METHODS

New procedures have recently been worked out to improve the power of chromatographic methods to separate polymer mixtures. One of them, the moving capacity gradient or gradient elution method, was suggested by Harteck and others[22-24] and the theory was worked out by Zhukhovitskii *et al.*[25]. This process consists in eluting the substances from the sorption column with a solution of continuously changing composition. The gradual replacement of the solvent or solution is accomplished in such a way that the sorption capacity for each substance continuously falls with time at each cross-section of the column. It is no longer sufficient to use only one material balance Eqn. (1) to represent this process, but a set of equations must be considered

$$-\frac{\partial c}{\partial x} = \alpha\frac{\partial c}{\partial v} + \frac{\partial m}{\partial v}, \qquad m = \varphi(c, \rho), \qquad (12)$$

where ρ is a parameter defining the sorption capacity for a given concentration of the substances but with a variable solution composition.

The solution to this set of equations indicates that the zone for each component should contract to a very narrow band. Thus, the gradient elution method can lead to greatly improved chromatographic separations.

Using this principle, Williams was able to separate two fractions of nylon of molecular weight 150 000 and 350 000 on a celite column[26]. Gradient elution was carried out with a solution of formic acid of continuously increasing concentration. The fraction of low molecular weight was eluted first (hydrolysis of the polymer took place during chromatography). Williams' work on the fractionation of polysiloxanes on activated charcoal, based on the same principle, was even more successful[27]. In these experiments the polymethylsiloxane was separated into a series of fractions, the first of which to leave the column contained components of low molecular weight. A continuous increase in molecular weight of the siloxane during chromatographic separation occurred when a set of solvents of increasing solvent power was used (methyl alcohol – ethyl alcohol – ethyl ether).

In order that equilibrium and kinetic factors in the sorption of polymers should act in the same direction, Mould and Synge[28] proposed the use of an electrokinetic ultrafiltration method, the idea of which was to move the polymer mixture through a porous block, under the action of electro-osmosis for example. Under these conditions both equilibrium and kinetic factors favour the displacement of the low-molecular-weight fractions. This method has been used to effect a molecular-weight separation of polysaccharides at a collodion membrane.

Considerable progress in the fractionation of polymers has been achieved by the use of a new chromatographic method – precipitation chromatography – previously developed for substances of low molecular weight[29]. Application of this method to the separation of polymer homologues is based on the well-known fractional precipitation of polymers by the addition of "poor" and "good" solvents to the solution. We owe to Williams and several other investigators[26,30-33] the successful realisation of the fractionation of polymers by precipitation and dissolution as a chromatographic column process. The process involves allowing the polymer solution to flow from the upper, hotter layer of a column of the finely ground material to the lower, cooler layer. If the solution is saturated, in equilibrium with the solid at the top of the column, and the temperature coefficient of solubility is positive, a precipitate is formed at the bottom. Such a displacement of substance along the column is analogous to the ordinary sorption chromatographic process, but with the only difference that repeated sorption and desorption are replaced by precipitation and dissolution. If there is no change in composition of the solvent during the process, and the temperature falls linearly along the column, the material balance equation for each cross-section of the column can be written

$$-\frac{dc}{dx}=\left(\frac{\partial m}{\partial v}\right)_x \qquad K\frac{dt}{dt}=\left(\frac{\partial m}{\partial v}\right)_x, \tag{13}$$

where t is the temperature, K is a constant defining the temperature gradient along the column, m is the amount of the substance in the precipitate, and the remaining symbols have the same significance as in Eqn.(1). From Eqn.(13) we obtain

$$\left(\frac{\partial x}{\partial v}\right)_m=-K\frac{dc/dt}{(\partial m/\partial t)_v}\,. \tag{14}$$

Thus the rate of movement of a zone is determined by the temperature coefficient of the solubility and the distribution of the substance along the column.

In actual fractionations which have already been carried out by precipitation chromatography, the effect of the temperature gradient is supplemented by gradient elution based on the introduction of a solution of variable composition into the column, beginning with a "poor" solvent and gradually adding a "good" solvent. A chromatographic apparatus operating on such a principle is shown in Fig.3. The column is filled with a suspension of glass powder in the "poor" solvent. The main part of the column A is placed in an aluminium jacket B, the upper part of which is heated by means of the heater C, while the lower part is cooled with water (cooling coil D). Thus the process takes place with a constant temperature gradient in the column. The mixed eluent of variable composition enters the upper part of the column from the mixer E, initially filled with the "poor" solvent. The "good" solvent, added to the mixer, continuously changes the composition of the solvent entering the column.

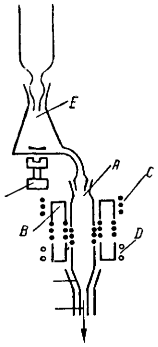

Fig. 3. Apparatus for fractionation of polymers by precipitation chromatography.

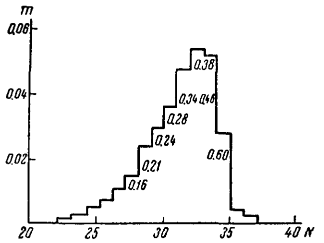

Fig. 4. Fractionation of polystyrene by precipitation chromatography. N = No. of fraction; m = amount of substance in fraction. The numerals on the graph indicate the specific viscosity of the fractions (in 0.5% solution in toluene).

The result of the fractionation of a sample of polystyrene of molecular weight 108 000 by the method described here is shown in Fig.4. The solvents used were ethyl alcohol and ethyl methyl ketone. The values shown along the curve for the viscosities of the polymer fractions indicate that the molecular weight of the polystyrene continuously increases as the solution leaves the column.

Precipitation chromatography enables very narrow fractions of polymer homologues to be further resolved[33]. Clearly the method has great possibilities.

V. POLYELECTROLYTES

Ion-exchange methods for the sorption of polymers have two main advantages over sorption methods based on van der Waals interaction between sorbent and sorbate: the existence of a large number of synthetic ion-exchange resins, possessing a great variety of properties, and also the possibility of specifying beforehand the sorption capacity of polyelectrolytes. The latter parameter depends on the formation of an electrovalent bond between specific groups in the polymers and in the sorbents. The synthesis of ion-exchange resins possessing considerable intramolecular porosity has enabled sorbents to be produced which absorb large quantities of polyelectrolytes. Such materials have been synthesised using very small quantities of cross-linking agent, for example divinylbenzene, the substance most widely used for combining linear polymeric molecules into three-dimensional structures. By varying the degree of cross-linking of the ion-exchanger, sorbents can be produced which are able to absorb small ions but not large ions. On this principle – the "molecular" or "ion-exchanger" sieve principle – various ionised substances can be separated according to their molecular weights. The simplest task here is to isolate polyelectrolytes from simple ions. For example, Amberlite IR-4B is an excellent sorbent for galacturonic acid, but it does not sorb polygalacturonic acid[34]. Polymannuronic (alginic) acid and its monomer behave similarly. The products of the enzymatic hydrolysis of polygalacturonic acid are absorbed by Amberlite IR-4B to an increasing extent as hydrolysis proceeds. The behaviour of phosphoric and polymetaphosphoric acids on this sorbent follows the same pattern. The definite effects observed with monomer–polymer systems become much less clearly defined with polymer homologues which are linear polyelectrolytes (polysulphostyrene[35]), although these too have been fractionated on a set of columns.

A new principle for the separation of ionised from unionised substances, that of ionic exclusion[36], based on the greater ability of the latter to penetrate the grains of a swollen ion exchanger, has been employed to separate weak and strong polyelectrolytes[37]. Lignosulphonic and weak polyacids in sulphite liquors have been separated by this method. Application of the molecular sieve principle as well has enabled this system to be fractionated also into polyelectrolytes of low and of high molecular weight.

VI. SORPTION OF PROTEINS BY ION-EXCHANGE RESINS

Biologically active polymers – proteins and nucleic acids – occupy a special place among soluble polyelectrolytes. Sorption methods have long been successfully applied to the purification and separation of these classes of compounds, especially proteins and enzymes. The numerous investigations in this field have been reported in great detail in a number of papers and books, especially in the reviews by Zittle[38] and by Moore and Stein[39]. The first of these papers discusses the equilibrium and the kinetic aspects of the sorption of proteins on both mineral and organic sorbents. The second gives a detailed account of work in the field of column chromatography. Finally, the application of chromatographic methods to the separation and analysis of proteins and nucleic acids has been reviewed by Sober and Peterson[40]. To avoid duplication, and since the results obtained during the past two years do not involve new principles, readers are referred to the above reviews. However, no mention is made in these papers of recent work on the mechanism and the laws governing the sorption of proteins by ion-exchange resins. An account of this work is given below.

The sorption of proteins by ion-exchange resins is governed by two main factors: the size of the absorbed ions and the occurrence of intermolecular interactions of opposite sign (*e.g.* Coulombic attraction and repulsion, resulting from the simultaneous presence of both positive and negative charges in proteins).

Application of the molecular-sieve principle enables proteins of high molecular weight to be separated from those of low molecular weight. Insulin, a protein of molecular weight 12 000, is sorbed in large amounts on sulphonated ion-exchange resins having a swelling factor of about 4.[41] Under the same conditions blood-serum proteins are absorbed in very small amounts. The synthesis of more cross-linked (less swollen) sulphonated resins provides an opportunity for the separation of polypeptides and proteins by this method, as well as of oligopeptides of different molecular weights[42].

Fractionation of proteins on the molecular-sieve principle using the hydrogen form of sulphonated resins should be carried out at 2°–5° to avoid catalytic hydrolysis of the peptide link. Denaturation phenomena are usually absent: desorbed insulin, for example, retains its biological activity. The preparation of sulphonated resins having swelling factors of 6–12 has led to the production of sorbents which now absorb blood-serum albumin and globulin in appreciable quantities (up to 10–20 mg g^{-1}).

However, the establishment of sorption equilibrium on resins of normal grain size is very slow, in this case taking several days or even weeks. A substantial increase in the capacity of sulphonated cation-exchange resins for sorbing proteins, and a marked reduction in the time required for the establishment of equilibrium, are achieved by using sorbents of very small particle size[43] (less than 0.05 mm). Under these conditions a considerable number of proteins are absorbed in amounts exceeding 100 mg g^{-1}. The adsorbabilities of different proteins and also the effect of the medium on sorption characteristics cannot be described in terms of the usual ion-exchange mechanism. However, a recently developed theory of the sorption of dipolar ions (amino-acids[44]) has provided a unified explanation of many unexpected experimental facts observed in the sorption of proteins.

Amino-acids and peptides of low molecular weight display a number of sorption properties denied to ions bearing one or more charges of the same sign. Thus, the amounts of dipolar ions (amino-acids) absorbed by the hydrogen form of sulphonated resins are approximately hundredfold greater than the amounts absorbed by the same resins in its salt form. Since the constant for the exchange of hydrogen ions with sodium ions on sulphonated resins is close to unity, this sorption phenomenon observed with amino-acids cannot be regarded as due to ion exchange. This, together with many other observations, has led to the following mechanism for the sorption of dipolar ions (amino-acids

$$R_1SO_3^- \; H^+ + H_3N^+ R_2COO^- = R_1 \, SO_3^- \, H_3N^+R_2 \, COOH. \tag{15}$$

It follows that dipolar ions absorbed on the hydrogen form of sulphonated cation exchangers are converted into cations. When a neutral solution surrounds the sorbent, this can only be explained as a large sorption effect causing a marked change in properties of the sorbed ion. The desorption of amino-acids by solutions of mineral acids is an ordinary ion-exchange process, since in such an experiment the amino-acid occurs as the cation both in the sorbed state and in solution. The sorption of an amino-acid on a sulphonated cation exchanger in the salt (*e.g.* sodium) form cannot take place in accordance with Eqn. (15). Consequently it is not the cation of the amino-acid but the zwitterion (dipolar ion) which should be present in the sorbed state on the salt form of resins. In conformity with this, the sorption capacity of sulphonated resins for zwitterions of low molecular weight is negligible: electrostatic attraction is accompanied by repulsion due to the presence of charges of like sign on sorbent and sorbate.

The quantity of zwitterions sorbed on sulphonated cation-exchange resins in the salt form can be substantially increased by diminishing in some way the effective repulsion caused by the negative charge on the carboxyl group. This can be achieved by decreasing the degree of ionisation of the carboxyl groups, changing from aqueous to aqueous–acetone solutions, by increasing the ionic strength of the solution and creating a screening shell around the ionised group, or finally by increasing the distance between the amino and carboxyl groups, using polypeptides instead of amino-acids[44]. In the last case the sorbed ion can without difficulty orient on the sorbent in such a way that the repulsion effect is diminished. The above considerations enable us to assess the sorption capacities of proteins on the salt and the hydrogen forms of sulphonated resins in terms of the distance between the amino and the carboxyl groups in the sorbed proteins. Zwitterions in which groups

TABLE. Sorption of proteins by the sulphonated cation-exchange resin SBS.

Protein	Sorption of protein, mg g^{-1}; resin in		Protein	Sorption of protein, mg g^{-1}; resin in	
	H form	Na form		H form	Na form
γ-Globulin	171	0	Adrenocorticotropic hormone	117	63
Serum albumin	145	0	Myogen	47	26
Ovalbumin	96	0	Chymotrypsinogen	90	105
Insulin	125	30			

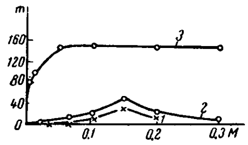

Fig. 5. Sorption of proteins from solutions containing NaCl on SBS sulphonated resins in the sodium form (m = quantity of protein sorbed, mg g^{-1} resin; M = molarity of NaCl):
1) serum albumin; 2) γ globulin; 3) insulin.

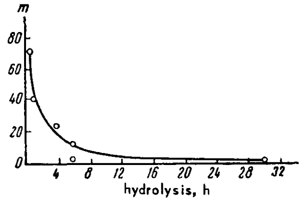

Fig. 6. Dependence of sorption of hydrolysis products of serum globulin on extent of hydrolysis; m = sorption expressed in mg-equiv. of nitrogen in the absorbed hydrolysis products (carboxylic cation-exchanger KMT in hydrogen form).

having unlike charges (NH_3^+, COO^-) are close together should be sorbed mainly on the hydrogen form of resins, and should not be sorbed, or be sorbed to a small extent, on resins in the salt (sodium) form. When the distance between the groups is relatively great (or in the presence of a great excess of positive charges), sorption of the proteins should occur on both salt and hydrogen forms of the resins. The data in the Table show that proteins can belong to either class of substances[43].

Biologically active proteins should belong predominantly to the second class of substances, which are sorbed on the salt forms of resins. Indeed, Coulombic attraction to other protein molecules in a solution of low ionic strength can occur only with proteins of this type. If, however, one of the interacting protein molecules contains oppositely charged groups situated close together, mutual attraction is possible only if the functional groups in the second macromolecule have the correct topography.

The sorption of proteins by sulphonated ion-exchange resins in salt form can be substantially intensified by increasing the ionic strength of the solution (Fig. 5). Nevertheless, the amounts of proteins sorbed under these conditions are small. Another way of increasing the sorption of proteins on the sodium sulphonate form of a resin is to use aqueous–acetone solutions[43].

Carboxylic cation exchangers sorb proteins in accordance with somewhat different laws. As zwitterions, many proteins are not sorbed on the salt forms of these exchangers[45], and the majority are sorbed in only small amounts. Nevertheless, proteins can be sorbed in large amounts on special types of carboxylic resins in the hydrogen form, which can swell greatly. The resin KMT, which incorporates a small quantity of cross-linking agent, proved to be such a cation exchanger. However, additional complications arise which are not observed in the sorption of proteins by sulphonated resins. Thus it has been shown that amino-acids are not sorbed by the same KMT resin in the hydrogen form, although it sorbs proteins. As the proteins are hydrolysed (Fig. 6), the sorption of the resulting polypeptides diminishes. This is the opposite rule to that observed in the molecular-sieve phenomenon, for the sorption capacity increases instead of decreasing with growth in the molecular weight of the polypeptides. There are grounds for assuming that this is connected with the formation of hydrogen bonds between the peptide groups of the polypeptides and the functional groups in the sorbent[46].

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THE DISCOVERY OF ELEMENT 103

S.S.Rodin

In April 1961, as the result of numerous experiments, a team from California University Radiation Laboratory consisting of A. Ghiorso, T. Sikkeland, A. Larsh, and R. Latimer obtained evidence of a new artificial synthetic element of atomic number 103.[1,2] In honour of the founder of their laboratory, Nobel prizewinner E. O. Lawrence, they proposed to name this new element lawrencium (symbol Lw).

Element 103 was obtained by the bombardment of californium with boron ions accelerated to 70 MeV energy by the linear accelerator HILAC. An alpha-activity was observed to result from this irradiation which could only be explained by the disintegration of a new element with atomic number 103. However, this activity is so small that it amounts to no more than several alpha-particles an hour. For this reason it is not yet possible to observe the mendelium disintegration products, which would confirm the atomic number of the element responsible for the new activity. Nonetheless, on the basis of nuclear data this activity can be positively ascribed to the element with atomic number 103. The method used by the team to obtain and identify the radiations is shown schematically in Fig. 1. In principle, the method is based on the approach used in the preparation of element 102. The californium target weighed 3 μg and had the following isotopic composition:

$^{249}\mathrm{Cf}$ — 3.3%, $^{250}\mathrm{Cf}$ — 32.8%, $^{251}\mathrm{Cf}$ — 12.3% and $^{252}\mathrm{Cf}$ — 50.8%.

The californium was deposited on a nickel foil 0.0015 mm thick in the form of a circle 2.5 mm in diameter. The success of the experiment was strongly dependent on the purity of the target; the purification consisted of meticulous use of ion-exchange columns and specially pure reagents. The last stage in the purification of the target from undesirable traces of lead and bismuth was accomplished by heating the target *in vacuo* by electron bombardment. Traces of lead and bismuth must be reduced to the minimum, since when these elements are irradiated by heavy ions they give a large yield of elements disintegrating with a half-life of 25 sec and emitting alpha-particles of energy 8.8 MeV. This activity can completely obscure the alpha-activity of element 103.

The current of ^{10}B or ^{11}B ions passing through the very thin target was not allowed to exceed 0.5 μA, to avoid melting the target. The atoms formed in the bombardment were ejected from the target into the surrounding

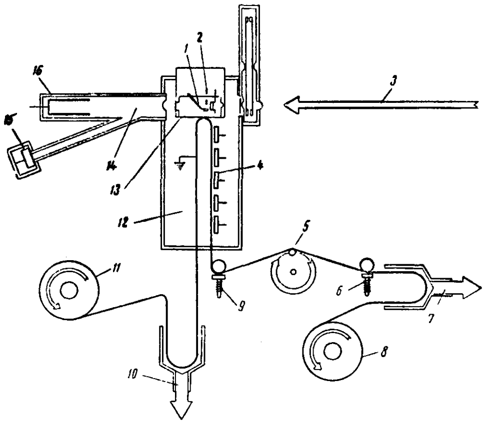

Fig. 1. Diagram of the apparatus for obtaining element 103: 1) target (-400 V); 2) collimator; 3) beam of heavy ions; 4) silicon alpha-particle counters; 5) motor; 6) brake; 7) suction; 8) take-up spool; 9) brake; 10) suction; 11) feed spool; 12) helium; 13) casing (-150 V); 14) vacuum; 15) silicon counter for measuring ion beam energy; 16) Faraday cylinder.

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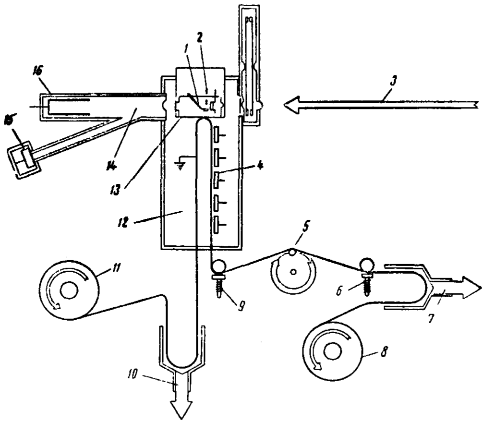

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space, which was filled with helium. A slow flow of gaseous helium carried the electrically charged products towards a thin copper conveyor belt. This belt was intermittently drawn along through a short distance in such a way that the atoms collected on it were presented to each of five silicon counters†. The pulses generated by the alpha-particles were passed to preamplifiers within the shielded area. They were then further amplified and analysed by two separate electronic systems. One system consisted of five separate 100-channel pulse analysers, while the other was a complex assembly using a memory device comprising five paper tapes on which the necessary marks were made by punching. With the second of these devices it was possible to determine the time at which each pulse was registered from the conveyor belt.

The crystalline silicon counters played a very important part in these experiments, and were developed by S.Borkowski and D.Blankenship of the Oak Ridge National Laboratory, who helped to make the silicon counters needed for this work. These counters were made from silicon plates 6 × 10 mm in size, fixed in a mounting and covered by a gold layer of thickness about 20 $\mu g\,cm^{-2}$. At first the counters were very unstable in operation, since they were in a helium atmosphere and subjected to very intensive beta-radiation fields. The use of charge-sensitive preamplifiers reduced these effects, but it was found during the experiments that the silicon crystal counters periodically had to be replaced by new ones.

The energy of the boron ions was also determined by means of a silicon counter, calibrated against nuclear photographic plates.

The whole system was calibrated and checked in the absence of a current of accelerated ions either by means of recoil nuclei from ^{233}U‡ collected on the conveyor belt, or by means of the alpha-particles formed in the disintegration of ^{212}Po. For this purpose the samples mentioned were placed in front of the counter installation. A preliminary study of reactions with the accelerated heavy ions was made by bombarding ^{147}Sm, which formed short-lived emitters. Lead and bismuth were also used in test bombardments, and produced various alpha-emitters with energies from 7 to 9 MeV.

When californium was bombarded with boron ions, the disintegration of element 103 was observed with half-life 8 ± 2 sec and emission of alpha-particles of 8.6 MeV energy. In these experiments alpha-particles with energies 8.4 and 8.2 MeV and half-life 15 sec, probably due to element 102, were also observed. Fig. 2 shows the spectrum of alpha-particles registered by the first counter during the last series of experiments. These activities were observed over many weeks, when bombarding a californium target with ^{10}B or ^{11}B ions. When Pb, Bi, ^{240}Pu, and ^{241}Am are bombarded under similar conditions, the new activities are not formed. The scientists who obtained the isotope of element 103 assume for several reasons that its mass number is 257. Thus, in bombarding ^{250}Cf, ^{251}Cf, and ^{252}Cf with ^{11}B ions the isotope ^{257}103 is formed after the emission of 4, 5, and 6 neutrons, while in bombarding with ^{10}B ions the same results are obtained with the emission of 3, 4, and 5 neutrons.

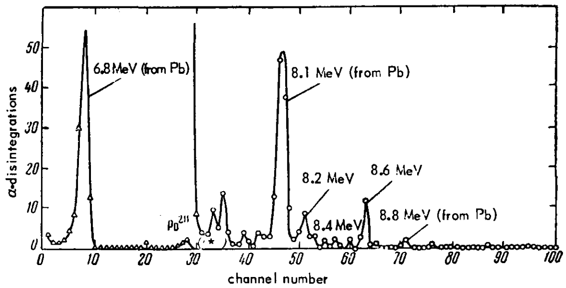

Fig. 2. Alpha-spectrum from the first counter.
*(From Pb)

The nuclear reactions taking place can be represented as:

$$
\begin{aligned}
{}^{250}\mathrm{Cf} + {}^{11}\mathrm{B} &\rightarrow {}^{257}103 + 4n \\
{}^{251}\mathrm{Cf} + {}^{11}\mathrm{B} &\rightarrow {}^{257}103 + 5n \\
{}^{252}\mathrm{Cf} + {}^{11}\mathrm{B} &\rightarrow {}^{257}103 + 6n \\
{}^{250}\mathrm{Cf} + {}^{10}\mathrm{B} &\rightarrow {}^{257}103 + 3n \\
{}^{251}\mathrm{Cf} + {}^{10}\mathrm{B} &\rightarrow {}^{257}103 + 4n \\
{}^{252}\mathrm{Cf} + {}^{10}\mathrm{B} &\rightarrow {}^{257}103 + 5n
\end{aligned}
$$

Furthermore, it is known from other experiments that in the nuclear interaction of boron with transuranic elements the most probable reactions are those with neutron emission. The excitation functions of ^{11}B and ^{10}B ions for the formation of alpha-activity with energy 8.6 MeV are consistent with the above conclusion. The form of these functions is such that the observed activity could not positively exclude reactions of the type (B, p × n), leading to the formation of light isotopes of element 102. The final proof of the existence of an isotope of element 103 was then obtained when element 102 was formed by bombarding a californium target with ^{12}C ions, when it was observed that the activity with energy 8.6 MeV decreased by a factor of two, while the 8.2 MeV activity (which basically belongs to isotope ^{255}102) increased by nearly 20 times. On the other hand, experiments with ^{240}Pu have shown that the cross-section of (^{12}C, α × n) reactions is greater, and that of (^{12}C, p × n) reactions less, than the cross-section of similar reactions in the bombardment of californium by boron ions.

The formation of light isotopes of mendelevium, which could emit alpha-particles with energies in the range 8.2–8.6 MeV was excluded in the experiments on the bombardment of ^{243}Am by ^{12}C ions.

Rather more than twenty years have passed since the discovery of the first transuranic elements neptunium and plutonium, and in this time eleven new transuranic elements have been prepared artifically.

The discovery of each transuranic element has been attended by enormous difficulties. All these elements are radioactive, and they have been discovered by means of various methods in nuclear chemistry, a very new science. Physicists have made important contributions to the discovery of these elements by helping to predict the basic properties of as yet undiscovered elements and to obtain various "atomic missiles", without which the synthesis of new isotopes of transuranic elements would have been impossible. For example, in the discovery of element 103

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† Solid state Au–Si surface barrier detectors (Ed. of Translation).

‡ Reference 2 quotes ^{230}U here (Ed. of Translation).

it was necessary to obtain, from the artificial element plutonium, adequate quantities of the transuranic element californium of great purity and of known isotopic composition. The californium so obtained was used as a target, and work with it was made extremely difficult by its high neutron activity.

The description of the experiments leading to the discovery of element 103 shows that a method of elimination was used. The use of this indirect method of proof calls for a colossal amount of work, since it was necessary to subject a very large number of different targets to irradiation by various ions.

It is interesting to note that the method described had previously been used, in the early days of the discovery of transuranic elements, by the Soviet scientists G. N. Flerov and K. A. Petrzhak, to demonstrate the spontaneous fission of uranium. More recently, the same method was used by G. N. Flerov and his colleagues in the discovery of element 102.

The discovery of an element with atomic number 103 is a significant event, since this element is the last member of an actinide group in the Periodic Table.

The next new chemical element that may be artificially obtained by man in the laboratory is that with atomic number 104. This element will have properties completely different from those of the other artificial elements produced already with atomic numbers from 93 to 103. Element 104 will be similar in its physical and chemical properties to hafnium and zirconium, since it occupies a position in the Periodic Table immediately below them. Various compounds of this new element will be relatively easy to separate from compounds of the actinide elements, by reason of the large difference in properties. A comparatively simple method of extraction can be employed for this separation in place of the complex and laborious method of ion exchange chromatography.

The series of elements beginning with element 104 will be the fourth so-called series of transition metals. If these elements can be prepared, they will have atomic numbers from 104 to 112. The elements from 112 to 118 complete the seventh row of the Periodic Table; they will also have different properties. But it must be pointed out here that steadily increasing difficulties will be met in the discovery of heavier elements. If the half-life of element 103 is 8 sec, then the predicted half-life for element 110 comes to 0.01 sec. Such short half-lives will very seriously limit the possibility of discovering new isotopes of heavy elements.

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1. Science News Letter, 79, 259 (1961).
2. Phys. Rev. Letters, in the press. [See Phys. Rev. Letters, 6, 473 (1961) (Ed. of Translation)]

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IDENTITY REACTIONS, INVOLVING THE TRANSFER OF IDENTICAL RADICALS IN SOLUTIONS (THE STEPWISE TRANSFER OF RADICALS)

G. G. Petukhov

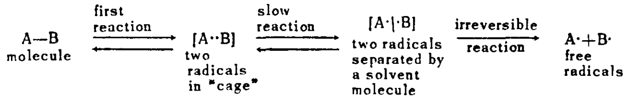
CONTENTS

I. INTRODUCTION

Many important chemical processes in gases and in solutions involve the formation and the reactions of free radicals, several radical reactions being known which are common to both states of aggregation. Liquid–phase reactions, however, have some additional features: thus, in solutions, each individual solute particle is surrounded by a "cage" of solvent molecules. This impedes the breakdown of the solute molecules into free radicals, since, owing to the slow diffusion of the latter in liquids, most of those which are formed recombine immediately. This primary recombination lowers the initial yield of formation reactions in solutions as compared with gases. When, however, the free radicals are able to escape from the "cage", the surrounding layer of solvent molecules now prevents their recombination and favours reaction between the radical and a solvent molecule.

With the thermal decomposition of phenylphenylsulphonyl diimide (A – B) in benzene as example, Rosenthal and Overberger[1] illustrate the mechanism of formation of free radicals, and their escape from the "cage", by the following scheme

$$(A\cdot = C_6H_5N_2\cdot \text{ and } B\cdot = C_6H_5SO_2\cdot)$$



The principle of the primary recombination of free radicals, put forward earlier by Franck and Rabinowitch[2], is valid only for inert solvents[3], *i.e.* those in which the escape of the radicals from the "cage" into the "bulk" of the solvent takes place by diffusion.

When a free radical R· is able to abstract an X atom from a solvent molecule RX, escape of radicals from the "cage" into the bulk can occur by stepwise radical transfer in addition to diffusion. The transfer of one atom from a reactant molecule to the free radical leads to the production of a new radical and molecule which are identical with the previous ones

$$R\cdot + RX \rightleftarrows RX + R\cdot \qquad (1)$$

Thus the transfer of identical radicals, or the so-called stepwise radical transfer, means the reaction of a molecule RX with the corresponding radical R· according to Eqn. (1). The regeneration of radicals by the solvent molecules can be repeated many times. The result is that the free valence moves in a stepwise manner from one molecule to the next, as illustrated by the collision of a moving sphere with a stationary row of spheres, when the motion of the first sphere is transferred to the last sphere of the row.

These considerations are inadequate for a complete description of the effect of the solvent on the course of radical reactions. Recent work indicates that free radicals can interact with solvent molecules to give unstable intermediate complexes, which then form the active centres between which reaction takes place.

Russell[4] points out that the course of the photochemical chlorination of 2, 3-dimethylbutane is changed by introducing an aromatic compound into the reaction medium. The effect of the solvent is explained by the chlorine atom forming a π complex with the aromatic nucleus. The complex is less reactive, and hence a more selective chlorinating agent, than free atomic chlorine. A similar phenomenon has been observed by Walling and others in the photochemical chlorination of some hydrocarbons[5]. The marked influence of solvents (benzene, carbon disulphide, chlorobenzene) on the relative ease with which hydrogen atoms attached to primary, secondary, and tertiary carbon atoms can be replaced by chlorine is due to the formation of relatively stable π complexes.

In the photolysis of iodobenzene, diphenylmercury, and tetraphenyl-lead in cumene, Bryce-Smith *et al.*[6] observed a difference in the composition of the isomeric reaction products, and concluded that phenyl radicals give intermediate compounds with the solvent during photolysis.

It is now firmly established that the phenylation of aromatic compounds by phenyl radicals takes place via π and σ complexes. The view that complexes are formed between the radicals and the solvent is not incompatible with reaction (1).

The heat ΔH of transfer of identical radicals ($R' = R$) is zero. In the case of different radicals ($R' \neq R$) ΔH differs slightly from zero[7]. The rate of stepwise transfer of a free radical depends on the activation energy of the process. Semenov showed by a simple calculation that this type of radical transfer often predominates over diffusion in solutions[3]. Assuming an activation energy of 5 kcal, the stepwise transfer of radicals at 400°K is 60 times as rapid as diffusional transfer. With large activation energies, on the other hand, the rate of diffusion will exceed that of estafette radical transfer. With an activation energy of 10 kcal, for example, the velocity ratio will be 10, diffusion being predominant.

The reaction between the $CH_3\cdot$ radical and CH_4 in the gas phase has an activation energy[8] of ~ 11.2 kcal mole^{-1}. Unfortunately, no experimental data have been published on the activation energy of liquid-phase stepwise reactions.

Although the estafette transfer of radicals is relatively unimportant in most of the cases investigated, some authors ascribe to it a great part in radical processes.

The opinion is held that exchange between radicals and the solvent may increase the life of the free radicals. Thus, Waters[9] and Semenov[3] consider that, when acetyl peroxide is boiled in acetic acid, the $CH_3COO\cdot$ radical may possess an abnormally long life as a result of regeneration by exchange with the solvent.

However, Fry *et al.*[10] have shown that the decomposition of acetyl peroxide in acetic acid $^{14}CH_3COOH$ is accompanied by hardly any stepwise transfer of acetoxy radicals, for the methane evolved in the reaction contains no more than 1% of radioactive carbon. Analogous results have recently been obtained by Razuvaev *et al.*[11] for the decomposition of acetyl benzoyl peroxide in acetic acid $CH_3.^{14}COOH$. The transfer of acetoxy radicals was determined from the radioactive $^{14}CO_2$ obtained by decarboxylation of $CH_3.^{14}COO\cdot$ radicals.

Many workers have investigated reactions of this type, but a detailed study has been made only of those involving the splitting off of hydrogen from hydrocarbons by methyl radicals in the gas phase. Little research has been done on the stepwise transfer of radicals in the liquid phase, and most of this work is confined to a qualitative assessment of the reaction; quite often contradictory views are encountered. The results of work in this field have not yet been systematised.

In the foreign literature, reactions involving the transfer of identical radicals have been called "identity reactions"[12].

The present paper is concerned mainly with an examination of liquid-phase identity reactions. For purposes of comparison, reactions involving the transfer of methyl radicals are considered first, as they have been studied in the gas phase.

The stepwise transfer of radicals is accompanied not only by purely chemical changes, but can be followed from the change in optical activity of the molecule involved. If RX is an optically active molecule, in which the activity is due to the asymmetry of $R\cdot$, this optical activity is not retained when X is split off[13]. Thus the stepwise transfer will result in a racemisation of RX.

The transfer of identical radicals can be monitored much more simply and more accurately by means of labelled atoms. Various isotopes of carbon and hydrogen can be used for this purpose, but hydrogen isotopes introduce a large isotope effect[14]. Either the solvent or the source of free radicals can be labelled. In the former case, interaction between radicals and solvent is determined from the isotopic composition of the products formed by combination of the radicals, and in the latter case from the change in isotopic composition of the solvent. Most of the work has been carried out by the first method.

Neither method is reliable with all radicals. As will be shown below, participation of the solvent in the formation of a dimer is not always a proof of the stepwise transfer of radicals. The appearance of activity in the solvent can also result from intramolecular splitting off of an atom from a solute molecule by the labelled radical. More trustworthy evidence of stepwise radical transfer is obtained by using both methods, which makes it possible to check and compare results obtained in different ways.

II. REACTIONS INVOLVING THE TRANSFER OF METHYL RADICALS IN THE GAS PHASE

The simplest example of radical transfer is the interaction between hydrogen atoms and the hydrogen molecule H_2. This is accompanied by the interconversion of ortho and para forms of hydrogen, caused by the magnetic field of the free radical[15]

$$H\cdot + H_2\,(\text{para}) \rightleftarrows H_2\,(\text{ortho}) + H\cdot$$

Other radical-transfer reactions are the reversible reaction of atomic hydrogen with a hydrocarbon molecule[16] and of alkyl radicals with molecular hydrogen[17].

During the past decade a detailed quantitative investigation has been made of the transfer of methyl radicals in the gas phase. A reaction of this type is the splitting off of a hydrogen atom from a methane molecule by a methyl radical:

$$CH_3^{\cdot} + CH_4 \rightleftarrows CH_4 + CH_3^{\cdot}$$

A competing reaction in this case is the dimerisation of the radicals. The gas-phase transfer of methyl radicals has been studied during the photolysis of acetone in the presence of methane. Different workers have employed compounds labelled with deuterium or radiocarbon ^{14}C for this purpose.

Photolysis of a mixture of acetone and deuteromethane at 354° gives[18] CH_3D, CD_3H, $C_2H_3D_3$, and C_2D_6. Irradiation of this mixture is stated to induce the following basic reactions

$$CH_3COCH_3 \xrightarrow{h\nu} 2CH_3^{\cdot} + CO\,,$$

$$CH_3^{\cdot} + CD_4 \xrightarrow{k_1} CH_3D + CD_3^{\cdot}\,, \qquad (2a)$$

$$CH_3^{\cdot} + CH_3COCH_3 \xrightarrow{k_2} CH_4 + \cdot CH_2COCH_3\,, \qquad (2b)$$

$$CD_3^{\cdot} + CH_3^{\cdot} \rightarrow C_2H_3D_3\,,$$

$$2CD_3^{\cdot} \rightarrow C_2D_6\,.$$

The ratio of the rate constants k_1/k_2 was found from a mass-spectrographic determination of the 17/16 mass ratio (CH_3D/CH_4). The velocity constant k_1 was calculated as

$$1.8 \times 10^8 \exp(-\,12.93 \pm 0.65\ \text{kcal}/RT)\ \text{litres mole}^{-1}\ \text{sec}^{-1}\,.$$

The activation energy of reaction (2a) is $E_{2a} = 12.9 \pm 0.65$ kcal mole^{-1}. It was proved in separate experiments that no deuterium exchange takes place between CD_4 and CH_3COCH_3. No methane was formed when acetone was heated to 354° in the absence of u.v. irradiation.

Other investigators[19] used a mixture of deuteroacetone and methane, which also was subjected to photolysis at 360°–428°

$$CD_3COCD_3 \xrightarrow{h\nu} 2CD_3^{\cdot} + CO\,,$$

$$CD_3^{\cdot} + CH_4 \xrightarrow{k_1} CD_3H + CH_3^{\cdot}\,, \qquad (3)$$

$$CD_3^{\cdot} + CD_3COCD_3 \xrightarrow{k_2} CD_4 + {}^{\cdot}CD_2COCD_3\,.$$

Mass-spectrographic determination of the 19/20 mass ratio (CD_3H/CD_4) yielded the ratio of the velocity constants k_1/k_2.

The rate constant was calculated[18] as $k_1 = 0.17 \times 10^3$ litres mole^{-1} sec^{-1} at 180°. The activation energy of reaction (3) was $E_3 = 14.1$ kcal mole^{-1}. The slight difference in activation energy (1.15 kcal mole^{-1}) between reactions (3) and (2a) is ascribed to the isotope effect in the splitting off of deuterium.

In order to eliminate the isotope effect in this reaction, radiocarbon ^{14}C was also used

$$CH_3^{\cdot} + {}^{14}CH_4 \rightarrow CH_4 + {}^{14}CH_3^{\cdot}\,. \qquad (4)$$

The reaction was carried out by exposing to u.v. radiation a mixture of acetone and radioactive methane at partial pressures of 50 and 62–425 mm Hg respectively. The reaction velocity was determined from the radioactivity of the ethane formed by recombination of the free methyl radicals[20]. The rate constant of reaction (4) was found to be

$$\log k_1\ (\text{litres mole}^{-1}\ \text{sec}^{-1}) = 8.83 - (14.65\ \text{kcal})/2.303\,RT.$$

This value is very close to that obtained previously for reaction (3).

The ratio of the velocity constants of the reactions

$${}^{14}CH_3^{\cdot} + CH_3COCH_3 \xrightarrow{k_1} CH_3^{\cdot} + {}^{14}CH_3COCH_3, \qquad (5a)$$

$${}^{14}CH_3^{\cdot} + CH_3COCH_3 \xrightarrow{k_2} {}^{14}CH_4 + {}^{\cdot}CH_2COCH_3, \qquad (5b)$$

was found to be $k_1/k_2 = 0.036$ at 350°. In this case the extent to which the exchange of methyl radicals [reaction (5a)] occurs is about 3% of the abstraction of hydrogen by these radicals according to reaction (5b).

The exchange of methyl radicals with ethane, methyl ether, acetone, and propene (CH_3R) has also been investigated[21]. The compound was heated at 550°–575° with deuteroacetaldehyde CD_3CDO, the thermal decomposition of which yields CD_3 radicals, which interact with the CH_3R

$$CD_3^{\cdot} + CH_3R \xrightarrow{k_1} CD_3R + CH_3^{\cdot}\,, \qquad (6a)$$

$$CD_3^{\cdot} + CH_3R \xrightarrow{k_2} CD_3H + CH_2R^{\cdot}. \qquad (6b)$$

The ratios of the velocity constants for reactions (6a) and (6b) (k_1 for the exchange reaction and k_2 for the splitting off of hydrogen) were found from mass-spectrographic determinations of the CD_3R/CD_3H ratios: for ethane the CD_3CH_3/CD_3H ratio is 1/1500, for methyl ether $CD_3OCH_3/CD_3H = 1/2800$, for acetone $CD_3COCH_3/CD_3H = 1/90$, and for propene $CD_3.CH:CH_2/CD_3H = 1/19$.

Comparison of the ratio found for acetone ($CD_3COCH_3/CD_3H = 1/90$) with the ratio of the velocity constants for the analogous reactions (5a) and (5b) ($k_1/k_2 = 0.036$) shows that, although the values obtained by different workers differ, they are of the same order of magnitude.

The decomposition of acetyl peroxide was investigated in toluene medium[22] in order to study the possible liquid-phase exchange of methyl radicals. As expected, no exchange took place between methyl radicals of the peroxide and the methyl group of the toluene. The decomposition of acetyl peroxide in $C_6H_5CD_3$ does not lead to the formation of CHD_3 or CD_4, and also no toluene $C_6H_5CH_3$ was detected after the reaction.

The absence of an exchange reaction in this case can be explained by the fact that methyl radicals do not form intermediate complexes with aromatic compounds. This is consistent with Antonovskii and Berezin's observation[23] that, when acetyl peroxide undergoes decomposition in tritiobenzene, the resulting methyl radicals split off the benzene hydrogen atoms more readily than the tritium atom. The large isotope effect (6.02 ± 0.07) indicates that the methyl radicals capture the hydrogen atoms, not in an intermediate complex, but by directly attacking the benzene ring.

In the gas phase, as several workers have suggested[7], the regenerative exchange of methyl radicals takes place *via* a transition state, involving a "coupling" of the bond system

$$H_3C\cdots\cdots H\cdots\cdots CH_3,$$

with three delocalised electrons. The energy of this system can be defined as the energy required to remove the hydrogen atom to infinity. If a methyl radical reacts with a more complex paraffin hydrocarbon molecule HR, the energy required to split off a hydrogen atom in the initial and final states is decreased by the coupling energy. In this respect Polanyi's rule is valid for the reaction

$$CH_3^{\cdot} + HR \rightleftarrows CH_4 + R^{\cdot},$$

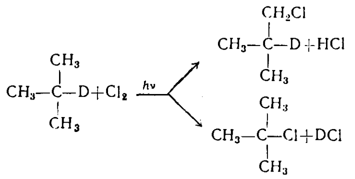
with few exceptions: the activation energy of the reaction and the bonding energy D(R–H) are linearly related. These quantities decrease as the radical becomes more complex. This question has been discussed in detail by Bagdasar'yan[7].

A considerable amount of work has been published on the stepwise transfer of other, more complex radicals in various solvents. The reactions of t-butyl, cyanoisopropyl, and trichloromethyl radicals will be examined in section III; those of radicals such as benzyl, diphenylmethyl, and 2-phenylbutyl in section IV. The stepwise transfer of phenyl and acyloxy radicals will be discussed separately because these groups have several peculiar features.

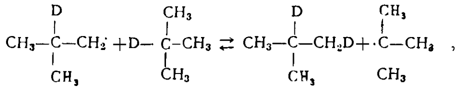
III. REACTIONS INVOLVING THE TRANSFER OF ALIPHATIC RADICALS

The stepwise transfer of t-butyl, cyanoisopropyl, and trichloromethyl radicals in the liquid phase has been investigated.

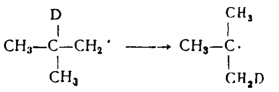
Brown and Russell[24] investigated the possibility of t-butyl radical transfer during the photochemical chlorination of 2-deutero-2-methylpropane in the liquid phase, and found that exchange does not occur between this radical and the corresponding hydrocarbon under the conditions indicated below. The photochemical chlorination of 2-deutero-2-methylpropane in the liquid phase at -15° involves the replacement of hydrogen by chlorine both in the methyl group and at the tertiary carbon atom



It is quite possible that chlorination is accompanied by the formation of free radicals, which can undergo either exchange or rearrangement. If such exchange (7a) or rearrangement (7b) takes place during the photochemical chlorination



$$CH_3-\underset{CH_3}{\overset{D}{C}}-CH_2^{\cdot} + D-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \rightleftarrows CH_3-\underset{CH_3}{\overset{D}{C}}-CH_2D + {}^{\cdot}\underset{CH_3}{\overset{CH_3}{C}}-CH_3\,, \qquad (7a)$$

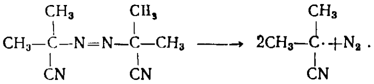


$$CH_3-\underset{CH_3}{\overset{D}{C}}-CH_2^{\cdot} \longrightarrow CH_3-\underset{CH_2D}{\overset{CH_3}{C}}{}^{\cdot}\,, \qquad (7b)$$

the relation between the quantities of deuterium chloride and the tertiary chloride formed will be complicated. It was established that equimolecular amounts of these compounds were formed. It would appear, therefore, that neither hydrogen exchange between the radicals and the hydrocarbon (7a) nor rearrangement of the free radical (7b) takes place during photochemical chlorination. The obvious explanation was that reaction between chlorine and the radical takes place considerably more rapidly than exchange or displacement of hydrogen atoms. Thus the presence of three methyl groups in the t-butyl radical $(CH_3)_3C\cdot$ does not increase the ability of the radical to split off hydrogen by stepwise transfer.

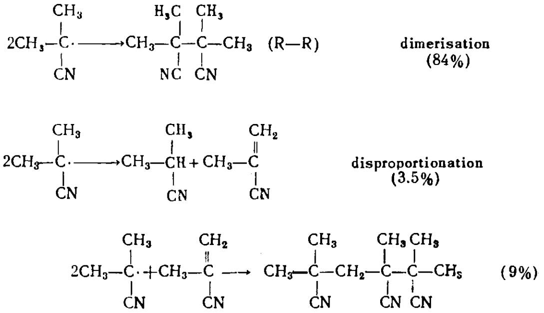
It is interesting to compare these results with those obtained with the cyanoisopropyl radical[25], which is extremely reactive and acts as an initiator for the polymerisation of many vinyl monomers. It might be supposed that the presence of the cyano group in the $CN.C(CH_3)_2^{\cdot}$ radical would have a definite effect, which could be observed from the exchange reaction.

Cyanoisopropyl radicals are easily obtained by the decomposition of azo-2, 2′-di-isobutyronitrile



$$CH_3-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_3 \longrightarrow 2CH_3-\underset{CN}{\overset{CH_3}{C}}\cdot+N_2 .$$

Studies of the decomposition products of this compound in various solvents showed that the main reaction undergone by the resulting radicals is dimerisation[26]. In toluene, for example, the decomposition is represented by the scheme



$$2CH_3-\underset{CN}{\overset{CH_3}{C}}\cdot \longrightarrow CH_3-\underset{NC}{\overset{H_3C}{C}}-\underset{CN}{\overset{CH_3}{C}}-CH_3 \quad (R-R)$$

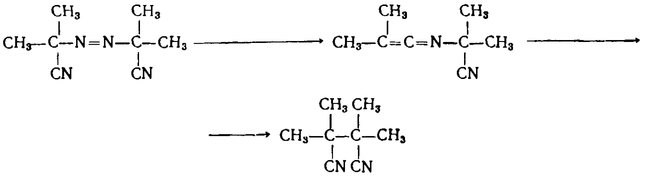
dimerisation (84%)

$$2CH_3-\underset{CN}{\overset{CH_3}{C}}\cdot \longrightarrow CH_3-\underset{CN}{\overset{CH_3}{CH}}+CH_3-\underset{CN}{\overset{CH_2}{\overset{\|}{C}}}$$

disproportionation (3.5%)

$$2CH_3-\underset{CN}{\overset{CH_3}{C}}\cdot+CH_3-\underset{CN}{\overset{CH_2}{\overset{\|}{C}}} \longrightarrow CH_3-\underset{CN}{\overset{CH_3}{C}}-CH_2-\underset{CN}{\overset{CH_3}{C}}-\underset{CN}{\overset{CH_3}{C}}-CH_3 \quad (9\%)$$

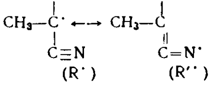
Actually, the interaction of the cyanoisopropyl radicals is more complicated than this. In the decomposition of azo-2, 2′-di-isobutyronitrile (RN.NR) the dimer tetramethylsuccinonitrile (R.R) can be obtained[27] by isomerisation of the less stable intermediate compound, dimethyl-*N*-(2-cyano-2-propyl)ketenimine (R.R′)



$$CH_3-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\overset{CH_3}{C}=C=N-\underset{CN}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{CN}{\overset{CH_3}{C}}-\underset{CN}{\overset{CH_3}{C}}-CH_3$$

i.e. $RN = NR \rightarrow R-R' \rightarrow R-R$.

The formation of the intermediate compound (R.R′) indicates that the radicals can rearrange and interact during the course of this reaction



$$\underset{(R^{\cdot})}{CH_3-\underset{C\equiv N}{\overset{CH_3}{C}}\cdot} \longleftrightarrow \underset{(R'^{\cdot})}{CH_3-\underset{C=N^{\cdot}}{\overset{CH_3}{\overset{|}{C}}}}$$

Hammond *et al.*[27] point out that dimethyl-*N*-(2-cyano-2-propyl)ketenimine polymerises styrene considerably more slowly than does azo-2, 2′-di-isobutyronitrile. This is explained by the primary decomposition of the compound R.R′ occurring *via* an intermediate complex of the radicals with the solvent or the monomer

$$R-R' \rightarrow \overline{2R^{\cdot}}$$

$$\overline{2R^{\cdot}}+C_8H_8 \rightarrow R^{\cdot}+[C_8H_8 \rightarrow R^{\cdot}],$$

$$[C_8H_8 \rightarrow R^{\cdot}] \rightleftarrows C_8H_8+R^{\cdot}$$

They point out that the cyanoisopropyl radical (R·) can behave as an electron acceptor, and will therefore give complexes with aromatic compounds.

Chemical changes of this type undergone by cyanoisopropyl radicals may have prevented Fedotova and Lazaris[25] obtaining definite evidence for the occurrence of stepwise transfer of this radical in the decomposition of azo-2, 2′-di-isobutyronitrile (labelled with ^{14}C in the nitrile group) dissolved in isobutyronitrile at 102°. The activity shown by the solvent should be a measure of the nitrile obtained by stepwise transfer and by disproportionation of the cyanoisopropyl radical. On dilution of the solution the percentage activity corresponding to disproportionation should remain constant, while stepwise transfer should increase with dilution. The molar ratio of the reactants was varied between wide limits (from 1 : 57 to 1 : 510), but no substantial change was observed in the activity in the isobutyronitrile (from 6.1 to 9.2%).

These workers consider that stepwise transfer of the cyanoisopropyl radical is absent owing to the large stabilisation energy of this radical. The appearance of activity (6.1–8.1%) in the isobutyronitrile is ascribed wholly to disproportionation, but some increase in activity (by 2–3%) with dilution is ascribed to experimental error. No other results have been published on the abstraction of hydrogen atoms from other organic molecules by the cyanoisopropyl radical.

Razuvaev *et al.* have investigated the possibility of the stepwise transfer of the trichloromethyl radical with displacement of hydrogen or chlorine[28]

$$CCl_3^{\cdot}+{}^{14}CCl_4 \rightleftarrows CCl_4+{}^{14}CCl_3^{\cdot}, \qquad (8a)$$

and

$$CCl_3^{\cdot}+{}^{14}CHCl_3 \rightleftarrows CHCl_3+{}^{14}CCl_3^{\cdot}. \qquad (8b)$$

A mixture of CCl_4 and $^{14}CHCl_3$ was therefore heated in the presence of Raney nickel in a stream of nitrogen at 80° for 10 h. In this case the primary reaction in the formation of CCl_3 radicals can only be the interaction of CCl_4 and Ni. If the resulting CCl_3 radicals then reacted according to Eqn. (8a), the C_2Cl_6 obtained would be active. The C_2Cl_6 and CCl_4 isolated from the reaction were not active, indicating that reactions (8a) and (8b) had not occurred.

The absence of reaction (8b) has been demonstrated also in the u.v. irradiation of a mixture of CCl_4 and $^{14}CHCl_3$: the CCl_4 isolated after exposure was inactive, although the C_2Cl_6 did show activity. The CCl_4 and C_2Cl_6 isolated after exposure of a mixture of CCl_4, CH_3OH, and $^{14}CHCl_3$ to u.v. radiation contained hardly any activity, showing that the CCl_3 radical does not abstract hydrogen from the alcohol. These workers explain the impossibility of abstracting hydrogen from the alcohol or from chloroform and the absence of stepwise transfer with the CCl_3 radical by the considerable stabilisation energy of this radical, which is estimated as 12 or 19 kcal $mole^{-1}$ by Schumacher and Wolf[29] and by Miller and Willard[30] respectively.

A postulated stepwise transfer of the CCl_3 radical of only 2–3% could have remained unnoticed, since the original $^{14}CHCl_3$ was feebly active (with a count of 900 min^{-1}).

No other work has been published on the transfer of the CCl_3 radical. The reactivity of the trichloromethyl radical has been investigated by Kharasch *et al.*[31]

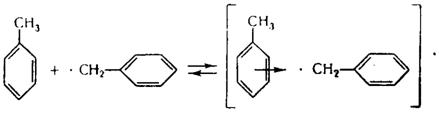
Thus the work which has been considered shows that – (1) the t-butyl, cyanoisopropyl, and trichloromethyl radicals undergo little or no exchange by estafette transfer in the liquid phase; (2) the presence of functional groups in these radicals has practically no effect on the rate of exchange.

IV. REACTIONS INVOLVING THE TRANSFER OF ARYL RADICALS

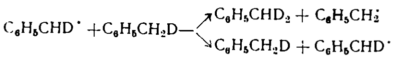
The liquid-phase stepwise transfer of the phenyl, benzyl, methylbenzyl, diphenylmethyl, and 2-phenylbutyl radicals has been investigated. Results obtained for the phenyl radical will be discussed separately in the next section.

The transfer of benzyl radicals has been investigated by several workers. Benzyl radicals are not very reactive, their stabilisation energy being[32] 21.5 kcal $mole^{-1}$, and they hardly undergo any exchange with toluene. In fact, u.v. irradiation of dibenzylmercury in deuterotoluene yielded 1, 2-diphenylethane containing $< 1\%$ of the deuterium in the original toluene[33]. Similar results were obtained for the thermal decomposition of dibenzylmercury in [1-^{14}C] toluene. The 1, 2-diphenylethane which was isolated contained only 1.5% of active carbon.

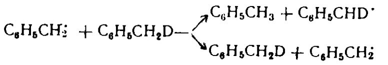
These data agree well with interesting observations by Cassidy and coworkers[34] who showed that the pyrolysis of toluene vapour at low pressures followed by rapid cooling to -78° yields a pyrolytic mixture containing benzyl radicals, which exist for 1½ h. During this period the radicals can be easily titrated with iodine to benzyl iodide. These workers point out that the radicals exist in the form of a complex in the toluene solution



Furthermore, stepwise transfer of the benzyl radical does not occur[24,35] in the liquid-phase photochemical chlorination of $C_6H_5CH_2D$ at 80°. Substitution of a methyl hydrogen could be accompanied by the formation of benzyl radicals of the types $C_6H_5CH_2^{\cdot}$ and $C_6H_5CHD^{\cdot}$. It was possible that the benzyl radicals might exchange with the toluene according to the following scheme


(A)

$$C_6H_5CHD^{\cdot} + C_6H_5CH_2D \rightarrow \begin{cases} C_6H_5CHD_2 + C_6H_5CH_2^{\cdot} \\ C_6H_5CH_2D + C_6H_5CHD^{\cdot} \end{cases}, \qquad (A)$$


(B)

$$C_6H_5CH_2^{\cdot} + C_6H_5CH_2D \rightarrow \begin{cases} C_6H_5CH_3 + C_6H_5CHD^{\cdot} \\ C_6H_5CH_2D + C_6H_5CH_2^{\cdot} \end{cases}. \qquad (B)$$

The exchange of the radicals with the hydrocarbon could be detected from the formation of $C_6H_5CHD_2$, Eqn. (A), or, less reliably, from the formation of non-deuterated toluene Eqn. (B).

An experimental test showed that $C_6H_5CHD_2$, Eqn. (A), is formed only in small amounts, which is explained by the considerably higher speed of the interaction of the radicals with chlorine than the abstraction of hydrogen from the toluene.

There are indications that, in contrast to the benzyl radical, the *p*-methylbenzyl radical exchanges readily with *p*-xylene. Cadogan *et al.*[36] conclude from an investigation of the reaction of benzoyl peroxide with *α*-deutero-*p*-xylene that transfer of *p*-methylbenzyl radicals

$$CH_3C_6H_4CH_2^{\cdot} + CH_3C_6H_4CH_2D \rightarrow CH_3C_6H_4CH_3 + CH_3C_6H_4CHD^{\cdot} \qquad (9a)$$

occurs to a greater extent than their dimerisation

$$2CH_3C_6H_4CH_2^{\cdot} \rightarrow CH_3C_6H_4CH_2CH_2C_6H_4CH_3.$$

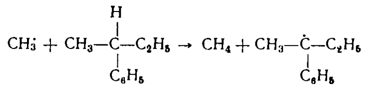
This conclusion is based on the fact that the deuterium content of the 1, 2-di-*p*-tolylethane isolated is greater than that of the xylene taken. If this reaction product had been formed by the recombination of radicals produced initially, its deuterium content should have been the same as that of the radicals, *i.e.* as that of the solvent. This discrepancy is explained by the occurrence of reaction (9a) with preferential displacement of hydrogen.

On this evidence, the increased reactivity of the *p*-methylbenzyl radical compared with the benzyl radical can be ascribed only to the influence of the methyl group. No quantitative assessment of the reactivity of the methylbenzyl radical is given in the paper.

Insignificant radical exchange is observed in the decomposition of various peroxides in aromatic hydrocarbons[37], but the stepwise transfer of methylbenzyl radicals has not been investigated in this connection. Wang and Cohen[38] investigated the stepwise transfer of the diphenylmethyl radical $(C_6H_5)_2CH^{\cdot}$ in diphenylmethane. This radical, like benzyl, is unreactive and stabilised, so that its stepwise transfer is improbable. When azobisdiphenylmethane $(C_6H_5)_2CH.N:N.CH(C_6H_5)_2$ decomposes in diphenylmethane $(C_6H_5)_2{}^{14}CH_2$ at 60°, the resulting $(C_6H_5)_2CH.CH(C_6H_5)_2$ contains only 1.5% of the total activity.

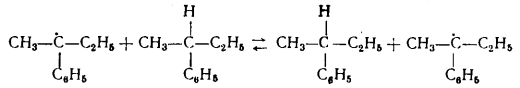
The stepwise transfer of the 2-phenylbutyl radical has been investigated in the decomposition of acetyl peroxide in optically active 2-phenylbutane[22].

Decomposition of the peroxide yields methyl radicals, which remove the hydrogen from the tertiary carbon atom of the 2-phenylbutane

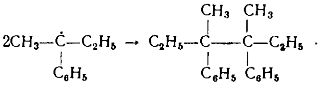

(A)

$$CH_3^{\cdot} + CH_3{-}\overset{H}{\underset{C_6H_5}{C}}{-}C_2H_5 \rightarrow CH_4 + CH_3{-}\underset{C_6H_5}{\dot{C}}{-}C_2H_5 \qquad (A)$$

The radicals thus produced (A) can then undergo stepwise transfer with a solvent molecule or may dimerise


(9b)

$$CH_3{-}\underset{C_6H_5}{\dot{C}}{-}C_2H_5 + CH_3{-}\overset{H}{\underset{C_6H_5}{C}}{-}C_2H_5 \rightleftarrows CH_3{-}\overset{H}{\underset{C_6H_5}{C}}{-}C_2H_5 + CH_3{-}\underset{C_6H_5}{\dot{C}}{-}C_2H_5 \qquad (9b)$$


(B)

$$2CH_3{-}\underset{C_6H_5}{\dot{C}}{-}C_2H_5 \rightarrow C_2H_5{-}\overset{CH_3}{\underset{C_6H_5}{C}}{-}\overset{CH_3}{\underset{C_6H_5}{C}}{-}C_2H_5. \qquad (B)$$

Free 2-phenylbutyl radicals (A) cannot maintain optical activity[13], so that, if reaction (9b) takes place, the optical activity of the 2-phenylbutane should fall. It has been found experimentally that the decomposition of acetyl peroxide in optically active 2-phenylbutane is accompanied by the formation of the inactive 3, 4-dimethyl-3, 4-diphenylhexane (B), while the 2-phenylbutane isolated from the reaction was only slightly racemised[22]. This shows that stepwise transfer might occur but only to a slight extent.

These workers remark that, although the results showed the absence of radical transfer on a large scale, it does not necessarily follow that transfer is entirely absent. If it is postulated that the extent of the reaction is slight, it is possible that in many cases the transfer of radicals could have remained unnoticed.

Thus the above data on the regenerative exchange of some aryl radicals indicate that benzyl and diphenylmethyl radicals react by a stepwise mechanism to only a very slight extent, not exceeding 1.5–2%. The exchange of methylbenzyl radicals has not been assessed quantitatively.

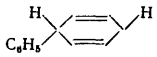
V. REACTIONS INVOLVING THE TRANSFER OF PHENYL RADICALS

The exchange reaction has been investigated in greatest detail in the case of phenyl radicals. This is because the transfer of radicals in aromatic compounds is accompanied by homolytic (amphoteric) substitution. The mechanism of homolytic substitution has been studied in detail by many workers, and fully described by Hey[39]; therefore it will be mentioned only briefly here when the need arises.

Ideas on the mechanism of the reaction between phenyl radicals and benzene have greatly changed during the development of the chemistry of free radicals. Until recently it was considered that phenyl radicals could react with benzene in three ways

$$C_6H_5^{\cdot} + C_6H_6 \rightarrow C_6H_5{-}C_6H_5 + (H\ )\,, \qquad (10a)$$

$$C_6H_5^{\cdot} + C_6H_6 \rightarrow C_6H_6 + C_6H_5^{\cdot}\,, \qquad (10b)$$

$C_6H_5^{\cdot} + C_6H_6 \rightarrow$ 

(A). (10c)

The three reactions were considered independently and serious objections were raised to each in turn. Reaction (10a) is considered improbable, since the evolution of atomic hydrogen is energetically unfavourable[40]. Besides, repeated attempts to confirm the formation of atomic hydrogen during the reaction were not successful. Rafikov and Kudinova's results[41] for the determination of the very small amounts of hydrogen formed cannot be accepted as conclusive, which these workers admit.

It is doubtful whether a hydrogen atom in benzene could be directly replaced by a phenyl radical. A more probable situation is one in which the hydrogen atom is removed by means of another radical, so that any overall assessment of the energy involved will include the energy of formation of a new bond with the hydrogen atom. In such a situation the removal of a hydrogen atom will be energetically feasible[42]. Originally, however, reaction (10b), the transfer of radicals, was regarded as the direct removal of a benzene hydrogen by phenyl radicals.

In fact, such a view is not confirmed by an experimental determination of the isotope effect. In the opinion of several investigators[23], as noted above, the direct removal of hydrogen atoms by radicals according to reaction (10a) is characteristic only of reactive radicals such as $CH_3^{\cdot}$ and ·OH. More complicated radicals are able to yield complexes with solvent molecules, a process favoured by the presence of substituents.

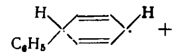
This hypothesis has recently been confirmed experimentally by Hey *et al.*[43] in the case of phenyl radicals. They found no isotope effect for the abstraction of hydrogen during the phenylation of tritiobenzene with benzoyl peroxide. This fact indicates the formation of a complex between the radical and the benzene, but does not suggest a mechanism involving the direct capture of hydrogen by phenyl radicals.

As already pointed out, the formation of complexes between radicals and solvent molecules does not exclude stepwise radical transfer: on the contrary, it is a necessary stage in the latter. Exchange occurs between the component parts of the complex, within the latter, in the course of reaction (10c). The result of this reaction is an unstable complex compound for which there is very convincing experimental evidence. In a recent investigation of the polymerisation of styrene and its benzene solutions in the presence of various peroxides, Dannley *et al.*[44] noted that the quantity of initiator fragments incorporated is greatly dependent on the presence of the solvent. They point out that polystyrene obtained in the absence of solvent contains 88–95% of all the aroyloxy groups of the peroxides, including *p*-nitrobenzoyl peroxide. In contrast to this, polymers obtained in benzene solution had a far lower content of ArCOO groups, and in the case of this latter initiator no *p*-nitrobenzoyloxy groups were detected at all. The phenomenon is explained by the ability of benzene to capture these free radicals.

Bagdasar'yan *et al.*[45] conclude from an investigation of radical phenylation using deuterated aromatic compounds that radical substitution takes place by reaction (10c), since changes in temperature and in the peroxide concentration have no effect on the deuterium content of the biaryls. The "cage effect" is also absent, since decomposition of *p*-nitrobenzoyl peroxide in benzene does not yield dinitrobiphenyls or biphenyl itself, but only nitrobiphenyls. The reaction between benzoyl peroxide and deuterobenzene produced biphenyl in which 45% of the phenyl radicals are derived from the solvent. These workers consider that formation of biphenyl has occurred *via* the complex A. The rather low content of deuterium in the biphenyl (45% instead of the calculated 50%) is explained by errors in the measurements.

The existence of an intermediate radical A has been established by DeTar and Long[46], who were able to isolate tetrahydroquaterphenyl and dihydrobiphenyl from the reaction between benzoyl peroxide and benzene, these products having been formed by dimerisation or the removal of hydrogen from the intermediate radical A.

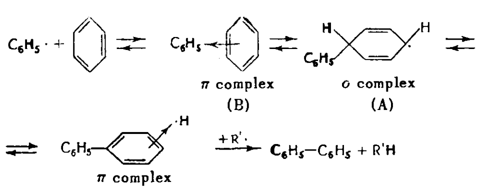
Thus, according to the latest results, the mechanism of homolytic arylation and the transfer of phenyl radicals in benzene are as follows. The first stage in the process is the direct addition of a phenyl radical to an aromatic nucleus to form the intermediate complex A (reaction 10c); the second stage is the transfer of a hydrogen atom to some radical fragment, this reaction taking place by the interaction of the complex A with another radical



$+ R'^{\cdot} \rightarrow R'H + C_6H_5C_6H_5\,.$ (10d)

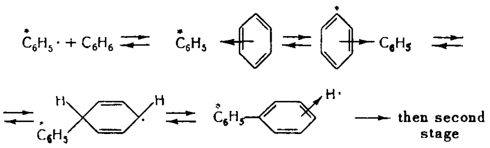
The radical R′· may be of the same nature as R·. Razuvaev and his coworkers consider that exchange of phenyl radicals can continue to occur within the complex A until the complex undergoes the second stage in the reaction[47]. This interpretation derives from the hypothesis[42] that reaction (10c) involves interconversion of the π and σ forms of the complex A (scheme 1).

Scheme 1



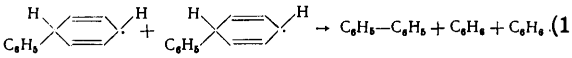
The exchange of phenyl radicals takes place, in Razuvaev's opinion, within the π complex (B). As can be seen from the scheme, this can pass into the σ complex (A) and enter the second stage of the reaction, or alternatively radical transfer can occur within (B) (scheme 2).

Scheme 2



If isomerisation of the π complex (B) and removal of a hydrogen atom by a second radical in the second stage are assumed to be fast, transfer of the phenyl radical will be determined by the presence of foreign radicals. In this way the regenerative exchange of radical fragments depends on the total concentration of radicals in the solution. This phenomenon has been observed in several experiments, which will be discussed below.

The discussion of reactions (10c) and (10d) shows some inconsistency. On the one hand, free radicals form complexes (A) with the aromatic compound (reaction 10c); and on the other, hydrogen is split off from this complex by free radicals (reaction 10d). In the writer's opinion, this discrepancy can be resolved by assuming that the removal of hydrogen from the complex (A) is effected by another complex radical. The first complex compound, by losing a hydrogen atom, is immediately converted into a biaryl. The other complex, by capturing a hydrogen atom, splits into two molecules



(10e)

The aryl radicals taking part in some processes, such as the decomposition of peroxides into reactive complexes, may be different. The biaryls formed according to this scheme always consist of radicals from the substance which has decomposed and from a solvent molecule. Such a phenomenon is consistent with the experimental results, the solvent molecules acting in this case as "carriers" of free radicals.

Certain difficulties are involved in the detection and the quantitative determination of the transfer of phenyl radicals. Estimation of the stepwise reaction from the active benzene formed from phenyl radicals (by reaction 10b) is not always reliable. In the decomposition of labelled benzoyl peroxide, for example, active benzene can be obtained by another reaction occurring in parallel (see reactions 10d and 10e). A similar phenomenon is observed in the decomposition of pentaphenylphosphorus.

Unfortunately the second method – use of a labelled solvent and the estimation of radical transfer from the isotopic composition of the biphenyl – is also unjustified in the case of benzoyl peroxide. In several cases, therefore, the question of the occurrence of an identity exchange still remains unsettled.

In order to detect reaction (10b), the decomposition of many organic and organometallic compounds containing carbon and hydrogen isotopes has been investigated, a labelled solvent being used as well. These compounds used as sources of radicals included diphenylmercury, benzoyl peroxide, pentaphenylphosphorus, nitrosoacetanilide, lead tetrabenzoate, diphenyliodonium iodide, etc.

The first experimental data on the transfer of phenyl radicals in benzene were obtained by Razuvaev *et al.*[48] who showed that this reaction takes place during the decomposition of diphenylmercury in deuterobenzene. These results were later confirmed by Korshunov and Orlova[49] using benzene labelled with ^{14}C. Heating and u.v. irradiation of a solution of diphenylmercury in deuterobenzene yields biphenyl containing up to 14.5% of phenyl groups from the solvent. On the other hand, use of diphenylmercury labelled with ^{14}C and benzene in the molecular proportions 1 : 25 in this reaction enabled the escape of radicals from the organometallic compound into the solution to be determined as radioactive benzene. After the reaction, the benzene was found to contain 7.9% of the activity of the diphenylmercury[47]. The biphenyl obtained consisted of 61.5% of phenyl groups from the mercury compound and 38.5% from the solvent. The formation of active benzene (~ 7.9%) may perhaps be a quantitative indication of the transfer of phenyl radicals in the decomposition of diphenylmercury. In both cases, however, the biphenyl contains considerably more benzene rings from the solvent.

It is interesting that escape of phenyl radicals into the bulk of the solvent is not observed in the thermal decomposition of diphenylmercury in benzene containing finely divided metals such as platinum and copper[47]. Under these conditions biphenyl contains only phenyl radicals from the organometallic compound, the solvent taking practically no part ($<$ 1.5%) in its formation. Almost all the phenyl radicals from the mercury compound recombined at the surface of the metals.

Bryce-Smith *et al.*[6] were able to isolate hydrobiphenyl from the photochemical decomposition of diphenylmercury in benzene in a current of nitrogen, but no mechanism for the formation of this compound is given.

As already pointed out, Bagdasar'yan *et al.*[45] found that the biphenyl resulting from the reaction of benzoyl peroxide with deuterobenzene contained up to 45% of phenyl radicals from the solvent. Razuvaev *et al.*[47] used benzene labelled with ^{14}C in this reaction, and found the biphenyl to contain 42% of active benzene rings.

In order to obtain direct confirmation of radical transfer, use was made of benzoyl peroxide containing radiocarbon ^{14}C in the ring. Decomposition of this peroxide in benzene at a molecular ratio of 1 : 10 was accompanied by the formation of radioactive benzene containing ~ 9% of the total activity of the peroxide. When the molecular ratio was lower (1 : 13) the quantity of radioactive benzene increased to 12%. The biphenyl obtained in these experiments contained 63% of phenyl groups from the peroxide and 37% from the solvent.

The relatively high discharge of phenyl fragments from the peroxide into the solution suggests that part of the radioactive benzene is formed in the latter case not only by transfer (scheme 2) but also by reaction (10d) or (10e).

It is difficult to judge the relative importance of the different processes. The isotopic composition of the biphenyl obtained in this reaction evidently also gives no answer to this question. In order to obtain a more rigorous proof of radical transfer, an investigation was made of the decomposition of mercurous acetate initiated with benzoyl peroxide in ^{14}C-labelled benzene medium[50]. The phenylmercury chloride isolated on treatment of the reaction mixture contained 6.2–12% of active phenyl groups from the benzene. The formation of active phenylmercury acetate is explained by labelled phenyl radicals regenerated by a transfer reaction attacking the mercury salt. This hypothesis is confirmed by the fact that, in the decomposition of labelled benzoyl peroxide in the presence of a mercury salt in benzene solution, the solvent after the reaction also contains a certain number of active molecules[51]. Mercuration of the benzene by the mercury acetate is excluded under these conditions (heating at 80° for 2 h).[52]

The photochemical decomposition of benzoyl peroxide under the influence of u.v. radiation takes place by a different mechanism from that of the thermal decomposition. The biphenyl obtained in labelled benzene contains only 9% of phenyl groups from the solvent. It is interesting that regeneration of C_6H_5 radicals does not occur under these conditions. When benzoyl peroxide labelled with ^{14}C in the ring is decomposed in benzene, the latter remains inactive after the reaction. It is assumed that photolysis of the peroxide involves the participation of excited molecules but not of free radicals.

Razuvaev *et al.* have observed the participation of the solvent in the formation of biphenyl by the decomposition of pentaphenylphosphorus in benzene[53]. The biphenyl obtained in an experiment with deuterated benzene contained 18% of deuterated phenyl groups, whereas use of radioactive benzene yielded a biphenyl containing only 5% of labelled radicals from the solvent[54]. Decomposition of deuterated $[1-5-D_5]$ pentaphenylphosphorus in ordinary benzene solution yielded 11.9% of deuterium which had passed into the solution in the form of benzene. The resulting biphenyl contained 83.0% of phenyl groups from the phosphorus compound. In the experiment with radioactive pentaphenylphosphorus, 16.5% of the original activity was found in the benzene, while the biphenyl contained 88.5% of phenyl fragments from the parent substance.

In many papers the participation of the solvent in the reaction, established from the composition of the dimer R–R, is regarded as proof of the transfer of identical radicals. However, the incorporation of part of the solvent molecule in the dimer is not always confirmation that stepwise transfer has taken place. This follows from the work of Razuvaev *et al.*[47] on the decomposition of lead tetrabenzoate and nitrosoacetanilide in benzene labelled with ^{14}C. They showed that the biphenyl obtained in these reactions contains equal quantities of phenyl groups from the benzene and from the above substances. Nevertheless, transfer of radicals definitely does not take place in this case.

Actually, no transfer of phenyl radicals from the lead salt to the benzene is observed in the decomposition in ordinary benzene of lead tetrabenzoate labelled in the nucleus with ^{14}C. The benzene isolated after the reaction has remained inactive[47]. Similar results were obtained for the decomposition of nitrosoacetanilide[51].

It is interesting that phenylmercury acetate obtained by the decomposition of nitrosoacetanilide in ^{14}C-labelled benzene in the presence of metallic mercury at 35°–40° showed no activity[55].

Finely divided metals have no influence on the mechanism of the decomposition of such compounds. This is evident from the fact that the isotopic composition of the biphenyl formed by the decomposition of nitrosoacetanilide in ^{14}C-labelled benzene does not change in the presence of freshly precipitated copper[55].

The reaction between diphenyliodonium iodide and labelled benzene in the presence of metallic mercury at 80° yields practically non-radioactive phenylmercury iodide and iodobenzene. Consequently, the solvent does not take part in the reaction.

The decomposition of the double diazonium salt $(C_6H_5N_2)_2ZnCl_4$ in labelled benzene at 80° also takes place without the formation of free radicals[55]. The main product of this reaction, chlorobenzene, is practically inactive.

The latter reactions are doubtless of homolytic type, but they proceed by a crypto-radical mechanism.

Thus the stepwise transfer of phenyl radicals is not characteristic of the decomposition of a number of "organo-elementary" compounds in benzene solution. The regenerative exchange of C_6H_5 radicals is completely absent in many of the reactions studied; it takes place to a slight extent (not exceeding 5–8%) in the thermal decomposition of diphenylmercury, benzoyl peroxide, and pentaphenylphosphorus.

VI. REACTIONS INVOLVING THE TRANSFER OF ACYLOXY RADICALS IN CARBOXYLIC ACIDS

It is sometimes suggested that regenerative exchange of acyloxy radicals can take place readily in carboxylic acids[3,9]

$$\mathrm{RCOO^{\cdot} + RCOOH \rightleftarrows RCOOH + RCOO^{\cdot}}, \tag{11a}$$

but such views are unfortunately expressed without experimental proof.

Most of the experiments on the transfer of acyloxy radicals have been carried out with acyl peroxides. The decomposition of many peroxides is accompanied by the formation of RCOO· and R· radicals

$$\mathrm{(RCOO)_2 \rightarrow 2RCOO^{\cdot}\,;\;\; RCOO^{\cdot} \rightarrow R^{\cdot} + CO_2}. \tag{11b}$$

Both these radicals are able to split off the hydroxyl hydrogen in carboxylic acid medium, with regeneration of an acyloxy radical; in the case of the RCOO· radical this occurs by reaction (11a), and in the case of R· as follows

$$\mathrm{R^{\cdot} + RCOOH \rightarrow RH + RCOO^{\cdot}}. \tag{11c}$$

In many cases the decomposition of acyloxy radicals RCOO· into R· and CO_2 is an exothermic process, as shown by the heats of decomposition, which have been determined for several radicals. In the case of R = CH_3, C_2H_5, and n-C_3H_7 their values are 17, 14, and 13 kcal mole^{-1} respectively[56].

In contrast to the decomposition of these radicals, that of the benzoyloxy radical is thermoneutral, and therefore $C_6H_5COO\cdot$ can exist for a longer period and the possibility of its exchange with the solvent is increased.

Thus the concentration of R· radicals in the decomposition of peroxides is governed by the stability of the acyloxy radicals RCOO·, *i.e.* by the rate of decarboxylation (11b).

Under the same conditions, therefore, the extents to which reactions (11a) and (11c) take place will differ with different peroxides. The stepwise transfer (11a) may be expected to be considerably more marked with the more stable acyloxy radicals RCOO·.

Fry *et al.*[10] found that the methane evolved in the decomposition of acetyl peroxide in acetic acid $^{14}CH_3COOH$ contained ~1% of the activity of the acid. On this basis they assume that formation of $^{14}CH_4$ is due to decarboxylation of the acid radicals $^{14}CH_3COO\cdot$, which could have been produced by reaction (11a) or (11b).

In Szwarc's opinion[57], acetoxy radicals are unstable and decompose almost completely. In many solvents they do not escape from the reaction "cage". In cyclohexane, however, the acetoxy radical does not exhibit its normal instability. Shine[58] points out that, when acetyl peroxide decomposes in cyclohexane, only 65−75% of CO_2 is evolved. The rest of the acetoxy radicals form esters with the cyclohexane. He considers that free acetoxy radicals are not formed in this reaction.

Results obtained by Szwarc and Smid[59] provide some confirmation that the more stable acyloxy radicals can undergo reaction (11a). Thus methane and ethane were detected among the products of the decomposition of benzoyl peroxide in acetic and propionic acids respectively. In contrast to this, methane and fluoroform are not formed in the analogous reactions of propionyl peroxide in acetic and trifluoroacetic acids respectively. The authors conclude that the ethyl radicals formed by decarboxylation of the unstable $C_2H_5COO\cdot$ are incapable of splitting off carboxylic hydrogen from acetic and trifluoroacetic acids.

In the case of benzoyl peroxide, 3−7% of its radicals attack the bond between hydrogen and the acid radical (RCOO−H), but which of the two possible radicals ($C_6H_5COO\cdot$ or $C_6H_5\cdot$) abstracts the hydrogen has not been established. It is suggested that formation of a hydrogen bond between the stable $C_6H_5COO\cdot$ radical and the carboxyl group of the acid is more probable.

In order to demonstrate the stepwise transfer of acyloxy radicals in carboxylic acids, Razuvaev *et al.*[11] have investigated the behaviour of benzoyloxy and *m*-nitrobenzoyloxy radicals, which are more stable than acetoxy radicals, in acetic and benzoic acids labelled with ^{14}C in the carboxyl group. The evolution of labelled $^{14}CO_2$ indicated that such exchange had occurred. When benzoyl, acetyl benzoyl, and *m*-nitrobenzoyl peroxides decompose in $CH_3{}^{14}COOH$ and $C_6H_5{}^{14}COOH$ media at 70°−100°, the carbon dioxide evolved contains 2−25% of $^{14}CO_2$.

When benzoyl and acetyl benzoyl peroxides decompose in benzoic acid (molecular ratios of 1 : 7.5−50) the activity increases to 6.4%. The increase in activity is especially marked in the decomposition of *m*-nitrobenzoyl peroxide in [α-^{14}C] benzoic acid, the quantity of active $^{14}CO_2$ increasing to 12.6% and 21.2% respectively.

The interaction of the R· radical of the peroxide with the carboxylic hydrogen of the acid according to reaction (11c) has been determined for the decomposition of benzoyl and *m*-nitrobenzoyl peroxides in CH_3COOD, dehydrogenation of the carboxyl being estimated from the isotopic composition of the RD formed. In the case of the phenyl radical, 3% of the deuterium is split off from the CH_3COOD, and 1.2% in the case of nitrophenyl. Thus the quantity of labelled $^{14}CO_2$ is by no means completely balanced by the deuterated benzene or nitrobenzene. For example, with *m*-nitrobenzoyl peroxide the ratio $NO_2C_6H_4D/^{14}CO_2$ is only 0.01.

Consequently the carboxylic hydrogen of the acid is split off mainly by the acyloxy radical of the peroxide according to Eqn. (11a)

$$RCOO^{\cdot} + R'^{14}COOH \rightleftarrows [RCOO^{\cdot}HOO^{14}CR'] \rightleftarrows RCOOH + R'^{14}COO\cdot$$
$$R'^{14}COO\cdot \rightarrow R'^{\cdot} + {}^{14}CO_2.$$

Stepwise transfer depends greatly on the temperature and the peroxide concentration, the amount of active $^{14}CO_2$ increasing as the concentration and the temperature fall. Thus lowering the temperature from 100° to 70° in the decomposition of *m*-nitrobenzoyl peroxide in acetic acid causes an increase in the activity of the $^{14}CO_2$ evolved from 21.2% to 24.6%. This fully agrees with the fact that the difference in stability between the $CH_3COO\cdot$ and *m*-$NO_2C_6H_4COO\cdot$ radicals is still greater at the lower temperature.

It is interesting that the $^{14}CO_2/CO_2$ (total) ratio obtained[11] in the decomposition of benzoyl peroxide in $CH_3{}^{14}COOH$ is 0.046, in good agreement with Szwarc's results (CH_4/CO_2 ratio = 0.044).[56]

Stepwise transfer of acyloxy radicals in carboxylic acids takes place *via* an intermediate complex of the radical with the acid [RCOOHOOCR′]. The great ease with which the carboxylic hydrogen is split off by the acyloxy radical coincides with the possibility of its forming a hydrogen bond with the acid[59].

It is clear from the above that the transfer of identical radicals ($CH_3COO\cdot$ radicals in acetic acid, and $C_6H_5COO\cdot$ radicals in benzoic acid) takes place to the extent of 1−2.3%.

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On the whole, reactions involving the transfer of different radicals belong to a very widespread class of chemical changes. Many cases are known in which such changes take place at a fast rate and are clearly in the nature of chain reactions. The transfer of identical radicals considered here is a particular case of this general class of chemical reactions.

It might be expected at first glance that the regenerative exchange of identical radicals would take place just as readily as exchange reactions involving different radicals. The available experimental data, however, contradict such an assumption. In all the examples investigated, as has been pointed out, stepwise transfer of radicals of one kind has occurred to only a slight extent, not more than by 1−5%. Thus even in the case of methyl and phenyl radicals such an exchange must be regarded as a subsidiary process. The main reactions undergone by radicals generated under the conditions investigated are recombination and disproportionation at the sites at which they have been produced.

This conclusion is not unexpected in the case of the unreactive stabilised radicals which have been mainly studied. The transfer of reactive radicals has been investigated only in the cases of methyl and phenyl. The interaction between $CH_3^{\cdot}$ and CH_4 has been investigated only in the gas phase, as it is impossible in the liquid phase. The reaction between $C_6H_5^{\cdot}$ and benzene is complicated, owing to complex formation between the reactants. Although several aspects of this question still remain somewhat obscure, a number of facts confirm the occurrence of transfer with a small proportion (~5−8%) of the radicals.

With regard to the stepwise reaction as a whole, it must be recognised that the amount of work published on this question is very small. Therefore it does not appear possible at the present time to reach a definite conclusion concerning the role of stepwise transfer of identical radicals in the migration of reactive centres throughout the volume of a reacting system and in increasing the life of radicals as kinetically independent units in many processes. The latter is the main feature of all exchange reactions and is widespread in the chemistry of free radicals. The same cannot be said with regard to identical radicals.

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MOLECULAR COMPOUNDS OF 1,4-DIOXANE

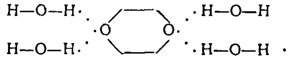
A.V. Dombrovskii

CONTENTS

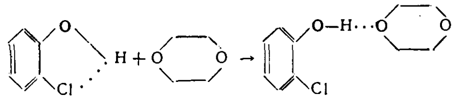
In contrast to its isomeric 1,3-dioxane, 1,4-dioxane is capable of forming molecular compounds (dioxanates) with many organic and inorganic compounds. The structure of dioxanates or other etherates has not yet been conclusively elucidated. It is considered that, depending on the properties of ether and ligand, the bond in these molecular compounds may be formed by: a) van der Waals forces; b) donor–acceptor interaction (resulting in compounds with an oxonium structure); c) hydrogen bonds with compounds containing active or mobile hydrogen atoms. Syrkin and Anisimov believe that the oxonium structure arises more frequently in dioxanates than in the molecular compounds of diethyl ether, for example[1].

1. MOLECULAR COMPOUNDS OF DIOXANE WITH COMPOUNDS CONTAINING ACTIVE OR MOBILE HYDROGEN ATOMS

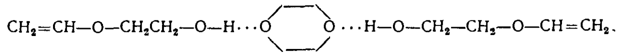
The ability of dioxane to dissolve, or mix with, compounds containing active or mobile hydrogen atoms is usually attributed to the formation of molecular compounds, involving the hydrogen bond. Physicochemical investigations of the water–dioxane system (vapour pressure, density, heat of mixing)[2-5] support this view. From their study of the heat of mixing of dioxane with water Fedos'eva *et al.*[4] inferred that dioxane forms with water a molecular compound of the type:



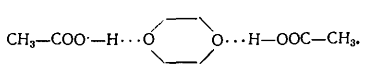
Freimann[5] and Gordy[6] measured the i.r. absorption spectra of dioxane and of ether solutions of alcohols and phenols and concluded that the OH groups of these hydroxylic compounds form hydrogen bonds with the oxygen atom in ethers. The reactivity of the OH group in *o*-chlorophenol, lowered by the *ortho*-effect, is increased[7] by the addition of 15% dioxane, which loosens the intramolecular hydrogen bond in *o*-chlorophenol and forms new hydrogen bonds between the phenolic OH group and the oxygen atoms in dioxane.



Measurements of the Raman spectra and the refractive index of the dioxane solution of ethylene glycol monovinyl ether[8] indicate unequivocally the presence of intermolecular hydrogen bonds:



The compounds of dioxane with organic acids are also formed primarily by hydrogen bonding. From their measurements of viscosity, density, surface tension, and refractive index in the dioxane–acetic acid system, the formation of the diacetate was inferred[9]:



The dioxanates of most strong acids are well-defined compounds with sharp melting points. They readily decompose in water, owing to the smaller proton affinity of dioxane compared with that of water[10]. Mezhennyi[11,12] found that at 20° dioxane dissolves, with heat evolution, up to 45 mole % of hydrogen chloride: the electrical conductivity of dioxane solutions of HCl is small (less than $10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$), and decreases with further dilution. This is in agreement with the earlier data by Meisenheimer[13], who found that the dissociation of HCl in dioxane is negligibly small.

Favorskii[14] was the first to show that a crystalline compound of composition $C_4H_8O_2.H_2SO_4$ (m.p. 101°) separates on mixing cold ether solutions of sulphuric acid with dioxane. A point corresponding to the dioxanate prepared by Favorskii has been identified[15] on the melting point diagram of the dioxane–sulphuric acid system. Syrkin and Anisimov[1] studied the polar properties of this dioxanate and found its dipole moment to be 4.63 D. The increase in the polarisation of the compound $D.H_2SO_4$† with dilution of the dioxane solution may, in the authors' opinion, be taken as evidence that both hydrogen bonds and oxonium structures are formed.

Pyrosulphuric acid forms dioxanate $D_2.H_2S_2O_7$, whose composition has been established by thermal analysis[16,17]. With 70% perchloric acid dioxane forms[18,19] in the cold a crystalline dioxanate hydrate, $D.HClO_4.H_2O$, m.p. 80°. Phosphoric acid dioxanate $D.2H_3PO_4$ (m.p. 87°) is recommended for use in reactions to be carried out in anhydrous media. The dioxanates $3D.4HNO_3$ and $2D.2HNO_3$ have also been described[21].

2. MOLECULAR COMPOUNDS WITH METAL HALIDES

A large number of dioxanates of metal halides are known. Salts of other anions do not normally react with dioxane. Dioxanates are prepared by allowing a mixture of dioxane and a metal halide to stand for several days, and subsequently evaporating the solution over sulphuric acid to incipient crystallisation. They are also prepared by mixing alcoholic solutions of metal halides with dioxane. They are crystalline compounds, coloured or colourless, readily soluble in alcohol, as a rule, and sometimes in acetone or ether. They are decomposed by water, and lose dioxane on being heated.

Lithium and caesium halides, from fluorides to iodides, are soluble in dioxane[22]. This property is particularly useful for separating lithium salts from the chlorides and bromides of other alkali metals[23]. Rheinboldt and his

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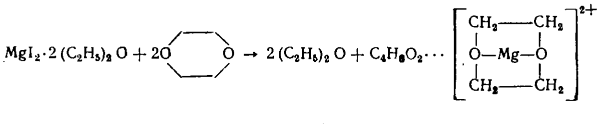
† D stands for dioxane

coworkers[24-26] established that dioxane forms the following dioxanates with alkali halides: D.LiCl, D.LiBr, D_2.LiI, D_3.NaI, D.KI, as well as $D_2.NH_4I$. NaCl, KCl, NH_4Cl, NaBr, KBr, and NH_4Br do not form dioxanates.

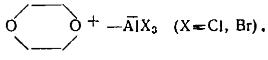
A large group of dioxanates of bivalent metal halides has been described[25-33]: $D_2.MgCl_2$, $D_2.MgBr_2$, D_2MgI_2, $D.CaCl_2$, $D.CaBr_2$, $D.CaI_2$, $D.SrBr_2$, $D_2.SrI_2$, $D_2.BaI_2$, $D_2.ZnCl_2$, $D_2.ZnBr_2$, $D_2.ZnI_2$, $D.CdCl_2$, $D.2CdCl_2$, $D.CuCl_2$, $D.CuBr_2$, $D.HgCl_2$, $D_2.HgCl_2$, $D.HgBr_2$, $D_2.HgBr_2$, $D_2.HgI_2$, $D.HgI_2$, $D_2.CrBr_2$, $D_2.MnBr_2$, $D_2.MnI_2$, $D_2.FeCl_2$, $D_2.FeBr_2$, $D_2.FeI_2$, $D_2.CoCl_2$, $D_2.CoBr_2$, $D_3.CoI_2$, $D_4.CoI_2$, $D.NiCl_2$, $D.NiBr_2$, $D.NiI_2$, and of the mercuric salts of pseudo-halide groups[32], $D_2.Hg(CN)_2$ and $D_2.Hg(SCN)_2$. In addition to those enumerated, a large number of dioxanates of metal halide hydrates[34] are also known, *e.g.* $D.CuCl_2.H_2O$, $D_3.ZnCl_2.H_2O$, $D.CaCl_2.H_2O$, *etc.* $SrCl_2$, $BaCl_2$, and $BaBr_2$ do not form dioxanates[25].

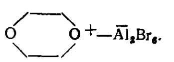
The tendency to form dioxanates, and the stability of the dioxanates, increase from chlorides to iodides in bivalent metal halides. Dioxanates are more stable than etherates. Esefov[33] showed that dioxane can displace diethyl ether from magnesium iodide etherate and form a stable dioxanate, whose structure he represented by the following formula (A):


(A)

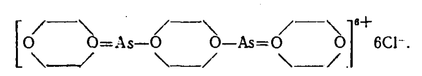
Dioxanate (A) does not decompose till 355°–365°.

Dioxanates formed by the halides of trivalent elements are also of interest. Boron trifluoride dioxanate, $D.BF_3.2H_2O$, is actually a salt-like compound with an ionic coordinate link[35]. With aluminium halides dioxane forms several compounds. Solutions of aluminium bromide in dioxane conduct electricity, and slowly deposit crystals of composition $D.AlBr_3$. Sheka and Karlysheva[37] prepared the dioxanates $D.AlCl_3$ and $D_2.AlCl_3$ and found their dipole elements (μ) to be 5.19 D and 5.21 D respectively. They also determined the dipole moment (μ = 5.23 D) of the dioxanate $D.AlBr_3$ obtained earlier[36]. The large dipole moments of these dioxanates are attributed to the considerable polarisation of the link between the oxygen atom in dioxane and the aluminium atom. The structure of these dioxanates can therefore be represented by the following general formula:



Characteristic in this respect[37] is the dioxanate $D.Al_2Br_6$, which is not dissociated in benzene solution. Its dipole moment is 4.62 D, and the compound is therefore assigned the unsymmetrical structure 

The dioxanate $D.SbF_3$ can be used[38] as a mild fluorinating agent. It reacts with $C_6H_5CCl_3$ forming a mixture of $C_6H_5CF_3$ and $C_6H_5CClF_2$. Arsenic trichloride froms two dioxanates, $D.AsCl_3$ (m.p. 68°)[39] and $D_3.AsCl_3$ (m.p. 62°)[40]. The latter is an ionic compound, whose complex cation contains arsenic, and whose outer sphere contains chloride ions. These can be precipitated from alcoholic solution with silver nitrate, although no such precipitation occurs with $AsCl_3$ itself. Accordingly the structure of arsenic trichloride dioxanate may be represented as follows:



The benzene solutions of the halides of tetravalent tin, titanium, and zirconium form the following crystalline dioxanates with dioxane: $D.SnCl_4$,[41,42] $D_2.SnCl_4$, $D.SnBr_4$,[41,43] $D_2.SnBr_4$,[40,43] $D.TiCl_4$,[44] $D_2.TiCl_4$,[44,45] $D_2.ZrCl_4$ and $D_2.ZrBr_4$.[45] Their composition was determined from analytical data and from cryoscopic molecular weight determinations. The stability of the dioxanates formed by the tetrachlorides of Group IV elements increases with the covalent radius of the metal atom[45].

Mixed alkyl and aryl magnesium halides also form crystalline dioxanates, as first observed by Schlenk and Schlenk[46]. They are prepared by precipitation with dioxane from ether solutions of Grignard reagents, the dialkyl- or diaryl-magnesium compounds remaining in solution. Wittig and his collaborators[47,48] described a large group of dioxanates of the phenyl derivatives of lithium, beryllium, magnesium, zinc, cadmium, and aluminium, for instance $D_2.[(C_6H_5)_3MgLi]$, $D_5.[(C_6H_5)_4AlLi]$, etc.

Metal halide dioxanates are used in organic synthesis. It has been reported[49] that the dioxanates of aluminium, zinc, tin, and iron halides can be used as catalysts in reactions between fumaric acid and butanol, triethyleneglycol, glycerol, etc. The stable crystalline lithium borohydride dioxanate, $D.LiBH_4$, obtained in 86% yield by mixing dioxane with a solution of $LiBH_4$ in tetrahydrofuran, can be used[50] to reduce esters. Unlike $LiBH_4$ itself, this material is stable and therefore convenient to handle.

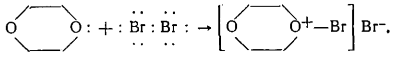
3. MOLECULAR COMPOUNDS WITH HALOGENS

There are no data in the literature regarding the reaction of dioxane with fluorine. With bromine, iodine, and interhalogen compounds dioxane forms crystalline molecular compounds. If bromine is added to dioxane in the cold, orange crystalline dioxane dibromine, $C_4H_8O_2.Br_2$, separates quantitatively[14,43,51]. Dioxane di-iodide $C_4H_8O_2.I_2$ is obtained[1,14,43,52] as dark crystals by mixing an ether solution of iodine with dioxane, and evaporating the solvent. The stability of halogen dioxanates (the strength of the oxygen–halogen bond) depends on the polarisation of the halogen molecule; the greater its polarisability, the stronger the molecular compound. Using the spectrophotometric method Lilich and Presnyakova[53] determined the stability constants (K_S) in 0.01 M carbon tetrachloride solutions of the dioxanates formed by halogens and interhalogen compounds (see Table). Their values for K_S

TABLE. Halogen dioxanates

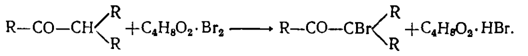
$D.X_2$	M.p. °C	K_s	μ, D
$D\cdot Br_2$	66	3.75	1.3
$D\cdot I_2$	85	10.5	0.95
D·BrI	58	163	—
D·ClI	65	632	—

accord well with the polarisability of the halogens. Compared with the constants for bromine and iodine dioxanates, K_S values for the dioxanates of interhalogen compounds are considerably higher, which is in full agreement with the high polarisability of ClI and BrI. Syrkin and Anisimov[1] compared the electron polarisation and dipole moments of $D.Br_2$ and $D.I_2$ at infinite dilution and found that dioxane dibromide is strongly ionised



This is further confirmed by the distance between bromine atoms, 2.31 Å, in crystalline dioxane dibromide[54] as compared with 2.28 A in the bromine molecule.

Dioxane dibromide has recently been recognised as a specific brominating agent[55]. Equimolar amounts of dioxane dibromide and a carbonyl compound react in ether solution or in the absence of solvent to give good yields of α-bromo-derivatives of aldehydes and ketones[55-63]:



$$R{-}CO{-}CH\begin{smallmatrix}R\\R\end{smallmatrix} + C_4H_8O_2\cdot Br_2 \longrightarrow R{-}CO{-}CBr\begin{smallmatrix}R\\R\end{smallmatrix} + C_4H_8O_2\cdot HBr.$$

R may be a hydrogen atom, alkyl, or a heterocyclic radical. The bromination of spiran compounds has been reported[64]. Dioxane dibromide is a mild reagent for brominating the carbon–carbon multiple bond in unsaturated compounds[65-67]. In the reaction with triarylethylenes dioxane dibromide replaces the single hydrogen atom by bromine[68,69]:

$$(C_{10}H_7)_2C{=}CH{-}C_6H_5 + C_4H_8O_2\cdot Br_2 \longrightarrow (C_{10}H_7)_2C{=}CBr{-}C_6H_5 + C_4H_8O_2 + HBr.$$

Benzene does not undergo bromination even on heating, while toluene, heated only to 40° forms quantitatively *p*-bromotoluene[55,62]. Depending on the relative amount of the reagent, phenol and its ethers yield mono- or di-substituted products[55,64,70,71]. Aromatic amines, (aniline, toluidines), their *N*-substituted derivatives[62,72], and *N*-arylamides of sulphonic acids[73] react similarly. Acid-labile compounds such as furan, thiophen, pyrrole derivatives, indole, and 2-methylindole, whose bromination by usual reagents is complicated by side-reactions, react with dioxane dibromide to give quantitative yields of substituted derivatives with one bromine atom in the heterocyclic nucleus[55,62].

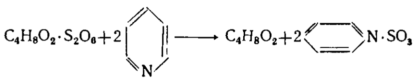
Dioxane di-iodide does not appear to have iodinating capacity[74]. For substitution iodination Terent'ev *et al.*[62] used the molecular compound formed by dioxane and iodine monochloride, $C_4H_8O_2.ClI$. With this reagent they carried out the iodination of phenol, salicylic acid, β-naphthol, resorcinol, and 2-methylindole, and obtained the corresponding mono-iodo derivatives in satisfactory yields.

4. MOLECULAR COMPOUNDS WITH VARIOUS OXIDES

With nitrogen dioxide, dioxane forms a crystalline dioxanate, $D.N_2O_4$, which has been used for nitrosating unsaturated compounds[75]. With sulphur dioxide it forms the dioxanates $D.SO_2$ and $D.2SO_2$, [76,77] which have been recommended for use as pesticides[78]. A dioxanate formed by rhenium oxide, $Re_2O_7.3C_4H_8O_2$ has also been described[79].

The dioxanate formed by sulphur trioxide is the most interesting. It was first obtained by Suter and his collaborators[80], who used it for sulphonating organic compounds. The direct action of sulphur trioxide upon dioxane produces decomposition and resinification. However, on mixing a sulphur trioxide solution (*e.g.* in dichloroethane) with dioxane in the cold a crystalline dioxanate of composition $D.S_2O_9$ is formed[81].

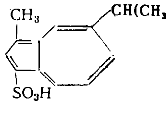
Mezhennyi and Kovganich[82] recently proposed a method for the preparation of sulphur trioxide dioxanate by direct reaction of dioxane vapours with gaseous sulphur trioxide. In the absence of moisture this compound is stable for several weeks. It is stable up to 80°, but above this temperature it decomposes violently with evolution of sulphur trioxide. It is practically insoluble in dichloroethane, benzene, and ligroin, but is readily soluble in dioxane, where it is present as $D.S_2O_6$. Mezhennyi and Martynenko[83] confirmed cryoscopically that in very dilute dioxane solutions sulphur trioxide is dimeric and that such solutions are completely non-conducting. Water instantly decomposes this dioxanate into sulphuric acid and dioxane. The dioxanate reacts violently and with the evolution of heat with pyridine[84] and ammonia[85], forming the adduct and ammonium sulphamate, respectively:



$$C_4H_8O_2\cdot S_2O_6 + 2NH_3 \longrightarrow H_2N{-}SO_3NH_4 + C_4H_8O_2.$$

Sulphur trioxide dioxanate has the remarkable property of sulphonating many acid-labile organic compounds which are resinified or polymerised by the usual sulphonating agents[86]. Sulphonation with sulphur trioxide dioxanate is carried out under mild conditions, usually at 0–20°, in an indifferent solvent (dichloroethane, methylene dichloride, ether). The resulting dioxanates of sulphonic acids can easily be decomposed into sulphonic acids and dioxane, and with alkalis and carbonates they form the salts of sulphonic acids, which are easily isolated.

Sulphonations of alkenes[80,87-89], alkynes[81], and cyclic alkenes[90-92] by sulphur trioxide dioxanate have been reported. In unsaturated aliphatic–aromatic compounds (*e.g.* styrene and its derivatives) the sulphonate group assumes a position in the side-chain, not in the aromatic nucleus[93-100]. At 20° benzene and *m*-xylene[80] form quantitatively the respective monosulphonic acids. Sulphonation of naphthalene[80], tetralin[101], anthracene, and guaiazulene[102] has also been described. The last compound gives a sulphonic acid of the following structure, in 53% yield:



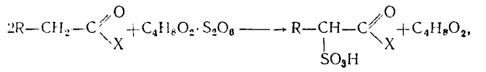
Alcohols and phenols form rapidly and quantitatively acid sulphate esters[103-104]

$$2R{-}OH + C_4H_8O_2\cdot S_2O_6 \longrightarrow 2R{-}OSO_3H + C_4H_8O_2.$$

This reaction is used for preparing the salts of acid sulphonic esters derived from higher alcohols, which are surface-active[105]. It has also been used as the basis of a method for the quantitative determination of mono- and poly-hydric alcohols[104,106]. Similarly primary aromatic amines are transformed quantitatively into sulphamic acids [104,107] by sulphur trioxide dioxanate:

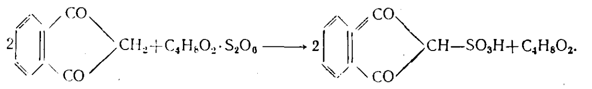
$$2Ar{-}NH_2 + C_4H_8O_2 \cdot S_2O_6 \longrightarrow 2Ar{-}NH{-}SO_3H + C_4H_8O_2 .$$

Sulphur trioxide dioxanate is an effective and specific sulphonating agent for aliphatic aldehydes [55,108], ketones [55,60,108–111], including cyclic ketones [55,108], and carboxylic acids and their derivatives [112,113]. The α-hydrogen atoms in these compounds undergo substitution by the sulphonate group, forming the corresponding sulphonic acids:

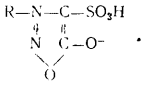


$$2R{-}CH_2{-}C(=O)X + C_4H_8O_2 \cdot S_2O_6 \longrightarrow R{-}CH(SO_3H){-}C(=O)X + C_4H_8O_2,$$

where X = H, Alk, OH, OAlk. Depending on the relative amount of reagents, α-mono- or α,α'-disulphonic acids may be obtained. Sulphonation of acetonitrile and isovaleronitrile proceeds likewise [112]. One H atom in the methylene group of the following 1 : 3 diketones is substituted by the sulphonate group (70–80% yields): 2-phenyl-1,3-indandione, dimedone, 5-phenyl-1,3-cyclohexadione, peri-1,3-naphthindandione, and dibenzoylmethane [114,115]. For example, the reaction with 1,3-indandione proceeds as follows:



The majority of heterocyclic compounds seem to be typical acid-labile substances. Terent'ev and Yanovskaya [116,117] showed however, that pyrrole and thiophen, as well as their alkyl derivatives, undergo sulphonation by sulphur trioxide dioxanate, forming good yields of mono-C-sulphonic acids. In sydnones [118] the single hydrogen atom in the heterocyclic ring undergoes substitution resulting in a sulphonic acid of the general formula:



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ANODIC SUBSTITUTION REACTIONS

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CONTENTS

1. INTRODUCTION

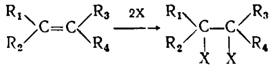
Among the processes occurring at the anode during the electrolysis of electrolyte solutions in the presence of organic compounds a group of processes can be distinguished which can be represented by the general equation,

$$RH \rightarrow RX\ ,$$

where X = F, Cl, Br, I, OH, CNS, CNSe, ONO_2, $O.CH_3$, SO_3H, N:N.Hal, etc.

These processes are usually described collectively as "anodic substitution". Depending on the nature of the substituting agent, anodic substitution can bring about fluorination, chlorination, bromination, iodination, hydroxylation, thiocyanation, selenocyanation, preparation of nitric esters, nitration, methoxylation, sulphonation, and diazotisation.

Addition to multiple bonds in organic compounds can also take place at the anode



$$R_1R_2C{=}CR_3R_4 \xrightarrow{2X} R_1R_2CX{-}CXR_3R_4$$

By analogy with "anodic substitution" such reactions could be termed "anodic addition" reactions. Since "anodic addition" reactions are comparatively few, and do not differ fundamentally from anodic substitution reactions, we will consider them together under the general term "anodic substitution".

2. MECHANISM OF "ANODIC SUBSTITUTION"

Anodic substitution processes can be divided into two main groups.

(i) Radical Processes

In radical processes the primary step at the electrode is the discharge of anions present in the solution, with the formation of free radicals

$$2X^- \xrightarrow{-2e} 2X^\cdot ,$$

which react with the organic substance

$$R{-}H + 2X^\cdot \longrightarrow R{-}X + HX...$$

Such a mechanism has been proposed by Knunyants and Sokol'skii[1] for all cases of electrochemical fluorination. Some workers, however, think this process more complicated. Thus Gramstad and Haszeldine[2] suggested that the formation of organic fluorine compounds involves reaction between the organic compound and higher fluorides of nickel formed on the anode.

In order to explain the formation of organic fluorine compounds during the electrolysis of a solution of an olefine in acetic acid containing potassium hydrogen difluoride, Schmidt[3] postulates the discharge at the anode of a complex of the organic compound with hydrogen fluoride, whereby the coordinate link in the complex is converted into a covalent bond.

Youtz[4] suggested a radical mechanism for electrochemical chlorination on the basis of measurements of anode potential during the chlorination of several organic compounds (malonic acid, phenol, and toluene).

This group includes, in addition to the above mentioned fluorination and chlorination, the reactions of bromination, thiocyanation, hydroxylation, preparation of nitric esters, iodination in part, and probably alkoxylation.

The mechanism of electrochemical alkoxylation is apparently that the bromine radicals formed at the anode react with the alcohol present as solvent, *e.g.* with methyl alcohol to form methoxyl radicals

$$Br^\cdot + CH_3OH \longrightarrow HBr + CH_3O^\cdot ,$$

which can effect the methoxylation of furan and its derivatives according to the equations considered below (see section on alkoxylation).

(ii) Chemical "Anodic Substitution" Reactions

The occurrence of such reactions is due to the accumulation in the layer adjacent to the anode, as a result of the anodic process, of products which can react with the organic compound. They include nitration, nitrosation, sulphonation, diazotisation, some cases of iodination, and also the addition of HOCl.

The addition of HOCl to ethylene during electrolysis in the presence of chlorides, for example, is due to the chlorine evolved at the anode dissolving to form hypochlorous acid, which reacts with the ethylene

$$Cl_2 + OH^- \longrightarrow Cl^- + HClO\ ,$$

$$HClO + CH_2{=}CH_2 \longrightarrow CH_2OH{\cdot}CH_2Cl$$

The formation of iodoform apparently takes place in an analogous manner, since alcohol is not a depolariser with respect to the platinum anode at which iodine is deposited.

In nitration and sulphonation the action of the electric current is essentially to produce concentrated solutions of nitric and sulphuric acids around the anode as a result of ionic migration.

3. ANODIC SUBSTITION REACTIONS: CONDITIONS

(*a*) Choice of Electrolyte and of Solvent

The solution in which anodic substitution is to be effected must be sufficiently conducting, and its electrolysis should involve the discharge at the anode of the anions required for the substitution. The choice of solvent is dictated by this requirement.

The only anodic process possible in the electrolysis of aqueous alkaline solutions is the discharge of hydroxyl ions, so that these solutions are most suitable for anodic hydroxylation.

Bromide, iodide, and thiocyanate anions are discharged with high efficiency from aqueous solutions of their salts, and therefore bromination, iodination, and thiocyanation are carried out in aqueous solutions, concentrated ammonium thiocyanate solutions being recommended for the last-named process.

The discharge of chloride ions requires a more positive potential than that of bromide, iodide, and thiocyanate ions. The chlorine evolved at the anode during the electrolysis of aqueous chloride solutions always contains some oxygen, since the discharge of hydroxyl ions accompanies that of chloride ions. If the substance is comparatively readily oxidised, some oxidation cannot be avoided during electrochemical chlorination in aqueous solutions. In such cases it is necessary to use non-aqueous solutions. The chlorination of benzene, for example, has been carried out in ether saturated with hydrogen chloride[5], in acetic acid saturated with lithium chloride[6], in a mixture of acetic and concentrated hydrochloric acids[7], and in methyl alcohol saturated with hydrogen chloride[8,9].

The discharge of fluoride ions requires a considerably more positive potential than that of hydroxyl ions, so that aqueous solutions are unsuitable for electrochemical fluorination. The chemical reactivity of elementary fluorine makes the choice of solvent extremely difficult. The only solvent which gives satisfactory results is apparently liquid hydrogen fluoride[10]. The electrical conductivity of pure hydrogen fluoride is slight[11], but it is a good solvent for most organic compounds (alcohols, ethers, carboxylic acids, nitriles, ketones, amines, etc.), forming electrically conducting solutions, which indicates that dissociation occurs on dissolution. Solutions in hydrogen fluoride differ fundamentally in the nature of their dissociation from aqueous solutions, for it is not the solute but the solvent, *i.e.* the hydrogen fluoride, which undergoes dissociation[12]. When alcohol and ether, for example, are dissolved in hydrogen fluoride, the dissociation which takes place can be represented by the following equations:

$$C_2H_5OH + HF \rightleftarrows C_2H_5OH_2^+ + F^-$$

$$C_2H_5OC_2H_5 + HF \rightleftarrows (C_2H_5)_2OH^+ + F^-,$$

i.e. the only anions present in the solution are fluoride ions, and electrochemical processes other than the discharge of fluoride ions are impossible.

A number of organic compounds, hydrocarbons for example, are almost insoluble in hydrogen fluoride and do not form electrically conducting solutions in it. It has been suggested that electrochemical fluorination of such compounds can be effected by adding to the hydrogen fluoride a small quantity of a substance which will make the mixture electrically conducting, *e.g.* water, mercurous cyanide, ammonia, methyl alcohol, acetic acid, pyridine, 2-fluoropyridine, or alkali-metal fluorides[10].

There are indications that electrochemical fluorination is possible by the electrolysis of an organic substance in anhydrous acetic acid saturated with potassium hydrogen difluoride[3,13], but this solvent is probably applicable only in rare instances.

Methoxylation and ethoxylation are carried out respectively in absolute methyl and ethyl alcohol in which a little ammonium bromide has been dissolved[14-17].

(*b*) Anode Material

The main requirement of an anode material for electrochemical substitution is that it shall be chemically inert. The choice of materials unaffected by anodic processes is very restricted.

Nickel is generally employed for electrochemical fluorination in liquid hydrogen fluoride[10], and a platinum anode is recommended for fluorinations in potassium hydrogen difluoride–acetic acid solution[3,13].

As already noted in sub-section (*a*), electrochemical chlorination in aqueous solutions may be accompanied by the discharge of hydroxyl ions, and a material of high oxygen overpotential must be used as anode to minimise possible oxidation processes. This requirement is best met by smooth platinum, the use of which is advisable for almost all electrochemical chlorination[5-9,18-30].

An attempt to use graphite or magnetite anodes in the chlorination of benzene did not give satisfactory results[7]. Chlorination of toluene at a graphite anode is accompanied by oxidising processes, leading to the formation of *o*- and *p*-chlorobenzoic acids[31].

It has been reported that benzene and ethylene can be satisfactorily chlorinated at a graphite anode impregnated with cyanuric acid[32], or by using anode rods made by compressing a mixture of 50 parts of graphite + 40 parts of sodium chloride + 10 parts of potassium iodide. The activity of such electrodes is apparently due to the formation of iodine chloride, which acts as a chlorine carrier. The use of anodes having this composition has a qualitative effect on the course of the chlorination. When, for example, toluene is chlorinated at a platinum anode, a mixture of *o*- and *p*-chlorotoluenes is formed[33], but on the pressed graphite anodes, 2,4-dichlorotoluene is also formed[34].

Platinum anodes are usually employed for bromination, iodination, methoxylation, and the preparation of nitric esters[14-16,35-46], although graphite anodes appear to be equally suitable for the first three processes[17,47,48], and thiocyanation is even more successful on graphite than on platinum[49-55].

Since anodic substitution is usually carried out in a bath without a diaphragm, the choice of cathode material is also fairly critical. Electrodes made of copper, nickel, iron, or other metal of low hydrogen overpotential are apparently the most suitable, since they are least likely to cause undesirable reduction processes.

(*c*) Current Density

In most cases current density has no effect on the mechanism of the discharge of anions until its limiting value is reached. However, products in which the hydrogen atoms have been completely substituted are more likely to be obtained at high current densities.

By employing a high concentration of organic acid and a low current density, for example, it is possible to obtain incompletely fluorinated propionic and butyric acids[56], whereas at current densities of ~400 A m^{-2} the hydrogen atoms are completely replaced by fluorine[57]. Increasing the current density favours the formation of polychloro-derivatives from benzene and its homologues[7]. Iodination of 8-hydroxyquinoline at 0.001 A cm^{-2} yields mainly a monoiodo derivative, whereas at 0.01 A cm^{-2} the chief product is diiodoquinolinol[44].

Increasing the current density has a favourable effect on the bromination of indigo[38] and on the formation of nitric esters from ethylene[45]. It may happen that at high current densities the rate of formation of inorganic radicals at the anode becomes greater than the rate at which they react with the organic compound, making additional processes possible. In the case of halogenation, for example, the free halogens may be evolved at the anode. This process is particularly dangerous with electrochemical fluorination, since the evolution of elementary fluorine at the anode leads to degradation of the organic substances. Thus electrochemical fluorination of succinic anhydride, for example, yields a mixture of the fluorides of perfluoropropionic and perfluorosuccinic acids, the yield of the latter increasing from 9.6% to 23.4% when the current density is decreased from 0.03 to 0.01 A cm^{-2}: *i.e.* increase in current density substantially accelerates decarboxylation processes[58].

The use of excessive current densities is undesirable also with other types of anodic substitution. Under these conditions an appreciable diminution in the yield has been observed in the bromination of indigo[38] and also, for example, in the preparation of iodoform[42].

It is clear from the above that each case should have an optimum current density, at which the process is carried out most efficiently. These optimum values usually lie within the range 100–1000 A m^{-2}.

Fluorination is normally carried out at ~200 A m^{-2}.[1,10,11,59] The optimum current densities (in A m^{-2}) for various processes are — preparation of chloral[32] 300, preparation of chloroform from alcohol[60] 400–800, and from acetone[29] 150, chlorination of higher ketones[61] 640–1250, chlorination of ethylene[30,62] 700–1500, chlorination of benzenesulphonic acid[63] 330, bromination of succinimide[40] 465, preparation of iodoform from acetone[43] 130, and thiocyanation[49–53] 200–300.

(*d*) Concentration of Organic Substance

Increasing the concentration of the organic substance has in most cases a favourable effect on the substitution process. In the bromination of acetone, for example, a high concentration of acetone in the solution favours the formation of bromoform[35], and increasing the concentration of alcohol undergoing iodination favours the formation of iodoform[41].

Many organic substances, however, have poor solubility in aqueous solutions, and therefore numerous attempts have been made to increase the concentration of the organic compound by using various solvents.

The use of solvents cannot be accepted as desirable, since they usually take part to some extent in the anodic process, and contaminate the reaction products. Instead of using solvents, it is sometimes better to stir vigorously the solution undergoing electrolysis[64], or to introduce the organic substance directly through a porous anode[32,65–68], since this practically eliminates any possible concentration effects and ensures the maximum possible concentration of the organic compound during the process. On the other hand, a large excess of the organic compound favours the formation of incompletely substituted derivatives: thus electrolysis of solutions of carboxylic acids containing comparatively low concentrations of hydrogen fluoride (1–5 moles of HF per mole of acid) results in partial replacement of the hydrogen atoms by fluorine, propionic acid giving a 10% yield of β-fluoropropionyl fluoride, and butyric acid a 20–30% yield of a mixture of α-, β-, and γ-fluorobutyric acids[56].

Another example of the effect of concentration of the organic substance on the substitution process is provided by the electrochemical fluorination of dimethyl sulphate. The main fluorination product of the electrolysis of a 5–10% solution of dimethyl sulphate in hydrogen fluoride is bistrifluoromethyl sulphate[69], but with a small concentration of hydrogen fluoride in the dimethyl sulphate (molecular ratio 1 : 5.5), the main product under the same conditions of electrolysis is fluoromethyl methyl sulphate[70].

(*e*) Solution pH

The optimum pH value is different for each individual substitution. Halogens, for example, react vigorously with alkalis, and therefore chlorination, bromination, and iodination are carried out in acid or neutral media. The main product of the chlorination of alcohol in acid medium is chloral[67,71], whereas in neutral or faintly alkaline medium chloroform is produced almost exclusively[18,20]. A neutral medium is necessary for the preparation of iodoform from alcohol[41] and of chloroform and bromoform from acetone[20,35] as well as in the bromination of succinimide[40] and the iodination of 8-hydroxyquinoline[44]. Other processes, such as the chlorination of ketones while preserving the carbonyl group[22,23,61], the chlorination of aniline[29,72,73], the bromination of indigo[38,72,73], etc , are carried out successfully in acid media.

Strongly alkaline media are more suitable for hydroxylation processes. An electrolyte of 25% caustic soda solution is recommended for the hydroxylation of ethylene[74].

We must consider here in more detail processes which require the medium to be kept neutral. Since the pH of the solution is continually changing during electrolysis, great attention has been paid to methods for buffering the medium in continuous-flow processes. Several ways of solving this problem have been suggested — (1) use of solutions of alkaline-earth salts (*e.g.* calcium chloride, barium chloride, etc.) as electrolyte[20,60,67,77], (2) employment of an additional (neutralising) cathode[20,43], (3) addition of hydrochloric acid to the solution[18], and (4) employment of a mercury-iron cathode[18,19].

A detailed consideration of the merits and defects of all these methods is beyond the scope of the present paper. The most reliable method is probably the continuous controlled acidification of the solution during electrolysis.

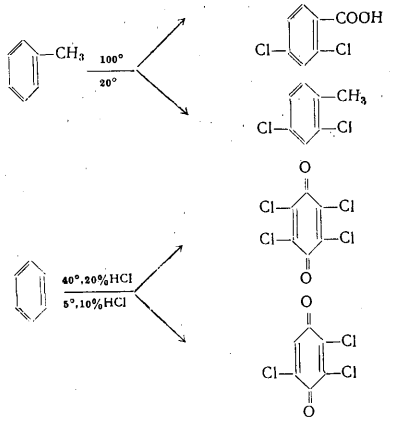
(*f*) Temperature

Temperature has a very important effect on the substitution process, but published information is inadequate for a complete explanation of the observed phenomena.

The role of temperature in electrochemical fluorination has been discussed in some detail[1]. As the temperature of fluorination is raised, the percentage of the most highly volatile products increases (see ref. 78) and the extent of degradation of the hydrocarbon skeleton decreases[79].

In a number of cases of chlorination, bromination, and iodination, a slight increase in temperature (to 40° – 60°) has a favourable effect on the substitution.

At still higher temperatures the yield of substitution products begins to fall owing to side-reactions. In electrochemical chlorination, for example, a rise in temperature usually results in more extensive oxidation, and also favours the formation of the more highly chlorinated products. This has been observed in the chlorination of benzene[28], toluene[31], benzenesulphonic acid[63], and aniline[75].



In other cases, for example in the chlorination of ketones[61], the bromination of succinimide[40], the iodination of 8-hydroxyquinoline[44], thiocyanation[51], and methoxylation[14], the use of low temperatures is recommended.

4. ANODIC SUBSTITUTION REACTIONS: APPARATUS

The apparatus for carrying out anodic substitution reactions in liquids is extremely simple, since in most cases other than nitration and diazotisation there is no need to separate the anodic and cathodic compartments by a porous diaphragm.

On a small scale the electrolytic cell can be a glass tube sealed at one end, in which are placed cylindrical electrodes. The required temperature is maintained by immersing the cell in a water-bath.

The reaction products in a number of cases of electrochemical chlorination, bromination, and fluorination are insoluble in the solution undergoing electrolysis, and separate as a heavy oil, which simplifies the treatment of the products. A laboratory type of cell suitable for carrying out such reactions has been designed by Izgaryshev and Polikarpov[36].

In order to obtain substitution products on a larger scale, it is advisable to use a cell fitted with a stack of electrodes of alternate polarity. The cell is provided with a jacket, a stirrer, and a reflux condenser in order to maintain the required temperature and avoid concentration effects and loss of the organic compound. An electrolytic cell of this type, intended for electrochemical fluorination, has been described in detail in Simons' monograph[59,80].

Electrochemical fluorination often results in the formation of gaseous products, which escape through the condenser and can be separated by intense cooling of the issuing gases.

The design of apparatus for carrying out the anodic substitution of gaseous substances presents great difficulty. One type of cell, intended for the addition of HOCl to ethylene and used in Stender's experiments[30], is shown in Fig. 1. The ethylene reaches the anode surface through a porous glass plate. This design of cell is extremely wasteful in ethylene, however, and cannot be accepted as satisfactory.

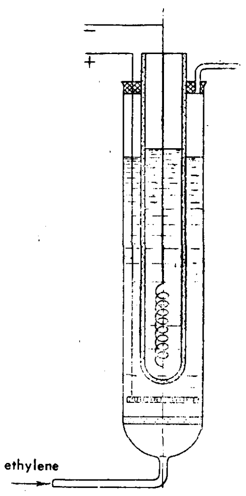


Fig. 1. Laboratory electrolytic cell for preparation of ethylene chlorohydrin.

McElroy's ingenious design of industrial cell for this process[81] is illustrated in Fig. 2. The gas is forced under pressure into the electrolytic cell, where it bubbles continuously through the solution. As reaction proceeds, the pressure drops and more ethylene is admitted.

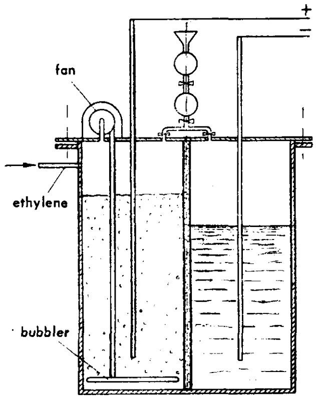


Fig. 2. Electrolytic cell for the industrial production of ethylene chlorohydrin.

Diazotisation and nitration should be carried out in a bath fitted with a diaphragm, since the products formed in these reactions are readily reduced at the cathode. The type of apparatus required for these reactions does not need to be specially described.

5. RANGE OF APPLICATION OF ANODIC SUBSTITUTION REACTIONS

In order to obtain a clear idea of the applicability of "anodic substitution" reactions in organic chemistry, the reactions which can be carried out electrochemically are summarised below.

A. Fluorination

(*a*) Fluorination of hydrocarbons and their chloro-derivatives. The electrochemical fluorination of saturated hydrocarbons is represented by the equation

$$C_nH_{2n+2}+2\,(2n+2)\,F\cdot \longrightarrow C_nF_{2n+2}+(2n+2)\,HF,$$

completely fluorinated compounds being formed. The current efficiency of formation of fluorocarbons is 10–30%.

Completely fluorinated analogues of octane, iso-octane, toluene, dodecane, and tetradecane have been prepared by the electrochemical method [82].

The electrochemical fluorination of hydrocarbons usually results in the complete replacement of all the hydrogen atoms by fluorine. Partly fluorinated compounds are formed in the electrochemical fluorination of halogenated hydrocarbons. The electrochemical fluorination of chloroform or methylene chloride [78,83], for example, yields a complex mixture containing CF_4, CHF_3, CH_2F_2, $CHClF_2$, CCl_2F_2, CH_2ClF, $CHCl_2F$, $CClF_3$, and CCl_3F. The proportions of the various species depend to a considerable extent on the experimental conditions.

Electrolysis of an HF–NaF mixture in the presence of $CHCl:CCl_2$ with vigorous stirring yielded the compound $CHFCl.CFCl_2$.[84] Similar products have been obtained by the electrochemical fluorination of brominated and iodinated hydrocarbons [85].

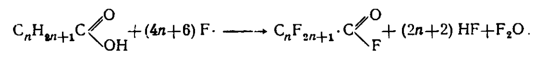
It is possible to add fluorine to the double bond of unsaturated compounds by electrolysis of a solution of potassium hydrogen difluoride in anhydrous acetic acid. In this electrolyte the efficiency of fluorination of vinyl chloride is a few per cent, but addition of fluorine to 1,1-diphenylethylene

$$(C_5H_5)_2C{=}CH_2+2F\cdot \longrightarrow (C_6H_5)_2CF\cdot CH_2F,$$

takes place with a current efficiency of ~ 70%.[3,13]

(*b*) Fluorination of carboxylic acids and their derivatives. Electrolysis of a mixture of acetic acid and hydrogen fluoride [86] or of potassium acetate in HF.KF yields a gaseous mixture containing fluoroform, carbon tetrafluoride, oxygen difluoride, difluoromethane, and methyl fluoride [86,87].

Electrolysis of higher carboxylic acids in hydrogen fluoride solutions leads to the formation of fluorides of completely fluorinated acids containing the same number of carbon atoms as the original acid



$$C_nH_{2n+1}C\langle{}^{O}_{OH}+(4n+6)\,F\cdot \longrightarrow C_nF_{2n+1}\cdot C\langle{}^{O}_{F}+(2n+2)\,HF+F_2O.$$

This reaction has been recommended for the preparation of fluorides of perfluorinated propionic [57,88], β-methoxy- and β-ethoxy-propionic [89,90], sebacic [91,92], benzoic, and phenylacetic acids [57,88].

Fluorides of fluorinated carboxylic acids can also be obtained by the electrochemical fluorination of anhydrides and chlorides of the corresponding carboxylic acids. The fluorination of acid anhydrides yields numerous fluorides of fluorinated carboxylic acids containing 2–13 carbon atoms in the chain [93,94].

The preparation of trifluoroacetyl fluoride by the electrolysis of acetic anhydride in hydrogen fluoride has been described in detail. The maximum yield of trifluoroacetic acid is achieved [95] by electrolysing a mixture of 40.5 g of acetic anhydride + 25.5 g of acetone + 80.0 g of anhydrous HF at 0.028 A cm^{-2}.

Anhydrides of dibasic acids yield fluorides of monobasic as well as dibasic acids. Thus the electrochemical fluorination of succinic anhydride followed by hydrolysis produced a mixture of perfluoropropionic and perfluorosuccinic acids. Electrolysis of an 8% solution of adipic anhydride yielded perfluorovaleric acid with a very small amount of perfluoroadipic acid [58].

Trifluoroacetyl fluoride has been produced on an industrial scale [59].

(*c*) Fluorination of ethers. Perfluorinated analogues of ethers have been obtained by electrolysis of solutions of the latter in hydrogen fluoride, *e.g.*

$$CH_3\cdot O\cdot CH_3+12F \longrightarrow CF_3\cdot O\cdot CF_3+6HF.$$

Completely fluorinated ethers containing 2–12 carbon atoms in the molecule have been prepared in this way [96,97].

Cyclic oxides of general formula $\overline{CH_2.[CH_2]_n.O}$, where $n = 2-4$, and their chloro-derivatives of the type $\overline{CHCl.[CH_2]_2.O}$, behave in a similar manner to ethers[98].

The fluorination of dioxan takes place in a rather unexpected manner, the ring opening at a C–C bond with formation of the diether $CF_3.O.CF_2.CF_2.O.CF_3$.[96]

(*d*) Fluorination of amines. Tertiary aliphatic and aromatic amines can be converted into perfluorinated derivatives electrochemically, *e.g.*

$$(CH_3)_3N+18F\cdot \longrightarrow (CF_3)_3N+9HF.$$

The fluorination of cyclohexylamine and of numerous other amines takes place in an analogous manner[10,99-101]. The benzene nucleus in aromatic amines is fluorinated to a perfluorocyclohexane nucleus during electrolysis.

The fluorination of several more complicated amines does not differ fundamentally[23,102-107].

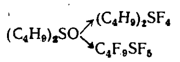
(*e*) Fluorination of nitriles. The electrochemical fluorination of nitriles can be represented by the equation[12]

$$C_nH_{2n+1}CN+2(2n+1)F\cdot \longrightarrow C_nF_{2n+1}CN+(2n+1)HF.$$

However, no concrete data have been published on the electrochemical fluorination of compounds of this type, apart from an indication[10] that electrolysis of a solution of acetonitrile in anhydrous hydrogen fluoride yields a minute amount of the compound $CF_3.CF_2.NF_2$.

(*f*) Fluorination of sulphur-containing compounds. Electrochemical fluorination of compounds containing $\rightarrow C.SH$ or $\rightarrow C.S.C \leftarrow$ groups can give the corresponding perfluorinated compounds, usually with considerable amounts of sulphur hexafluoride and numerous products of destructive fluorination. Table 1 lists the products obtained in the electrochemical fluorination of various representatives of this class.

The electrochemical fluorination of dibutyl sulphoxide can be represented as[110]



$$(C_4H_9)_2SO \begin{array}{l} \nearrow (C_4H_9)_2SF_4 \\ \searrow C_4F_9SF_5 \end{array}$$

Dimethyl sulphate on electrochemical fluorination forms bistrifluoromethyl or methyl monofluoromethyl sulphate depending on the conditions of electrolysis[69,70]. Methanesulphonyl fluoride yields a complex mixture of products[113]. Methanesulphonyl chloride is readily fluorinated electrochemically, with an almost quantitative yield of the perfluorinated derivative[114]:

$$CH_3SO_2Cl+6F\cdot \longrightarrow CF_3SO_2F+HCl+2HF.$$

The fluorination of ethanesulphonyl chloride, where the yield of perfluorinated derivative reaches 87%,[115] and of several other sulpho-derivatives takes place analogously. In particular, a method has been patented for obtaining the following fluorides of perfluorinated sulphonic acids:

$$n\text{-}C_5F_{11}SO_2F;\quad n\text{-}C_{16}F_{33}SO_2F;\quad n\text{-}C_{18}F_{37}SO_2F;\quad \text{cyclo-}C_6F_{11}SO_2F,$$

which are recommended as starting materials for the preparation of surface-active additives for chromium-plating baths[116,117].

Organic selenium compounds do not form fluorine-containing derivatives under the same conditions[108].

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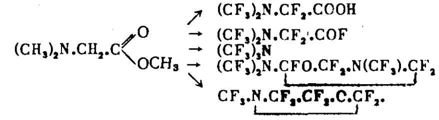
In all the above cases of electrochemical fluorination, a perfluorinated derivative of the original organic substance is formed, in varying yield. However, this is always accompanied by destructive fluorination. In the electrochemical fluorination of hydrocarbons, for example, the formation of fluorocarbons having a smaller number of carbon atoms than the original hydrocarbon is observed[82,118].

Destructive fluorination is still more marked in the case of compounds containing oxygen or nitrogen. Both monobasic and dibasic carboxylic acids are partly decarboxylated[58,87].

The electrochemical fluorination of acetone[86] yields a mixture of almost equal volumes of fluoroform and carbon tetrafluoride; alcohols split off the hydroxyl group, forming a complex mixture of fluorocarbons with larger and smaller numbers of carbon atoms than in the original alcohol: methyl alcohol yields CF_4, C_3F_8, and C_2F_6; phenol forms a mixture of fluorocarbons having five and six carbon atoms[82,119].

In the electrochemical fluorination of a solution of guanidine in anhydrous hydrogen fluoride, the only products formed at the anode are nitrogen, nitrogen trifluoride, and carbon tetrafluoride in the molecular proportions 1 : 6 : 2.22, the nitrogen trifluoride being formed[120] with a current efficiency of 47%.

The methyl ester of *NN*-dimethylglycine gives the following mixture of products[102]



$$(CH_3)_2N.CH_2.C\begin{array}{l}\nearrow O\\ \searrow OCH_3\end{array} \begin{array}{l} \nearrow (CF_3)_2N.CF_2.COOH \\ \rightarrow (CF_3)_2N.CF_2.COF \\ \rightarrow (CF_3)_3N \\ \rightarrow (CF_3)_2N.CFO.CF_2.N(CF_3).CF_2 \\ \searrow CF_3.N.CF_2.CF_2.C.CF_2. \end{array}$$

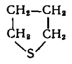
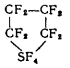
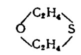
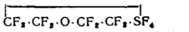
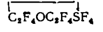
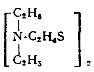
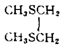
In the electrolysis of a solution of mercurous cyanide in hydrogen fluoride, destructive fluorination of the cyano-group results in the formation of nitrogen trifluoride and carbon tetrafluoride[10]. Fluorination of acetonitrile yields[10], in addition to its fluorinated analogue, considerable quantities of CF_4 and C_2H_5F. Pyridine on electrochemical fluorination forms nitrogen trifluoride and perfluoropentane as well as decafluoropyridine[105], while the main products of the fluorination of quinoline[10] are nitrogen trifluoride and the fluorocarbon C_9F_{18}. Destructive breakdown in the fluorination of sulphur-containing compounds has already been mentioned (see Table 1).

Owing to destructive fluorination, the formation of fluorine-containing compounds having the same carbon skeleton as the original substance does not usually exceed 20–30%.

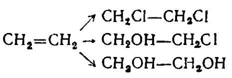
B. Chlorination

(*a*) Chlorination of hydrocarbons. There are no data on the electrochemical chlorination of individual saturated aliphatic hydrocarbons.

TABLE 1.

Starting material		Fluorination products obtained	Ref.
name	formula		
Carbon disulphide	CS_2	SF_6;CF_3SF_5; $CF_2(SF_3)_2$; $CF_2(SF_5)_2$	108
Dimethyl sulphide	$(CH_3)_2S$	SF_6; CF_4; CF_3SF_5; $(CF_3)_2SF_4$.	108
Dimethyl disulphide	$(CH_3S)_2$	SF_6; CF_3SF_5; $CF_3{\cdot}SF_4{\cdot}CH_2F$	109
Diethyl sulphide	$(C_2H_5)_2S$	C_2F_6; $C_2F{\cdot}SF_5$; $(C_2F_5)_2SF_4$	110
Dipropyl sulphide	$(n\text{-}C_3H_7)_2S$	SF_6; $C_3F_7SF_5$; $(C_3F_7)_2SF_4$	110
Dibutyl sulphide	$(n\text{-}C_4H_9)_2S$	SF_6; $C_4F_9SF_5$; $(C_4F_9)_2SF_4$	110
Dibutyl disulphide	$(n\text{-}C_4H_9S)_2$	SF_6; $C_4F_9SF_5$; $(C_4F_9)_2SF_4$	110
Di-t-butyl disulphide	$(t\text{-}C_4H_9S)_2$	products could not be separated	110
Tetrahydrothiophen		 SF_6; $(C_2F_5)_2SF_4$; $C_3F_7{\cdot}SF_4{\cdot}CF_3$; $C_4F_9SF_5$	110
Oxathiane		 SF_6; $(C_2F_5)_2O$; $C_2F_5OC_2F_4SF_5$; $C_2F_5SF_5$; 	110 109
Bis-(2-diethylaminoethyl) disulphide	 $\left[\begin{matrix}C_2H_5 \\ \mid \\ N{\cdot}C_2H_4S \\ \mid \\ C_2H_5\end{matrix}\right]_2$	SF_6; $(C_2F_5)_2NCF_2CF_2SF_5$	110
1,3,5-Trithiane	$(CH_2S)_3$	SF_6; CF_3; SF_6; $SF_5{\cdot}SF_2{\cdot}SF_5$; $(CF_2SF_4)_3$	109
1,2-Bismethylthioethane	 $\begin{matrix}CH_3SCH_2 \\ \mid \\ CH_3SCH_2\end{matrix}$	CF_3SF_5; $C_2F_5{\cdot}SF_4{\cdot}CF_3$; $(C_2F_4\ SF_4)_2$; $(C_2F_5)_2\ SF_4$; $CF_3{\cdot}SF_4{\cdot}CF_2{\cdot}CF_2{\cdot}SF_5$; SF_6	109
Methylthioacetyl chloride	CH_3SCH_2COCl	SF_6;$SF_3{\cdot}SF_5$; $(CF_3)_2SF_4$; SF_5CF_2COF; $SF_4{\cdot}CF_2{\cdot}CF_3$; $CF_3SF_4CF_2COF$ $CF_3SF_4CF_2CF_3$	111
Mercaptoacetic (thioglycollic) acid	$HSCH_2COOH$	SF_6; CHF_3; CO_2F_2; COF_2; C_2F_6; CF_3SF_5; CF_3COF; CF_4; $SF_3{\cdot}CF_2COOH$; CF_3CO_2F; $SF_5{\cdot}CF_2CO_2H$; SF_5CF_2COF	112

The only case of the electrochemical chlorination of an unsaturated compound which has yet been investigated is the chlorination of ethylene[30]. In aqueous solution, partial or complete hydroxylation is also possible, leading ultimately to the formation of three products:



$$CH_2{=}CH_2 \rightarrow \begin{cases} CH_2Cl{-}CH_2Cl \\ CH_2OH{-}CH_2Cl \\ CH_2OH{-}CH_2OH \end{cases}$$

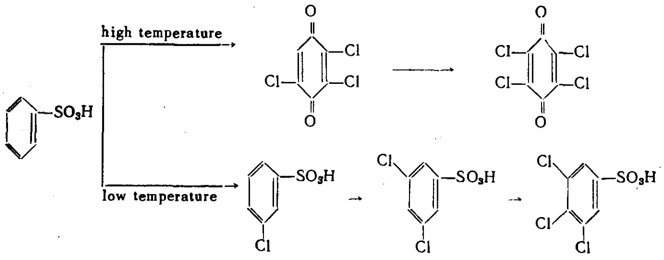
The aim of nearly all the research on this reaction has been to find optimum conditions for obtaining ethylene chlorohydrin[30,62,81,121-125] which is widely used as a solvent and in various organic syntheses. With a current density of 1400 A m^{-2} at a platinum anode at 25°, the yield of ethylene chlorohydrin[30] reaches 89.0% at a current efficiency of 85.5%.

A solid mixture of products containing up to 50% of chlorine has been obtained[126] by the electrochemical chlorination, with a platinum anode, of an emulsion of molten paraffins in concentrated hydrochloric acid at 90°.

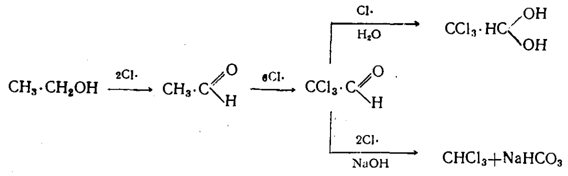
The electrochemical chlorination of aromatic hydrocarbons has been studied in considerably greater detail. Benzene is readily acted on by chlorine evolved at the anode, with the formation of a number of chlorinated products[5-9,27,32,127]. A certain amount of hydroxylation of the benzene nucleus occurs with the chlorination.

The chlorination of toluene is analogous to that of benzene, the nucleus being chlorinated first[7,31,34,35]. 1-Chloronaphthalene has been obtained electrochemically from naphthalene[9]. The possibility of chlorinating phenanthrene, anthracene, and biphenyl has also been reported[128].

Benzenesulphonic acid forms tri- and tetra-chloro-*p*-benzoquinone, together with the mono-, di-, and tri-chlorinated sulphonic acids[63]



(*b*) Chlorination of alcohols. When an attempt is made to chlorinate methyl alcohol electrochemically, formaldehyde is formed. The process of electrochemical chlorination has been studied in greatest detail with ethyl alcohol. The general course of the process can be represented by the scheme



In acid medium the main reaction product is chloral, but in alkaline medium it is chloroform. Since the latter is widely used as a solvent, a great amount of work has been done on the development of an industrial method for producing chloroform[18,19,128,129]. Under the optimum conditions of electrolysis, both the yield and the current efficiency[20,41,60] can reach 90%.

The maximum yield of chloral achieved[61-67,130] is 51.3%. Electrolytic chlorination of isopropyl alcohol produces a small amount of chlorine-containing compounds, the composition of which has not been investigated[20].

(*c*) Chlorination of aldehydes. As already indicated at (*b*), acetaldehyde is an intermediate product in the production of chloral and chloroform from ethyl alcohol. No special investigation has been made of the electrochemical chlorination of aldehydes.

(*d*) Chlorination of ketones. The electrochemical chlorination of acetone in acid medium yields monochloroacetone[21,23] with a current efficiency of up to 80%.

$$CH_3{-}CO{-}CH_3 \xrightarrow{Cl\cdot} CH_3{-}CO{-}CH_2Cl + HCl.$$

The chlorination of cyclohexanone and of several aromatic ketones — acetophenone, propiophenone, and benzophenone — also results in the formation of monochloro-derivatives[61]. The current efficiency of formation of chlorination products is 70–90%.

The chlorination of acetone in alkaline solutions takes place according to the following equation

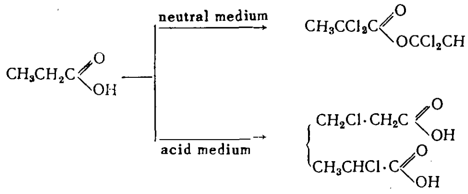
$$CH_3{-}CO{-}CH_3+4NaOH+6Cl\cdot \longrightarrow CHCl_3+CH_3COONa+3NaCl+3H_2O,$$

with the formation of chloroform and an acetate.

This reaction has been much studied[20,43,131–133] since the formation of chloroform from acetone requires a smaller expenditure of electrical energy than its preparation from ethyl alcohol. Under optimum conditions the yield of chloroform can reach 79%, and the current efficiency 60%.

Chloroform and acetic acid have been obtained by the electrochemical chlorination of ethyl methyl ketone in alkaline medium[20].

(*e*) Chlorination of carboxylic acids. Acetic acid is difficult to chlorinate electrochemically[134], and it is therefore a suitable solvent for electrochemical chlorinations in non-aqueous solutions[6,7]. The higher acids form chlorinated compounds. The electrochemical chlorination of propionic acid yields dichloroethyl αα-dichloropropionate, β-chloropropionic acid, and traces of α-chloropropionic acid[25].

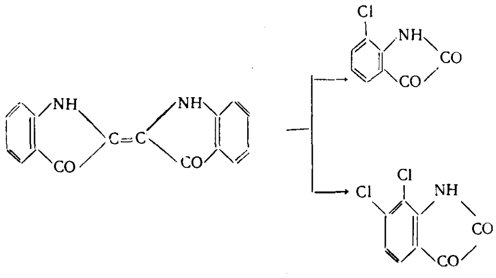


Butyric acid forms a mixture of β-chlorobutyric and ββ-dichlorobutyric acids, isopropyl β-chlorobutyrate, isopropyl dichlorobutyrate, and a little chloroform[25].

Pentyl chloride, 1,2-dichloropentane, and chloroform have been obtained from hexanoic acid[135].

(*f*) Chlorination of amines. Data are lacking on the electrochemical chlorination of aliphatic amines. Aniline on electrolysis in hydrochloric-acid solution is oxidised to a considerable extent, with the formation of Aniline Black and small amounts of chloroquinone, chloroaniline and tetrachloroquinone[29,72]. This last compound is formed in considerable amounts when solutions in concentrated hydrochloric acid are used[73].

(*g*) Chlorination of other compounds. The chlorination of indigo at a platinum anode in hydrochloric-acid solution yields mono- and di-chloroisatin[27]:



A product of formula $C_{21}H_{27}O_7N_2Cl_7$ has been prepared from brucine[136], but its nature could not be established.

Electrochemical chlorination of hydrogen cyanide in dilute hydrochloric acid yields cyanogen chloride; when concentrated hydrochloric acid is used, a crystalline compound having the composition $[HCNCl_2]_3.3HCl$ is formed[137].

Interesting work has been done on the electrochemical chlorination of sulphite liquor[138], a waste product from the manufacture of viscose rayon. Electrolysis of a mixture of sulphite waste liquor, caustic potash, and potassium chloride has yielded, for example, $CH_2Cl.CHO$, $CHCl_2.CHO$, and several other compounds which can serve as raw material for the manufacture of a number of organic compounds.

Electrochemical chlorination has been suggested as a method for delignifying straw and wood[139,140].

C. Bromination

(*a*) Bromination of hydrocarbons. Monobromobenzene is obtained with a current efficiency of up to 23% by the bromination of benzene[141]

$$C_6H_6+2Br\cdot \longrightarrow C_6H_5Br+HBr.$$

The electrolysis of the complex $AlBr_3.3C_6H_6$ between platinum electrodes has also been investigated[142].

When toluene is brominated electrochemically in the dark, bromination of the nucleus takes place, whereas under illumination benzyl bromide is the only product[47].

(*b*) Bromination of alcohols. Attempts to obtain bromoform by electrolysing a solution of an alkali-metal bromide together with alcohol did not give positive results[41,143]. Carbon dioxide and a minute amount of bromoform were isolated as products of the electrolysis. The maintenance of a strictly neutral medium is apparently of immense importance in this process, since there are indications that bromoform can be obtained when calcium bromide is employed as electrolyte[77].

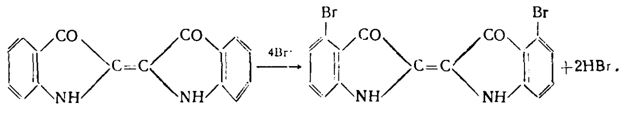
(*c*) Bromination of ketones. The only example of the electrochemical bromination of ketones described in the literature is that of acetone.

In acid medium, monobromoacetone is obtained in good yield[22]:

$$CH_3COCH_3+2Br\cdot \longrightarrow CH_3COCH_2Br+HBr.$$

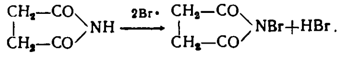
In alkaline medium, bromoform is produced in almost quantitative yield. This reaction is analogous to the preparation of chloroform from acetone[35,60,129,144].

(*d*) Bromination of other compounds. The principal reaction product in the electrochemical bromination of indigo is 5,5′-dibromoindigo[38,74,75], apart from small amounts of 2,4,6-tribromoaniline, 5-bromoisatin, and probably tribromophenol and formic acid



Attempts to introduce electrochemically four bromine atoms with the aim of obtaining the valuable dye 5,5′,7,7′-

-tetrabromoindigo proved unsuccessful. Bromination of succinimide gave a 54% yield of *N*-bromosuccinimide[40]



It has been reported that eosin can be obtained by the electrochemical bromination of fluorescein[145].

Pentabromoacetone is obtained by the electrolysis of a sulphuric-acid solution of citric acid and potassium bromide[146]. Since the bromination is quantitative, this reaction has been suggested for the estimation of traces of citric acid.

D. Iodination

Iodine radicals formed at the anode react with organic compounds only rarely: examples of electrochemical iodination are therefore very limited.

(*a*) Iodination of hydrocarbons. Benzene[141] does not interact with iodine radicals formed at the anode.

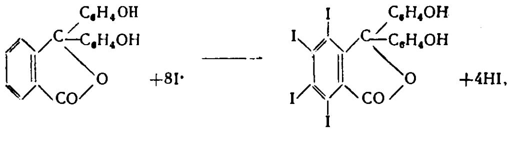
(*b*) Iodination of alcohols. The only case of the iodination of alcohols which has been investigated is the preparation of iodoform from ethyl alcohol, where iodination takes place[41,129,147-149] with a yield of 90–98%.

The electrochemical method of preparing iodoform from alcohol has been successfully employed[150,151] to synthesise iodoform containing the heavy isotope iodine-131.

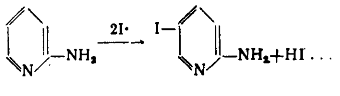
(*c*) Iodination of ketones. The preparation of iodoform from acetone has been investigated in detail, a 95% yield being achieved[42,43,152]. The reaction is completely analogous to the preparation of chloroform from acetone.

(*d*) Iodination of carboxylic acids. It has been reported[153] that propyl iodide is formed by the electrolysis of a mixture of potassium propionate and potassium iodide, and that potassium succinate and potassium iodide give β-iodopropionic acid. However, these results require verification.

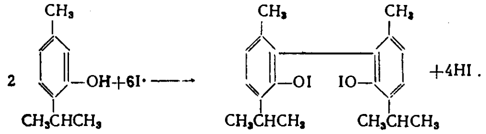
(*e*) Iodination of other compounds. The iodination of phenolphthalein yields tetraiodophenolphthalein[29]:



and 2-aminopyridine gives 2-amino-5-iodopyridine[154]

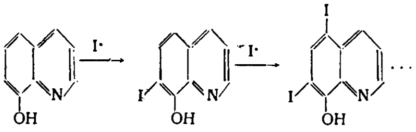


More complicated processes take place in the iodination of phenol and naphthol derivatives in alkaline solutions. Thymol, for example, forms bisthymol diiodide[155-157]:



The following compounds are similarly iodinated with the formation of dimeric products — 2-naphthol, resorcinol, salicylic acid, *p*-isobutylphenol, *p*-isobutyl-*m*-cresol, *p*-isobutyl-*o*-cresol, methyl-*o*-cresol, ethyl-*o*-cresol, propyl-*o*-cresol, isopentyl-*o*-cresol, propyl-*m*-cresol, and isopentyl-*m*-cresol[154].

8-Hydroxyquinoline forms mono- and di-iodo derivatives[44]

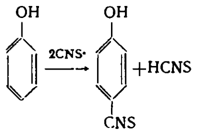


For the monoiodo derivative, the yield and the current efficiency are 68% and 34% respectively, whereas for 8-hydroxy-5,7-diiodoquinoline they are 82.4% and 32.4%.

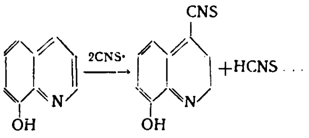
E. Thiocyanation and Selenocyanation

Until recently, thiocyanogen derivatives of aromatic compounds only had been obtained by the electrochemical method.

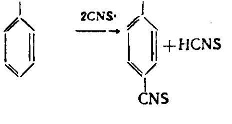
Thiocyanation of phenol gives a 67% yield of *p*-thiocyanatophenol[51]:



Thiocyanation of various phenol derivatives takes place similarly. Among these compounds are resorcinol (yield of thiocyanogen compound not indicated)[49], *o*-cresol[51] (72%), guaiacol[50] (20%), thymol[51] (76%), carvacrol[51] (50%), and diethylphenol[51] (82%). With all these compounds the thiocyanato-group enters the *para* position with respect to the hydroxyl group. An exception is provided by *m*-cresol, thiocyanation of which yields 2-hydroxy-5-thiocyanatotoluene. Thiocyanation of 8-hydroxyquinoline gives 8-hydroxy-4-thiocyanatoquinoline[51]:

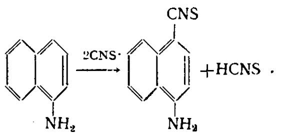


The thiocyanation of aromatic amines is completely analogous to that of phenols. With methylaniline, for example, a 41% yield of *p*-thiocyanato-*N*-methylaniline is obtained[52]



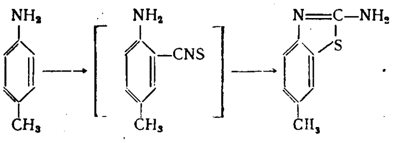
Thiocyanation of the following substances takes place in a similar manner — *o*-toluidine[49,51] (yield 44%), *N*-ethyl-*m*-toluidine[52] (60%), ethylaniline[51] (60%), propylaniline[52] (44%), butylaniline[52] (47%) dimethylaniline[50] (85%), diethylaniline[50] (68%), ethylbenzylaniline[52] (84%), anthranilic acid[52] (54%), and methylanthranilic acid[52] (63%). In all these examples the thiocyanato-group enters the *para*-position to the amino-group. Exceptions are *m*-toluidine, thiocyanation of which gives a 62% yield of 3-amino-5-thiocyanatotoluene[51], and *NN*-dimethyl-*p*-toluidine, from which a 21% yield of *NN*-dimethylamino-4-methyl-2-thiocyanatobenzene was obtained[50].

1-Naphthylamine gives 1-amino-4-thiocyanatonaphthalene[49]:



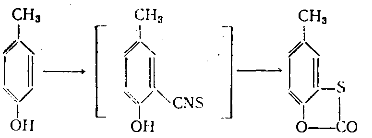
When the thiocyanato-group enters the *ortho* position to the active functional group in the molecule, a thiazole rearrangement takes place with amines, and a thiocarbonate rearrangement with hydroxy compounds.

For example, 2-amino-6-methylbenzothiazole is prepared from *p*-toluidine[53]:



Thiocyanation of the following amines takes place according to this scheme — phenetidine (yield 60%), anisidine (57%), *p*-ethylaniline (90%), and methyl *p*-aminobenzoate[53].

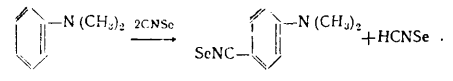
In the thiocyanation of *p*-cresol, the product rearranges to a methylphenylene thiocarbonate[51]



Since the rearrangement does not usually go to completion during electrolysis, it is advisable to boil the resulting solution under reflux for 1½–2 h.

An interesting application of electrochemical thiocyanation proposed in a German patent[158,159] is the electrolysis of an aqueous solution of lignosulphonic acid and a thiocyanate, sodium chloride being added to the solution to diminish the formation of polythiocyanogen. The water-insoluble thiocyanato derivative of the acid is precipitated during the electrolysis, and can be used as a starting material for the manufacture of plastics and as an insecticide.

Electrochemical selenocyanation can be carried out by analogy with thiocyanation. *NN*-Dimethyl-*p*-selenocyanatoaniline has been prepared from dimethylaniline with a current efficiency of 15–20%[160]:

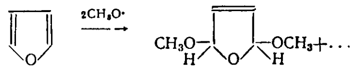


Selenocyanation of diethylaniline, methylaniline, and ethylaniline can be carried out similarly[160] with current efficiencies of 10–25%.

F. Alkoxylation

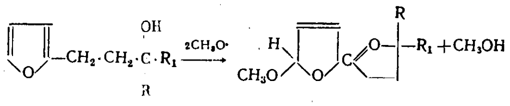
Alkoxylation is effected by electrolysing a solution of the organic substance in absolute alcohol containing an inorganic salt (*e.g.* ammonium bromide).

Methoxylation of furan[15] gave dihydrodimethoxyfuran with a current efficiency of 86%:



It has been possible in the same way to methoxylate furfuryl alcohol, furfuryl acetate, furfuraldehyde dimethylacetal[14], and other furan derivatives[161–163] to the corresponding dimethoxy derivatives.

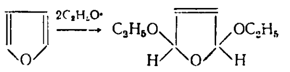
Electrochemical methoxylation has been applied to the synthesis of spiro compounds of the 1,6-dioxaspiro[4,4]-nonane group by the alkoxylation of furylalkanols, the reaction being represented by the general equation:



In this process, alkoxylation is accompanied by cyclisation, probably also initiated by the action of methoxy radicals[17].

The applicability of this reaction has been demonstrated with derivatives in which R = H, CH_3, $(CH_3)_2CH.CH_2$, C_2H_5, and R_1 = H, H, H, and CH_3 respectively. The yield of spiro compounds is 53–76%.

Ethoxylation of furan[16] can be carried out in a similar manner to methoxylation, the electrolyte being ammonium bromide in ethyl alcohol. Diethoxydihydrofuran is obtained with a current efficiency of ~ 74%:



G. Preparation of Nitric Esters

Electrolysis of nitrates in the presence of ethylene[45,46,164] gives a mixture of nitric esters according to the equation:

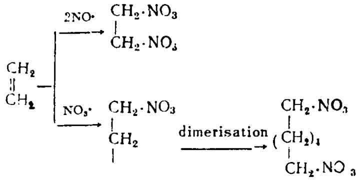


Table 2 lists the compounds which are formed by the electrolysis of solutions of organic acids in the presence of nitrates[153,165–173]. In most cases the olefines produced when aqueous solutions of the acids are electrolysed undergo reactions apparently similar to the formation of nitric esters from ethylene.

A process has been patented for the electrochemical preparation of cellulose nitrate[174–176] and is claimed to be completely safe.

TABLE 2. Products obtained in the electrolysis of solutions of carboxylic acids in the presence of nitrates.

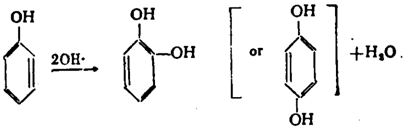
Initial acid		Products	Ref.
name	formula		
Propionic	CH_3CH_2COOH	$C_2H_5NO_2$ $C_2H_5ONO_2$; $O_2NO(CH_2)_2ONO_2$; $CH_3(CH_2)_3ONO_2$; $O_2NO(CH_2)_4ONO_2$	153 165
Butyric	$CH_3(CH_2)_2COOH$	$CH_3(CH)_2NO_2$; $(CH_3)_2CHONO_2$ $(CH_3)_3{\cdot}CCH_2CH_2CH_2ONO_2$; $CH_3(CH_2)_3\underset{ONO_2}{CH}\,CH_3$ $(CH_3)_2CH\underset{CH_3}{C}HCH_2ONO_2$; $CH_3-\underset{ONO_2}{CH}-\underset{ONO_2}{CH_2}$	166
Valeric	$CH_3(CH_2)_3COOH$	$CH_3(CH_2)_3ONO_2$; $CH_3-\underset{ONO_2}{CH}-\underset{ONO_2}{CH}-CH_3$	167
Isovaleric	$\underset{CH_3}{\overset{CH_3}{CH}}CH_2COOH$	$(CH_3)_2CHCH_2ONO_2$; $CH_3-\underset{ONO_2}{CH}-\underset{ONO_2}{CH}-CH_3$ $CH_3-\underset{ONO_2}{CH}-CH_2-\underset{ONO_2}{CH_2}$	168
Hexanoic	$CH_3(CH_2)_4COOH$	$CH_3(CH_2)_4ONO_2$; $CH_3(CH_2)_3\underset{O_2NO}{CH}-\underset{ONO_2}{CH_2}$	169
α-Methylbutyric	$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>CHCOOH$	$CH_3-\underset{O_2NO}{CH}-\underset{ONO_2}{CH}-CH_3$	170
β-Methylvaleric	$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>CHCH_2COOH$	$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>CH-CH_2ONO_2$	171
Heptanoic	$CH_3(CH_2)_5COOH$	$CH_3(CH_2)_5ONO_2$; $C_{12}H_{25}ONO_2$	171
Laevulinic	$CH_3CO(CH_2)_2COOH$	$\underset{ONO_2}{H_2C}-(CH_2)_2-\underset{ONO_2}{CH_2}$ $\underset{ONO_2}{H_2C}-CH_2-\underset{ONO_2}{CH}-\underset{ONO_2}{CH_2}$ $\underset{O_2NO}{CH_2}-\underset{ONO_2}{CH}-\underset{ONO_2}{CH}-CH_3$ $\underset{ONO_2}{H_2C}-\underset{ONO_2}{CH_2}$	172
β-Isopentyl-oxypropionic	iso-$C_5H_{11}O(CH_2)_2COOH$	iso-$C_5H_{11}O-CH_2-\underset{ONO_2}{CH}-O(CH_2)_2-CH(CH_3)_2$	172
Malonic	$HOOCCH_2COOH$	$(CH_2ONO_2)_2$; $(CH_2{\cdot}CH_2ONO_2)_2$	173
Adipic	$HOOC(CH_2)_4COOH$	$H_3C-CH_2-\underset{ONO_2}{CH}-\underset{ONO_2}{CH_2}$ $\underset{ONO_2}{H_2C}-\underset{ONO_2}{CH}-\underset{ONO_2}{CH}-\underset{ONO_2}{CH_2}$ $\underset{ONO_2}{H_3C}-CH_2-\underset{ONO_2}{CH}-\underset{ONO_2}{CH_2}$ $\underset{ONO_2}{H_2C}-\underset{ONO_2}{CH}-\underset{ONO_2}{CH}-\underset{ONO_2}{CH_2}$	171

H. Hydroxylation

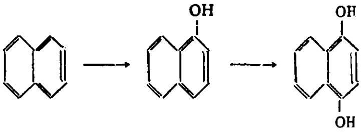
When ethylene is passed under pressure through an apparatus in which 25% caustic soda is being electrolysed, ethylene glycol is obtained[76]

$$CH_2{=}CH_2 + 2OH{\cdot} \longrightarrow HO{-}CH_2{-}CH_2{-}OH.$$

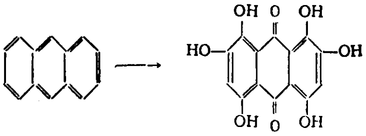
Anodic oxidation of phenol yields quinol and catechol[177,178]



Electrochemical oxidation of naphthalene leads to the formation of 1-naphthol and naphthalene-1,4-diol[179]:



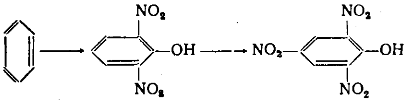
Oxidation of anthracene at the anode gave hexahydroxy-anthraquinone[180]



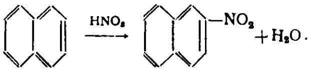
I. Nitration

Electrochemical nitration has been investigated only in the case of aromatic compounds.

Electrolysis of an emulsion of benzene in aqueous nitric acid at 70° has given dinitrophenol and picric acid[181]:



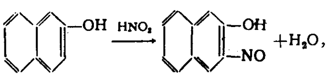
Under analogous conditions toluene and xylene give the same products as those obtained by chemical nitration[182,183], nitrobenzene yields *m*-dinitrobenzene[184], and nitration of naphthalene results in a 90% yield of mononitronaphthalene[185-187]:



J. Nitrosation

By analogy with nitration, several naphthalene derivatives have been nitrosated by electrolysis in an aqueous solution of sodium nitrite.

2-Naphthol gives a 53.8% yield of nitroso-2-naphthol[188]



and 1-naphthol and 1-hydroxynaphthalene-4-sulphonic acid are also nitrosated[189]. An attempted electrochemical nitrosation of ethers of phenol did not give positive results[190].

K. Sulphonation

Information on electrochemical sulphonation is extremely limited. Puls' reported electrochemical sulphonation of toluene[191] has been refuted by Fichter[192].

The only electrochemical sulphonation reactions which have been reliably demonstrated so far are the formation of methylsulphuric [193] and ethylsulphuric [143] acids:

$$ROH + H_2SO_4 \longrightarrow ROSO_3H + H_2O,$$
$$\text{where } R = CH_3;\quad C_2H_5.$$

induced by the high concentration of sulphuric acid around the anode. The main requirements of these reactions are a high anodic current density and the absence of stirring.

L. Diazotisation and Coupling

In order to effect diazotisation and coupling electrochemically, an equimolecular mixture of the amine, the coupling component (preferably in the form of a soluble salt), and sodium nitrite is subjected to electrolysis.

A large number of different types of dyes have been prepared in this way, *e.g.* Orange II, [194-196] Congo Red [194,196,197], Chrysamine G, [194,196] Bismarck Brown [196], and several others which are produced in bulk.

Azo dyes obtained electrochemically differ slightly in colour from samples prepared by chemical means.

An attempt has been made to apply electrochemical diazotisation to aliphatic compounds. The chief product of the diazotisation of glutamic acid is said to be an isodiazoate [198].

An interesting application of electrochemical diazotisation and coupling has been described in a series of American patents [199-201]. A method is disclosed of forming a dye directly in the pores of the fibrous material to be coloured. The material is impregnated with a solution containing the amine to be diazotised, sodium nitrite, and the coupling component. Metal printing moulds are pressed against the impregnated material, and an electric current is passed. Dye is formed at the points of contact with the anode, accurately reproducing the design of the mould. Later patents [202,203] propose certain modifications to this process: the porous material to be coloured is impregnated with a solution containing an already diazotised compound in the form of a diazonium salt, a coupling component, an inorganic salt to make the solution electrically conducting, and a compound which retards azo coupling, *e.g.* tartaric acid. When a current is passed, dye formation takes place at points of contact with the cathode, since the pH increases at these sites. The proposed method of dyeing, which is applicable to textiles, paper, and other fibrous materials based on cellulose, is of considerable interest.

Since dye is formed directly in the pores of the material to be coloured, this method of coloration approaches vat dyeing in fastness.

6. COMPARISON OF CHEMICAL AND ELECTROCHEMICAL SUBSTITUTION PROCESSES

It can be concluded, from the products obtained, that there is no fundamental difference between chemical and electrochemical substitution processes: the two methods generally lead to the same products. However, the electrochemical method possesses certain special features, which sometimes make it preferable for substitution reactions. In cases of halogenation, for example, the electrochemical method avoids the need to use the free halogen, and allows the halogen to be used up quantitatively, whereas in chemical halogenation one-half of the halogen is wasted in forming a hydrogen halide.

Elimination of the use of free halogen is especially desirable in fluorination processes, owing to the corrosive nature of elementary fluorine. Furthermore, the high cost of compounds of fluorine, bromine, and iodine, makes the more complete utilisation of the halogens particularly attractive.

Electrochemical thiocyanation, methoxylation, nitration, and hydroxylation are evidently of considerable practical interest; the first two processes have been said [15,50,51] to give more satisfactory results than do chemical methods.

Finally, the electrochemical deposition of azo dyes directly in the pores of the substrate also merits careful study. The method of anodic substitution may prove useful in the synthesis of derivatives of labile compounds, which undergo changes at elevated temperatures or under the influence of very active reagents.

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THE CHEMISTRY OF URANIUM FLUORIDES

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CONTENTS

1. INTRODUCTION

Uranium fluorides were prepared in the 19th and at the beginning of the 20th centuries[1,2], but little attention was paid to their properties, since they had no practical applications. The use of uranium for atomic fuel led to the problem of separating its isotopes. This was achieved in various ways, including a diffusion method based on the use of uranium hexafluoride[3]. The technology of the production of uranium hexafluoride and of metallic uranium enriched in the light isotope (^{235}U) is associated with the preparation of the lower fluorides, particularly the tetrafluoride. Atomic reactors do not achieve complete combustion of the fuel in the sense that the fissile material is not completely utilised; to achieve complete utilisation it is necessary to carry out several combustion cycles with intermediate regeneration cycles. Uranium hexafluoride is used in this field[4]. Methods for the extraction of uranium as UF_6 by dissolving the spent fuel in fused salts with subsequent fluorination by gaseous fluorine[5,6] are also being studied. This does not exhaust the applications of the fluorides, as their direct use as atomic fuel is at present being examined; for this they can be used either in molten[7] or in gaseous[8,9] form. These applications show the part which uranium fluorides play in the atomic energy industry. It is for this reason that the last twenty years have seen a marked increase in the study of their chemistry and technology.

2. URANIUM TRIFLUORIDE

Uranium trifluoride can be obtained by reducing anhydrous uranium tetrafluoride with hydrogen[10]. Traces of moisture and oxygen, which lead to contamination of the product with uranium oxides, must be completely absent.

A new method has recently been proposed[11] for preparing uranium trifluoride by reducing UF_4 with aluminium at high temperatures *in vacuo*. Uranium tetrafluoride, prepared by hydrofluorination of UO_2 at 650°, was mixed with aluminium filings and heated in a graphite crucible. The reaction

$$UF_4 + Al = UF_3 + AlF$$

begins at 800°, proceeds rapidly at 900°, and is complete in one and a half hours. Chemical analysis and X-ray diffraction showed that the reaction product is UF_3, containing less than 2% uranium dioxide. The AlF sublimed onto the walls of the apparatus. The residues contained ~90% UF_3.

A. Physical Properties

Uranium trifluoride is a violet-red crystalline substance with melting point 1495°.[12] At high temperatures disproportionation takes place:

$$4UF_3 = 3UF_4 + U.$$

D'Eye and Martin found the disproportionation slow at 1500° (~ 20% in 1 h).

From X-ray powder patterns, Zachariasen[13] found the uranium atoms in this compound to be hexagonal close-packed, with $a_0 = 4.146 \pm 0.003$ Å, $c_0 = 7.348 \pm 0.004$ Å, space group $P6_3/mmc$, with two UF_3 molecules in the unit cell. Uranium trifluoride is isomorphous with the fluorides of lanthanum, praseodymium, cerium, and neodymium[14]. Later, Staritzky and Douglas[15] determined the lattice parameters of UF_3 from X-ray oscillation photographs: $a = 7.179$ Å, $c = 7.345$ Å (± 0.001 Å); $c/a = 1.023$, ρ (calc.) = $= 8.965$, $Z = 6$, space group $P6_3/mcm$. Isomorphism of uranium trifluoride with the fluorides of the rare-earth elements has been confirmed[14] and the data of Zachariasen[13], who proposed a different structure for UF_3, have been refuted.

B. Chemical Properties

Uranium trifluoride is not hygroscopic, but is affected by moist air. When heated in air it is oxidised to oxide fluoride and at 900° is converted to U_3O_8. Disproportionation takes place on heating in an inert atmosphere.

It is insoluble in water but is oxidised appreciably to U^V, the rate of this reaction increasing considerably with increasing temperature. UF_3 is sparingly soluble in acids, but in the presence of oxidising agents it goes into solution as UO_2F_2. The ability of acids to dissolve UF_3 increases in the order $HCl < H_2SO_4 < HNO_3$. The presence of boric acid facilitates dissolution. The reaction of uranium trifluoride with chlorine at 350° yields $UClF_3$.[16,17]. Fluorine and other fluorinating agents (ClF_3, BrF_3, etc.) react readily with UF_3 to form uranium hexafluoride.

The reaction of UF_3 with metal fluorides has been studied. Thus the UF_3–BaF_2 system has been studied by X-ray diffraction, thermal analysis, and density measurement[12]. The solid solution of UF_3 in BaF_2 contains up to ~ 50 mole % UF_3, the lattice parameter a for BaF_2 decreasing from 6.189 kX to 6.034 kX†. The conjugate solid solution of BaF_2 in UF_3 contains ~ 20 mole % BaF_2. The densities found for the solid solutions indicate random distribution of the U^{3+} and Ba^{2+} cations in the cationic positions of the UF_3 lattice, the anionic lattice being incomplete. Pure UF_3 is hexagonal, $a = 4.131$ kX, $c = 7.335$ kX. The melting point of BaF_2 increases on formation of the solid solutions. A peritectic appears to exist at 1400°. UF_3 can also form solid solutions with SrF_2; for the specimen with 33 mole % UF_3 in SrF_2, $a = 5.821 \pm 0.005$ kX

3. URANIUM TETRAFLUORIDE

A. Preparation

The existing methods can be reduced to three main types. The first is based on preparation of uranium tetrafluoride from aqueous solutions of tetravalent uranium by the addition of fluoride ions to the solution. The second is based on direct fluorination of various tetravalent uranium compounds with hydrogen fluoride, and the third on preparation of uranium tetrafluoride from the hexafluoride.

The first papers elucidating the conditions for the preparation of uranium tetrafluoride were those of Bolton[1], who established that addition of hydrofluoric acid to uranium tetrachloride solution precipitates the tetrafluoride, and that the action of hydrofluoric acid on U_3O_8 yields a mixture of tetrafluoride and uranyl fluoride

$$U_3O_8 + 8HF = UF_4 + 2UO_2F_2 + 4H_2O.$$

Bolton later showed that a precipitate of the tetrafluoride can be obtained by reducing a boiling solution of uranyl fluoride with stannous chloride or by reducing ammonium uranate with ammonium carbonate in the presence of hydrofluoric acid.

Allen *et al.*[18,19] studied a number of reducing agents: $SnCl_2$, CuCl, $CrCl_3$, $TiCl_3$, and SO_2, for the preparation of U^{IV}. They found that all these compounds are effective, except sulphur dioxide, which does not reduce uranium, even when excess fluoride is present. It was found, however, that in the presence of Cu^{2+} ions at high temperatures, SO_2 reduces U^{VI} to U^{IV} as a result of the preliminary reduction of Cu^{2+} to Cu^{+}, which then reduces the uranium.

Methods based on the direct reduction of various uranium salts in the presence of fluoride ions are of particular interest. Thus the passage of SO_2 through a solution of uranyl nitrate in the presence of HCOOH and NH_4F (or NaF) leads to reduction of the uranyl nitrate[20] according to the equation:

$$UO_2(NO_3)_2 + 2SO_2 + HCOOH + 5NH_4F = NH_4UF_5 + 2NH_4NO_3 + 2NH_4HSO_3 + CO_2.$$

The rate of reaction increases with increase in temperature. The resulting NH_4UF_5 precipitate, when heated to 450°, decomposes to UF_4 and NH_4F.

A method has been proposed for preparing uranium tetrafluoride from solutions of uranyl nitrate in the presence of HF.[21] Rongalite ($NaHSO_2 . CH_2O . 2H_2O$) is recommended as reducing agent. Rongalite reduces hexavalent uranium in uranyl nitrate solution even at room temperature, but the reaction is slow in the absence of acid. Hydrogen ions accelerate the reaction, probably as a result of the process:

$$UO_2^{2+} + 2H^+ + 2e \longrightarrow UO^{2+} + H_2O.$$

Tetravalent uranium is precipitated quantitatively from solution as the fluoride. Reducing agents similar in character to sulphoxylate include thiourea dioxide, $(NH_2)_2CSO_2$, which has been used for the quantitative separation of platinum from solution[22]. Thionyl chloride and fluoride belong to the same group. A feature of all these compounds which distinguishes them from sulphoxylate is that reduction takes place without liberation of sulphur, and the solution is not contaminated by alkali metals.

Electrolytic methods for the reduction of U^{VI} solutions have recently been developed. Their chief advantage is that reduction takes place without introduction of foreign substances into the solution. Uranium can be precipitated from the reduced solutions in different hydrated forms, depending on the temperature: as $UF_4 . \frac{3}{4}H_2O$ at 95°–100°, and as $UF_4 . 2\frac{1}{2}H_2O$ at room temperature. This method can also be used to prepare double fluorides of uranium[23]; the double fluoride is precipitated in the cathode compartment by adding hydrofluoric acid and ammonium fluoride. Thermal decomposition of the resulting ammonium salt yields pure uranium tetrafluoride.

Most organic compounds do not reduce uranyl compounds under ordinary conditions, but reduction is possible in sunlight. Photo-reactions take place in, for example, solutions of methyl or ethyl alcohols, ethers, and glycol. In the presence of fluoride ions the reduction takes place with formation of tetrafluoride[24,25].

Uranium tetrafluoride is also obtained by electrolysis of a solution of the hexafluoride in water[26]. When UF_6 is dissolved in water, hydrolysis takes place with the formation of UO_2F_2 and HF. This solution contains sufficient fluoride ions for the formation of UF_4. Technological methods for the preparation of UF_4 and NH_4UF_5 or $NaUF_5$, based on electrolytic reduction in cells with diaphragms of ion-exchange membranes, have been described[27-30].

The most popular methods in uranium tetrafluoride technology are those in which purified U_3O_8 [31-33] or uranates[34] are dissolved in mineral acids. The resulting solutions are reduced (for example with $SnCl_2$) and the UF_4 is precipitated with hydrofluoric acid. Methods based on the direct reaction of uranium dioxide with hydrofluoric acid[35-37] have recently found extensive application. They provide for the use of UO_2 obtained from UO_3 by reduction with hydrogen. The uranium dioxide, in either tablet or powder form, is fluorinated with 40% hydrofluoric acid. Uranium tetrafluoride can be obtained by heating a suspension of U_3O_8 in aqueous hydrofluoric acid solution to boiling, and then adding a reducing agent ($SnCl_2$).[38]

Methods of the second type are based on the preparation of uranium tetrafluoride from uranium dioxide and hydrogen fluoride. A number of papers[39-43] describe the fluorination of uranium dioxide with gaseous hydrogen fluoride at high

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† 1 kX = 1.002 Å.

temperature. At the Second International Conference on the Peaceful Uses of Atomic Energy, brief details were given of methods which can be used under industrial or laboratory conditions for the preparation of UF_4 by the action of gaseous hydrogen fluoride on uranium dioxide at 600°–700°.[44–48] The most important feature of the proposed methods is the design of the apparatus for the fluorination, which can be carried out in a suspended layer, with tablets, or in a vibratory apparatus. Ammonium hydrogen fluoride can also be used as fluorinating agent[49,50].

Another group of methods involves preparation of uranium tetrafluoride from the trioxide by simultaneous reduction and fluorination. The freons CCl_2F_2,[51,52] $CFCl_3$,[52] $C_2Cl_4F_2$, $CClF_3$, $C_2Cl_3F_3$, and $CHCl_2F$ [53] are used for this purpose. For freon-12 (CCl_2F_2) the process is:

$$UO_3+2CCl_2F_2 \xrightarrow{360°-380°} UF_4+CO_2+COCl_2+Cl_2.$$

Fluorination with freon-12 [54,55] has been proposed for a technological scheme in which the uranium in solution is separated from impurities by means of hydrogen peroxide. This is also possible in the presence of fluoride ions; a sparingly soluble peroxofluoro compound of the type $3NH_4F.4UO_4$ or $(NH_4)_3U_4O_{16}F_3$ is formed. This compound is dried at 110° and heated at 450°–550° in a current of freon to yield the tetrafluoride:

$$3NH_4F\cdot4UO_4+{}^{13}/_2CCl_2F_2=4UF_4+3NH_3+2O_2+4CO_2+4Cl_2+{}^{5}/_2COCl_2+{}^{3}/_2H_2O.$$

NH_3, CO_2, and other volatile compounds are liberated, leaving the UF_4 as a crystalline mass. Pure uranium tetrafluoride can also be obtained by an analogous method from the double ammonium compounds (for example NH_4UF_5) by decomposing them at 400°–600°, when ammonium fluoride sublimes away[56].

The third type of method for preparing uranium tetrafluoride is based on reduction of the hexafluoride. Hydrogen can be used[57], reduction taking place at 250°–400°. It occurs at a measurable rate[58]. At 25° the reaction is ~30% complete after 30 min. The quantity of hydrogen taken for the reaction corresponds to a calculated $H_2 : UF_6$ ratio of 3 : 1. Uranium hexafluoride can be reduced to tetrafluoride by heating with gaseous HCl, HBr, or HI.[59,60] The reaction with HBr takes place at 100°, and that with HCl at 300°. Ethylene, trichloroethylene, propane, ammonia, $SiCl_4$, PCl_3, etc. can be used for the reduction. Smiley and Brater[57] studied direct reduction of UF_6 to UF_4 with trichloroethylene, carrying it out in both the liquid and gaseous phases in the range 74°–480°. The uranium hexafluoride was completely reduced, but the resulting tetrafluoride was contaminated with carbon, hexachlorobenzene, and other impurities.

The most efficient reducing agent for uranium hexafluoride is carbon tetrachloride, which reduces it to UF_4 rapidly at 100°–200°.[61] The reaction was carried out in an autoclave at 150°:

$$UF_6+2CCl_4=UF_4+Cl_2+2CCl_3F.$$

The concentration of intermediate fluorides UF_5, U_2F_9, and U_4F_{17} was reduced to a minimum (~1%) by removing the volatile products before the end of the reaction by reheating to the initial temperature. The optimum ratio of uranium hexafluoride to carbon tetrachloride was 1 : 4. The reaction involves formation of chlorofluoromethanes as intermediate products and is apparently autocatalytic; traces of UF_4 accelerate the reaction. The resulting uranium tetrafluoride was kept in a current of air at 120° to remove adsorbed gases. The authors established that the reaction takes place sufficiently rapidly at atmospheric pressure and can be used in industry for the continuous treatment of large quantities of UF_6 enriched in the light isotope.

Crystal hydrates of uranium tetrafluoride. A number of hydrates of uranium tetrafluoride have been described. Bolton[1] found that addition of hydrofluoric acid to uranyl chloride solution yielded a precipitate which after drying *in vacuo* or in air at 100° had the composition $UF_4.H_2O$. Khlopin and Gerling[62] prepared $UF_4.2H_2O$ by electrochemical reduction of uranyl sulphate in hydrofluoric acid. When this hydrate was dried over $CaCl_2$ or concentrated sulphuric acid, or by heating to constant weight at 100°–105°, $UF_4.\frac{1}{2}H_2O$ was obtained. Khlopin and Yashchenko[63] studied the physicochemical properties of the tetrafluoride prepared under various conditions and established that the air-dried tetrafluoride obtained by the electrochemical reduction of UO_2SO_4 solution in hydrofluoric acid solutions of concentrations from 4 to 20% always has the composition $UF_4.2\frac{1}{2}H_2O$, irrespective of the method of preparation. When this hydrate is dried to constant weight at 100°–105°, a compound of composition $UF_4.\frac{1}{2}H_2O$ is obtained.

Popov and Gagarinskii[64] established that the stable crystal hydrate is $UF_4.2\frac{1}{2}H_2O$, and that all crystal hydrates of lower water content are gradually converted to this form. Dawson *et al.*[65] found that UF_4 forms two hydrates: a higher hydrate $UF_4.2\frac{1}{2}H_2O$ with orthorhombic structure and a lower hydrate $UF_4.nH_2O$ with $0.5 < n < 2$ and a pseudo-cubic structure. The higher hydrate $UF_4.2\frac{1}{2}H_2O$ is stable *in vacuo* at 25° and in air up to 100°. Above this temperature it loses water rapidly to yield UF_4. With increase in temperature the hydrate $UF_4.2\frac{1}{2}H_2O$ loses water to give $UF_4.\frac{1}{2}H_2O$. The dehydration of $UF_4.\frac{1}{2}H_2O$ is much slower than the initial loss of water. Part of the water can be removed from the pseudo-cubic hydrate with dry methanol, whereas under the same conditions only adsorbed water can be removed from $UF_4.2\frac{1}{2}H_2O$. The hydrate $UF_4.2\frac{1}{2}H_2O$ is formed from the lower hydrate by placing it in 2–10% hydrofluoric acid.

There are reports on the relationship between the temperature of precipitation of UF_4 from solution and the composition of the resulting hydrates[26]. $UF_4.2\frac{1}{2}H_2O$ is formed below 40° and the monohydrate above 60°. Between 40° and 60° a mixture of the two hydrates is formed. Allen *et al.*[18,19] obtained $UF_4.\frac{3}{4}H_2O$ at 95°. The quantity of hydrate water in the uranium tetrafluoride molecule decreases with increase in the temperature of precipitation.

From X-ray diffraction, calorimetric, and tensimetric studies, Gagarinskii and Mashirev[66] concluded that the lower crystal hydrate of uranium tetrafluoride, with pseudo-cubic structure, previously assumed[65] to be $UF_4.nH_2O$ ($0.5 < n < 2$) has the composition $UF_4.0.4H_2O$. The water in excess of 0.4 molecules is not chemically combined with the UF_4 and does not form part of the composition of the crystal hydrate. When the lower crystal hydrate of uranium tetrafluoride is dehydrated *in vacuo* below 225°, the resulting phase retains a structure similar to that of the original compound. Hydration of the dehydrated salts obtained from various uranium tetrafluoride crystal hydrates gives the crystal hydrate from which the anhydrous salt was obtained. Thus, dehydration of $UF_4.2\frac{1}{2}H_2O$ yields a phase which retains a structure similar to that of the original hydrate, and this ensures that introduction of water into the lattice (the reverse process) gives the original compound. Anhydrous UF_4 prepared at high temperatures is not hydrated.

Dawson *et al.*[65] found from the thermogravimetric curve that the conversion of $UF_4.\frac{1}{2}H_2O$ to UF_4 takes place more slowly than the conversion of $UF_4.2\frac{1}{2}H_2O$ to $UF_4.\frac{1}{2}H_2O$. A similar observation was made by Gagarinskii and Mashirev[66], who established that in the dehydration of $UF_4.2\frac{1}{2}H_2O$, only that fraction of the water in excess of 0.4 moles per mole of UF_4 is removed fairly rapidly. As the water content is reduced to approximately 0.4 moles per mole of uranium tetrafluoride, almost no further dehydration takes place at 95°. Aqueous vapour pressures were measured at different water contents for specimens of partially dehydrated $UF_4.2\frac{1}{2}H_2O$ at 95°. The hydrate $UF_4.0.4H_2O$ is very stable, and a temperature of 400°–500° is required for its decomposition. Dehydration of crystal hydrates of uranium tetrafluoride is complicated by the two side reactions[18]:

$$UF_4+2H_2O \rightleftarrows UO_2+4HF,$$

$$2UF_4+O_2+2H_2O \rightleftarrows 2\,UO_2F_2+4HF.$$

Both these reactions take place readily at the high temperatures necessary to dehydrate uranium tetrafluoride crystal hydrates. It is thus very important to know the course of each individual reaction.

B. Physical and Physicochemical Properties

Uranium tetrafluoride is a crystalline solid, usually green, which is precipitated from aqueous solutions in two modifications, a coarse-grained green form and a finer pale blue form[63,64], which can be readily separated by elutriation.

The vapour pressure of uranium tetrafluoride was measured by Popov *et al.*[67] by a flow method. The carrier gas was argon, previously purified from oxygen and water vapour. Spectroscopic analysis showed that the uranium tetrafluoride specimen contained 0.01% iron and up to 0.001% each of silicon, magnesium, and calcium. They established that the vapour pressure of uranium tetrafluoride in equilibrium with the solid salt at 875°, 900°, and 950° satisfies the equation:

$$\log P_{mm}=12.945-16\,140/T$$

The discrepancies between experimental and calculated values of the pressure at 875°, 900°, and 950° were +2.0%, -2.5%, and +4.5% respectively. The vapour pressures of UF_4 in equilibrium with the liquid at 975° and 1000° lie on the straight line given by:

$$\log P_{mm}=8.003-10\,000/T.$$

The intersection of the two straight lines gives 969° for the melting point of uranium tetrafluoride, which agrees satisfactorily with the value 960° ± 5°, found from the heating curve[10].

The structure of UF_4 was studied by Zachariasen[13]. X-Ray single-crystal diffraction patterns for uranium tetrafluoride showed that it is monoclinic with twelve molecules in the unit cell, a = 12.79 ± 0.06 kX, b = 10.72 ± 0.05 kX, c = 8.39 ± 0.05 kX, β = 126° 10' ± 30', space group $C2/c$.

The higher crystal hydrate $UF_4.2\frac{1}{2}H_2O$ is orthorhombic and contains eight molecules in the unit cell, a = 12.75 ± ± 0.04 Å, b = 11.12 ± 0.04 Å, c = 7.05 ± 0.03 Å, space group *Pnam*. $UF_4.nH_2O$ (n = 0.75–2) has a pseudo-cubic lattice with a = 5.69 ± 0.01 kX, space group $Fm3m(O_h^5)$.[65]

The heat capacity, enthalpy, and entropy of uranium tetrafluoride have been determined[68] at temperatures from 20° to 350°K. The UF_4 specimen contained 2% UO_2F_2. It was assumed that the heat capacity of this impurity does not differ greatly from that of uranium tetrafluoride and introduces no serious error. The values of C_p were calculated from a smooth curve drawn through the experimental points. The enthalpies were calculated by integrating the function $dH = C_{sat}dT + VdP$, where C_{sat} is the heat capacity of the condensed phase in equilibrium with the saturated vapour, using Simpson's rule, with the values obtained for C. The entropies were obtained by the same method, integrating the function $dS = (C/T)dT$. Measurements of the heat capacity of uranium tetrafluoride were repeated by Osborne *et al.*[69], using uranium tetrafluoride containing 0.05% UO_2F_2. The heat capacity was measured from 5° to 300°K in an adiabatic calorimeter. C_p, $H^0 - H_5^0$, and $S^0 - S_5^0$ at 298.16°K are 27.37 ± 0.03 cal deg^{-1} mole^{-1}, 5389 ± 6 cal × × mole^{-1}, and 36.13 ± 0.04 cal deg^{-1} mole^{-1} respectively.

Lohr *et al.*[70] determined the magnetic entropy of uranium tetrafluoride from the difference between the entropies of UF_4 and ThF_4 assuming that, owing to diamagnetism, the entropy of ThF_4 is determined entirely by the lattice vibrations. The isomorphism, the slight (2.5%) difference in the unit cell volumes, and the small difference between the molecular weights of UF_4 and ThF_4 suggest that for these substances the entropies due to lattice vibrations should be close to one another. The magnetic entropy was found to be 2.17 e.u. at 298.16°K, that is, very close to the value of the spin magnetic entropy: $R\log(2S + 1) = R\log 3 = 2.18$.

The heat of hydration of uranium tetrafluoride

$$UF_4(\text{solid}) + 2\tfrac{1}{2}H_2O(\text{liquid}) = UF_4.2\tfrac{1}{2}H_2O(\text{solid}) + \bar{Q},$$

was determined by an adiabatic method[71] for two specimens, obtained by dehydrating $UF_4.2\frac{1}{2}H_2O$ *in vacuo* with gradual heating to 225°. The first specimen contained 0.28% H_2O, corresponding to the presence of 2.23% $UF_4.2\frac{1}{2}H_2O$, and the second specimen was anhydrous. The heat of hydration was found to be 8.21 ± 0.02 kcal mole^{-1} UF_4 at 20°. The authors checked this heat of hydration with two specimens of salt containing 2.5 and 2.43 moles H_2O respectively. In the first case the heat was found to be zero, while in the second case it corresponded to the heat evolved for hydration of $UF_4.2.43H_2O$ to $UF_4.2.5H_2O$. The dissociation pressure of $UF_4.2\frac{1}{2}H_2O$ was measured by Popov and Gagarinskii[64], who showed that the average dissociation pressure (mm Hg) of $UF_4.2\frac{1}{2}H_2O$ in the temperature range 20°–35° satisfies the equation:

$$\log P_{mm}=10.035\pm0.003-\frac{2920\pm3}{T}.$$

The dissociation pressure of the lower hydrate $UF_4.0.4H_2O$ is small[66], even at 95°, and much less than that of $UF_4.2\frac{1}{2}H_2O$. The heat of hydration of UF_4 with liquid water, calculated from the dissociation pressure of $UF_4.2\frac{1}{2}H_2O$ at various temperatures[64], was found to be 7.23 kcal mole^{-1}. Direct determination of the heat of hydration of UF_4 (obtained by dehydrating $UF_4.0.4H_2O$) on hydration to $UF_4.0.4H_2O$, gave 6.09 ± 0.01 kcal mole^{-1}.[66] The heat of hydration of UF_4 to $UF_4.2\frac{1}{2}H_2O$ is 8.21 ± 0.02 kcal mole^{-1}. The authors consider that in this case the phases being hydrated have different structures. The discrepancy between the calorimetric heat of hydration of UF_4 to $UF_4.2\frac{1}{2}H_2O$ (8.21 kcal mole^{-1}) and the same heat of hydration calculated from the dissociation pressure of the crystal hydrate $UF_4.2\frac{1}{2}H_2O$ (7.23 kcal mole^{-1}) arises because the latter refers not to the hydration of UF_4 but of a solid solution containing water.

C. Chemical Properties

Uranium tetrafluoride is sparingly soluble in water. The solubility in water, found by different authors, ranges from 1×10^{-4} M to 1.9×10^{-3} M. The most reliable value, obtained by Khlopin and Yashchenko[63] at 25° under conditions precluding oxidation, is 1.7×10^{-4} M.

A solution of $UF_4.2\frac{1}{2}H_2O$ in water gives an acid reaction. This has been attributed[63] to part of the water being not simply water of crystallisation but directly coordinated to the uranium. Thus it has been suggested that $UF_4.2\frac{1}{2}H_2O$ in aqueous solution is an acid capable of losing a proton. The pH was the same for different crystal hydrates and corresponded very closely to the presence in solution of two hydrogen ions per g-atom of uranium, agreeing with the coordination formula $H_2[UF_4(OH)_2]$. This formula was not considered to be proved conclusively. The equilibrium constants for the reactions

$$U^{4+} + HF \rightleftarrows UF^{3+} + H^+,$$

$$U^{4+} + 2HF \rightleftarrows UF_2^{2+} + 2H^+,$$

were estimated by Day *et al.*[72] as 10^6 and 10^8 respectively.

Uranium tetrafluoride is sparingly soluble in acids, the solubility increasing with increasing temperature. The solubility in 2 N H_2SO_4 is 2.9 g litre^{-1}. It is less in concentrated sulphuric acid than in dilute. Uranium tetrafluoride dissolves in sulphuric acid, when it is heated to fumes of SO_3 and subsequently diluted with water.

It is readily soluble in mineral acids in the presence of boric acid, owing to formation of the BF_4^- ion, and in a mixture of dilute sulphuric acid and silica, in which case $U(SO_4)_2$ and H_2SiF_6 are formed. It also dissolves in hot phosphoric acid. Nitric acid dissolves uranium tetrafluoride with oxidation of U^{4+} to UO_2^{2+}. The addition of boric acid, as with other acids, increases the solvent action of nitric acid.

Uranium tetrafluoride is soluble in certain electrolytes, for example, aluminium salts. This is due to the formation of the stable AlF_2^+ complex ion, which binds the fluoride ion and thus reduces its concentration. Uranium tetrafluoride prepared by the high-temperature method and containing no hydrate water is chemically inactive.

The sensitivity of uranium tetrafluoride to water vapour was studied in the temperature range 100°–500°.[73] It was shown that water vapour acts on uranium tetrafluoride above 100°. The constant for the reaction

$$UF_4 + 2H_2O \rightleftarrows UO_2 + 4HF,$$

and the heat of this reaction (-30 kcal) have been determined. The decomposition of UF_4 by water vapour is widely used in its analysis[74].

The reaction between uranium tetrafluoride and a current of dry oxygen[75] at 600°–900° can be used to prepare uranium hexafluoride under laboratory conditions. An interesting feature is that the preparation of UF_6 in this way does not require free fluorine. The main reaction

$$2UF_4 + O_2 = UF_6 + UO_2F_2,$$

starts above 750° and is accompanied by side reactions, for example, $UF_4 + UF_6 \rightleftharpoons 2UF_5$. The latter leads to an increased consumption of UF_4, condensation of UF_4 and UF_5 in the colder zones, and contamination of the uranium hexafluoride with UF_5. The rate of vaporisation of uranium tetrafluoride at 600°–900° is very low (1/50th of the rate of the main reaction). The rate constant for the decomposition of uranyl fluoride:

$$3UO_2F_2 = UF_6 + {}^2/_3U_3O_8 + {}^1/_3O_2,$$

is 7.6×10^{-5}–6.7×10^{-5} min^{-1} at 700° and 7.7×10^{-4}–7.8×10^{-4} min^{-1} at 800°. The rate constant for this reaction is fairly low at temperatures below 800° and is 1/50th of the rate constant for the reaction of uranium tetrafluoride with oxygen. The activation energy calculated from these data is 50 kcal mole^{-1}.

The kinetics of oxidation of uranium tetrafluoride with oxygen have been studied[76]. The rate of the reaction of uranium tetrafluoride with dry oxygen was determined by a thermogravimetric method in the temperature range 550°–815°. The reaction is first order. The reaction rate depends on the partial pressure of oxygen, and the rate constant is given by the expression $k = 8.31 \times 10^6 \times \exp(-45\,900/RT)$, where k has units of moles min^{-1} m^{-2}. For the reaction of UF_4 with dry air, the rate constant is given by $k_a = 8.24 \times 10^6 \times \exp(-47\,000/RT)$, which satisfies the relationship $k_a = 0.55\,k$ at each temperature. In calculating the rate constants, sublimation of uranium tetrafluoride and decomposition of uranyl fluoride were neglected. At each temperature[75], the rate of sublimation was 50 times less than the rate of the reaction with oxygen. The rate of decomposition of uranyl fluoride is also insignificant in the temperature range studied. Thus at temperatures where UF_5 is not formed the only reaction is

$$2UF_4 + O_2 = UF_6 + UO_2F_2.$$

The side reaction $UF_4 + UF_6 = 2UF_5$ was detected only above 750°. The quantity of uranium tetrafluoride taking part in this reaction increases from 1% at 750° to 30% at 815°. The standard heat of the reaction, estimated from the equation $\Delta H^0 = 22\,060 + 27.1\,T - 17.1 \times 10^{-3}\,T^2 + 158.3 \times 10^4\,T^{-1}$, was found to be $\sim$ -5 kcal (mole UF_4)$^{-1}$ between 550° and 815°.

Uranium tetrafluoride reacts with elementary fluorine. Labaton and Johnson[77] established that the preparation of UF_6 from the tetrafluoride involves formation of intermediate fluorides, which undergo further fluorination but at a lower rate than the rate of fluorination of the tetrafluoride.

Halogen fluorides, such as ClF_3 and BrF_3, react with uranium tetrafluoride. Its reaction with chlorine trifluoride was studied at temperatures from 17° to 193° by the change in weight of the solid phase[78]. The reaction rate passed through a maximum at 105°, decreased to a minimum at 148°, and subsequently increased. The decrease in rate between 100° and 150° arises because the reaction of chlorine trifluoride with the intermediate fluorides is probably slower than the reaction with uranium tetrafluoride, as was observed with fluorine.

At 17°–58° and 156°–194°, the Arrhenius equation relating rate constants and reaction temperature is applicable within the limits of experimental error. The activation energies of the fluorination reaction found for uranium tetrafluoride obtained by hydrofluorination are 5.6 kcal $\times$ mole^{-1} and 3.4 kcal mole^{-1}. It was shown that close to room temperature a linear relationship exists between the reaction rate and the partial pressure of chlorine trifluoride. In the range of gas velocities studied, the linear velocity of the gas did not influence the rate of reaction. Comparison of the results for the reaction between uranium tetrafluoride and chlorine trifluoride with those for the reaction with fluorine shows that the former takes place at much lower temperatures than the latter. For a given specimen, the activation energy is also lower than that for the reaction with fluorine (5.6 kcal mole^{-1} and 3.4 kcal mole^{-1} compared with 19.1 kcal mole^{-1}). Comparison of the rate constants after reduction of the values to the same partial pressure shows that at 265°, fluorination by chlorine trifluoride is 160 times faster than fluorination by fluorine. At higher temperatures the difference between the rates would be less, because the reaction of uranium tetrafluoride with fluorine increases more rapidly than that of the reaction with chlorine trifluoride.

The reaction of uranium tetrafluoride with bromine trifluoride was shown by Sharpe and Emeléus[79] to take place rapidly and quantitatively with formation of uranium hexafluoride. Uranium tetrafluoride reacts with CCl_4 [17] at 420° in an inert atmosphere. The reaction yields uranium monochlorotrifluoride $UClF_3$, which is also obtained by heating uranium tetrafluoride and tetrachloride in an inert atmosphere.

When a mixture of UF_4 and $CaSO_4$ in the molar ratio 1 : 2 is heated in a graphite crucible in an atmosphere of helium to 715° – 730°, a vigorous reaction takes place and is complete in 3 h.[80] The main products are CaF_2, U_3O_8, SO_2, and SO_3, identified by X-ray diffraction and chemical analysis. The loss in weight corresponds to the equation:

$$6CaSO_4+3UF_4=6CaF_2+U_3O_8+2SO_2+4SO_3.$$

The quantity of SO_2 evolved in the reaction exceeds that required by this equation. This is apprently due to reduction of the SO_3 by the crucible material. The reaction products were, moreover, found to contain a small quantity of $CaUO_4$ and traces of UO_2F_2. The presence of these compounds is probably due to reaction of the intermediate product UO_3 with $CaSO_4$ and CaF_2 to form $CaUO_4$ and UO_2F_2:

$$CaSO_4+UO_3=CaUO_4+SO_3,$$

and

$$CaF_2+2UO_3=CaUO_4+UO_2F_2.$$

The importance of the tetrafluoride in the atomic energy industry is due to the fact that metallic uranium is obtained by a metallothermic process using calcium or magnesium[81]. Dubrovin and Evseev[82] concluded, on the basis of thermodynamic calculations, that the reduction of uranium tetrafluoride by magnesium at 1400° would take place almost completely to form metallic uranium and MgF_2, since the equilibrium vapour pressure of magnesium at this temperature is very low (0.8 mm Hg). The higher the magnesium vapour pressure, the more rapid the reduction, estimated to be complete in a few tenths of a second.

4. DOUBLE FLUORIDES

Double fluorides are obtained by precipitating uranium tetrafluoride from aqueous solution in the presence of metal fluorides or by fusing UF_4 with a metal fluoride. The ammonium, sodium, and potassium double fluorides have been most studied.

Khlopin and Gerling[62] and Khlopin and Yashchenko[63] synthesised the salt $UF_4.NH_4F$ by the electrochemical reduction of a solution of uranyl fluoride in hydrofluoric acid in the presence of ammonium fluoride. The composition of the air-dried precipitate $NH_4UF_5.\frac{1}{2}H_2O$ remained almost unchanged on heating up to 105°. The electrical conductivity and pH of solutions of this compound were determined and used to calculate the molar conductance and solubility in water at 25° (1.4 M). The authors consider that the electrical conductivity and solution pH indicate that in aqueous solution NH_4UF_5 breaks down to ammonium fluoride and uranium fluoride. Alkalis readily decompose solutions of this compound. It dissolves slowly in hydrochloric, sulphuric, and nitric acids, and readily in concentrated solutions of Na_2CO_3, $NaHCO_3$, and $(NH_4)_2CO_3$.[83] Determination of the solubility is made difficult by the ready oxidation of U^{IV} to UO_2^{2+}; the presence of uranyl fluoride in solution prevents the double fluoride dissolving. Similar phenomena are observed for dissolution of NH_4UF_5 in solutions of ammonium and sodium carbonates. The solubilities for saturated solutions of NH_4UF_5 (calculated as anhydrous UF_4) in concentrated solutions of Na_2CO_3, $NaHCO_3$ (9.5%), and $(NH_4)_2CO_3$ are 6.6, 2.4, and 5.0 g per 100 ml of solution respectively. It was also observed that dilution of these solutions leads to hydrolysis with precipitation of hydrated uranium dioxide. Dilution with 6 to 12 times the volume of cold water yields a pale green precipitate which gradually becomes black. Dilution with hot water yields an immediate black precipitate. The reason for the different colours of the precipitate has not been established. The action of acetic acid on a carbonate solution of NH_4UF_5 yields a precipitate insoluble in excess acid. Oxalic acid does not yield a precipitate, owing to the formation of a readily soluble oxalate complex. On heating, carbonate solutions of the double fluoride undergo complete [in the case of $(NH_4)_2CO_3$] or partial (in the case of Na_2CO_3, etc.) decomposition with precipitation of uranium(IV) hydroxide.

Double compounds of the type $UF_4.nMF$ have been detected in a number of systems[5,6,84–89] studied in connection with the use of a mixture of molten fluorides for the extraction of uranium from spent fuel elements.

The NaF–UF_4 and LiF–UF_4 systems[88] have been studied by straightforward and differential thermal analysis, quenching, optical identification of solid phases, X-ray diffraction, and visual observation of polytherms. The LiF–UF_4 system (Fig. 1) contains only incongruently-melting compounds with peritectic points: 4LiF.UF_4 with 26 mole % UF_4 at 500°; 7LiF.6UF_4 with 40 mole % UF_4 at 610°, and LiF.4UF_4 with 57 mole % UF_4 at 775°. The eutectic of 4LiF.UF_4 and 7LiF.6UF_4 is formed at 27 mole % UF_4 at 490°. At 470° 4LiF.UF_4 breaks down to LiF and 7LiF.6UF_4. When specimens with 20–32 mole % UF_4 were quenched from temperatures > 490°, a metastable phase assumed to have the composition 3LiF.UF_4 was formed.

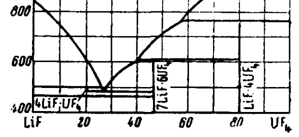

Fig. 1. The LiF–UF_4 system[88].

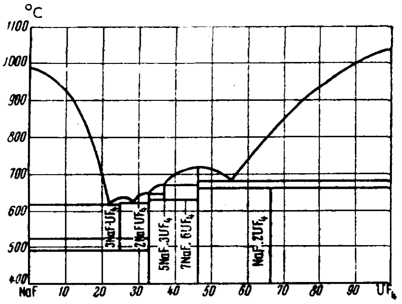

Fig. 2. The NaF–UF_4 system[88].

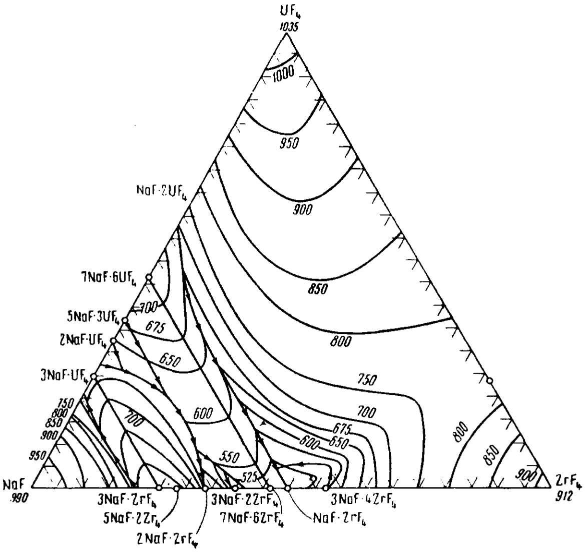

Fig. 3. The NaF–ZrF_4–UF_4 system[89].

The NaF–UF_4 system (Fig. 2) shows formation of the congruently-melting compounds 3NaF.UF_4 at 625° and 7NaF.6UF_4 at 718°, and incongruently-melting compounds with peritectic points, 2NaF.UF_4 with 32.5 mole % UF_4 at 648° and 5NaF.3UF_4 with 37 mole % UF_4 at 673°. Eutectics were found at 21.5 mole % UF_4 (618°), 28 mole % UF_4 (623°), and 56 mole % UF_4 (680°). The solid phase contains the compound NaF.2UF_4, which breaks down at 660° to 7NaF.6UF_4 and UF_4. The compound 3NaF.UF_4 undergoes a polymorphic transformation at 528°, and at 497° breaks down to NaF and 2NaF.UF_4. The compound 5NaF.3UF_4 breaks down at 630° to 2NaF.UF_4 and 7NaF.6UF_4. The α-2NaF.UF_4 phase described by Zachariasen[87] is in fact the compound 5NaF.3UF_4, and the γ-2NaF.UF_4 phase is metastable. Barton *et al.*[88] deny the existence of the compound NaF.UF_4, the polymorphism of 2NaF.UF_4, and the existence of solid solutions in the range 33.3–40 mole % UF_4, which were reported previously[87].

Phase equilibrium has been studied in the UF_4–ZrF_4 and NaF–ZrF_4–UF_4 systems[89]. Thermal, differential-thermal, microscope, optical, and X-ray diffraction studies, with chemical analysis of the phases isolated from the melt by filtration at high temperature, have been used to construct equilibrium diagrams for the UF_4–ZrF_4 and NaF–ZrF_4–UF_4 systems (Fig. 3). The UF_4–ZrF_4 system forms a continuous series of solid solutions with a minimum melting point of 765° at 77% ZrF_4. Sections of the ternary 3NaF.ZrF_4–3NaF.UF_4 system and of the 7NaF.6ZrF_4–7NaF.6UF_4 system consist of continuous solid solutions. The regions of primary deposition of the solid solutions 3NaF.U(Zr)F_4, 7NaF.6U(Zr)F_4, and U(Zr)F_4 occupy ~90% of the liquidus surface. No ternary eutectics or ternary compounds were detected.

The solubility of the inert gases He and Xe in an NaF–ZrF_4–UF_4 melt (50/46/4 mole %) was studied in the pressure range 0.5–2.0 atm at 600°, 700°, and 800°.[90] The dissolved gas was displaced from the fluoride melt by another inert gas and its concentration in the latter was measured by mass-spectrometry. It was found that the solubility increases linearly with pressure, decreases with decrease in atomic weight, and increased with temperature.

The Henry constants $10^8 K$, in mole (cm of melt)$^{-3}$, at atmospheric pressure and 600°, 700°, and 800° are respectively 20, 27, and 41 for He, and 2.0, 4.0, and 6.5 for Xe.

5. INTERMEDIATE FLUORIDES

The intermediate fluorides are compounds of formula UF_n, where $4 < n \leqslant 5$. U_4F_{17} ($UF_{4.25}$), U_2F_9 ($UF_{4.5}$), and UF_5 have been reported as distinct compounds. Besides these, there exist substances with more arbitrary fluorine : :uranium ratios; this casts doubt on their individuality and suggests that fluoride ions have been introduced into the crystal structure of the tetrafluoride.

There are few references to methods of preparing these compounds. The earliest papers include a report by Ruff and Heinzelman[2] on the reaction between anhydrous liquid hydrogen fluoride and uranium pentachloride. The uranium pentafluoride obtained disproportionates to UF_6 and UF_4. This method was subsequently developed by Carignan[91], who treated the chlorides UCl_5 and UCl_6 with anhydrous HF at temperatures from -33° to +25°. The pentafluoride, was obtained and volatile reaction products were removed by heating *in vacuo*. The reaction involves halide conversion and reduction:

$$2UCl_6 + 10HF \rightarrow 2UF_5 + 10HCl + Cl_2.$$

Agron and Weller[92] reported conditions for the formation of U_4F_{17} by the reaction between UF_4 and UF_6. These conditions are defined by: $12.75\ T - T \log P \leqslant 7143$ and $13.68\ T - T \log P \geqslant 7315$, where T is expressed in °K and P is pressure of UF_6 vapour in mm Hg. Under other conditions, U_2F_9 and UF_5 in α- and β-modifications are formed.

A similar reaction can be carried out between the liquid hexafluoride and tetrafluoride. Reaction for 1 week at 100° - 125° yields β-UF_5, but if the duration of reaction is insufficient for equilibrium to be reached, the product is U_2F_9.

Intermediate fluorides are formed on fluorination of the tetrafluoride, $UF_4 + \frac{1}{2}F_2 \rightarrow UF_5$. This reaction takes place at a temperature lower than that at which chiefly the hexafluoride is obtained (350°-360°). More details are being obtained. Labaton and Johnson[77] approached the chemistry of fluorination from the kinetic viewpoint. At 220°, no reaction takes place between fluorine and the tetrafluoride; at 300° and a hexafluoride pressure of 42 mm Hg, the reaction between UF_6 and UF_4 yields intermediate fluorides. Fluorides of composition $UF_{4.52}$–$UF_{4.12}$ were obtained, depending on the method of preparing the specimens used (dehydration of $UF_4.2\frac{1}{2}H_2O$, hydrofluorination of the dioxide). The same compositions were obtained in fluorination of UF_4 with fluorine. The formation of intermediate fluorides during the preparation of the hexafluoride is due to the concentration of fluorine being lower in the bulk of the tetrafluoride layer than at the surface, whereas the UF_6 concentration is sufficient for formation of intermediate fluorides by the reaction between UF_6 and UF_4. The rate of the reaction depends on the temperature. In accordance with the Arrhenius equation, the rate constants lie on a straight line plot of $\ln k$ *vs.* $1/T$, where k is the rate constant and T is in °K. The activation energies for three specimens of UF_4 lay in the range 15.5-19.9 kcal mole^{-1}, the higher value corresponding to specimens of greater crystalline complexity, as shown by X-ray diffraction. The formation of intermediate fluorides in the preparation of hexafluoride from tetrafluoride is, at first, the result of adsorption of fluorine on the surface of the particles of the substance being fluorinated and then penetration of the fluorine into the tetrafluoride lattice. The compositions of these compounds may not correspond to stoichiometric ratios.

A. Physical and Physicochemical Properties

This review of their preparation shows that intermediate fluorides should be regarded as comprising U_4F_{17} (probably), U_2F_9 (also obtained in a black modification), and UF_5 (α- and β-forms). Their crystal-chemical and thermodynamic data are given in Table 1.

B. Chemical Properties

A characteristic chemical property of the intermediate fluorides is disproportionation, which takes place on heating and in solution:

$$2UF_5 \rightleftarrows UF_4 + UF_6 \text{— thermal disproportionation,}$$

$$2UF_5 \xrightarrow{+2H_2O} UF_4 + UO_2F_2 + 4HF \text{— hydrolytic disproportionation.}$$

Both processes are connected with the uranium in the intermediate fluorides being present in both the hexavalent and tetravalent states. The thermal disproportionation has a definite pressure of volatile component (UF_6). Agron and Weller's results[92] lie on a straight line for $\log P$ *vs.* $1/T$ (Fig. 4). The diagram shows that the most stable compound is U_4F_{17}; at 300° its disproportionation pressure is ~1.5 mm, whereas that of α-UF_5 is ~400 mm.

TABLE 1. Crystal-chemical and thermodynamic characteristics of intermediate uranium fluorides.

Compound	Structure[93,94]	Thermodynamic characteristics[10]			Remarks
		$\Delta H_{298°}$, kcal mole^{-1}	$S_{298°}$, e.u.	$\Delta H_{298°}$, kcal mole^{-1}	
α-UF_5	tetragonal $a = 6.512 \pm 0.001$ Å $c = 4.463 \pm 0.001$ Å	—483.7±1.3	48.0±0.4	—458.2±1.4	$\alpha \rightarrow \beta$ change not known
β-UF_5	tetragonal $a_1 = 11.450 \pm$ $\pm 0{,}002$ A $c = 5.198 \pm 0.001$ Å	—485.2 ±1.4	43.3±0.5	—458.7 ±1.5	$\alpha \rightarrow \beta$ change takes place at $t° > 125°$ with disproportionation pressure 1.76 mm Hg
U_2F_9	cubic, mixed $(U^{4+}_{0.5} \cdot U^{5+}_{0.5})F_{4.5}$ or $(U^{4+}_{0.75} \cdot U^{6+}_{0.25})F_{4.5}$ $a = 8.454 \pm 0.002$ Å	—933.8±3	75.3±0.6	—884.0±3	
U_4F_{17}	not known	—1820±4	149±0.6	—1727.5±4	black product; all uranium atoms structurally equivalent, indicating intermediate valency 4.5

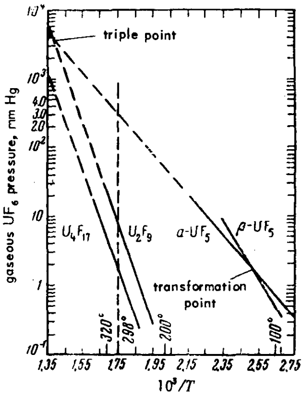

Fig. 4. Disproportionation pressure of U_4F_{17}, U_2F_9, α-UF_5, and β-UF_5[10].

Hydrolytic disproportionation takes place at different rates for different intermediate fluorides; U_4F_{17} is less reactive than U_2F_9 and UF_5, the hydrolytic disproportionation reaction in this case being:

$$2U_4F_{17} + 2H_2O \longrightarrow 7UF_4 + UO_2F_2 + 4HF.$$

Black U_2F_9 is affected by water only on boiling. Intermediate fluorides have been detected in the reduction of uranium hexafluoride to tetrafluoride, for example, by hydrogen or CCl_4. They thus take part in these processes and may be reduced to UF_4. These are all the available data on the chemical properties of these compounds.

6. URANIUM HEXAFLUORIDE

A. Methods of Preparation

The methods of preparing uranium hexafluoride can be classified according to the fluorinating agents employed. These include: 1) gaseous fluorine; 2) halogen fluorides, either liquid or gaseous (ClF_3, BrF_3, BrF_5, IF_7, etc.); 3) certain metal fluorides; 4) hydrogen fluoride.

Various uranium-containing materials are used for the preparation of the hexafluoride by means of gaseous fluorine. Ruff and Heinzelman[2] fluorinated metallic uranium or its carbide. Almost any uranium compound is fluorinated by fluorine under appropriate conditions to yield the hexafluoride, for example U_3O_8, UO_2, UF_4,[46,48,95,96] intermediate fluorides, uranyl fluoride[97], and sodium diuranate. Other uranium compounds proposed as starting materials include double salts of the type KUF_5 and K_2UF_6. Fluorination is carried out at 200° – 400°.[98]

The next most important methods of fluorination are those based on the use of halogen fluorides. These reactions can be used in the condensed phase. For this reason liquid halogen fluorides have been widely used in fluorination technology[99–105]. Fluorination can be carried out both in the gaseous phase [for example ClF_3 (gas) + U(solid)] and in the condensed phase [for example BrF_3 (liquid) + U (solid)]. Chlorine trifluoride and bromine trifluoride and pentafluoride have been used for fluorination of metallic uranium.

Halogen fluorides are used chiefly for extracting uranium from the irradiated uranium heat-producing blocks of nuclear reactors[4,84,105–108]. Dissolution of the irradiated uranium in halogen fluorides yields volatile and non-volatile fluorides of the fission elements and plutonium tetrafluoride. The uranium fluoride is distilled from the non-volatile fluorides and the residue is brought into solution by treating with aluminium nitrate. This is based on the reaction proposed by one of the authors of this article[109]:

$$Al^{3+}+RF_n \longrightarrow AlF_2^{+}+R^{n+}+(n-2)\,F^-,$$

where R is a fission element. Further extraction of this solution for plutonium and fission elements is possible using extracting agents stable to irradiation.

Halogen fluorides are used to prepare fluorides of a number of elements[110–114]. Their role as fluorinating agents is increasing as they have considerable advantages over elementary fluorine. The writers have synthesised a number of higher fluorides of transition elements by means of chlorine and bromine trifluorides and have shown the advantages of this method[115–117].

The reaction between certain higher metal fluorides and the compound to be fluorinated, for example UF_4, is also of interest. The addition of 2 moles of CoF_3 to 1 mole of UF_4 heated to 400° yields UF_6:

$$UF_4+2CoF_3=UF_6+2CoF_2.$$

The uranium hexafluoride is distilled off and the CoF_2 is regenerated by treatment with fluorine. Silver difluoride, palladium trifluoride, and platinum hexafluoride can be used in the same way.

The preparation of uranium hexafluoride using only hydrogen fluoride (without subsequent use of fluorine) is based on double decomposition with subsequent disproportionation. Ruff and Heinzelman[2] first prepared UF_6 in this way from uranium pentachloride:

$$UCl_5+5HF=UF_5+5HCl\ ,$$

$$3UF_5 \xrightarrow{175^\circ} U_2F_9+UF_6\ ,$$

$$2U_2F_9 \overset{200^\circ}{\rightleftarrows} 3UF_4+UF_6.$$

The uranium hexafluoride can readily be separated from the uranium tetrafluoride by heating, and from excess hydrogen fluoride by fractional distillation.

B. Physical Properties

Under ordinary conditions uranium hexafluoride is a white crystalline volatile substance which sublimes without melting. The known actinide hexafluorides UF_6, NpF_6, and PuF_6 have similar chemical and physical properties, but uranium hexafluoride is also the analogue of the higher fluorides of the chromium subgroup elements, MoF_6 and WF_6. A characteristic feature of the actinide hexafluorides is their lower stability and higher reactivity[118–122]. Weinstock and Malm's[121] physical properties for these compounds are given in Table 2.

The melting and boiling points of uranium hexafluoride have been determined many times[2,123–125] and, allowing for the difficulty of measurement, all the reported values agree well except the original data of Ruff and Heinzelman[2]. The vapour pressure of uranium hexafluoride over a wide range of temperature, for both liquid and solid states, has been determined by many authors[121–128]. On the whole the results show good agreement. The vapour pressures of solid and liquid uranium hexafluoride at different temperatures are expressed by the equations given in Table 3, which cover the whole temperature range studied. The critical temperature (230° ± 0.2°) and pressure (45.5 ± ± 0.5 atm) have been determined by Oliver *et al.*[126] and Llewellyn[128]. Llewellyn's value for the critical temperature is 245°± 5°.

TABLE 2. Physical properties of the hexafluorides[121].

Hexafluoride	M.p., °C	B.p., °C	Vapour pressure at 0°, mm Hg	Vapour pressure at the m.p., mm Hg
MoF_6	17.4	35.0	—	—
WF_6	2.3	17.06	370.7	414.9
UF_6	64.0*	56.5	17.5	1137.9**
NpF_6	54.4*	55.2	20.8	754.9**
PuF_6	50.8*	62.2	17.6	533.0**

* Triple point.

** Vapour pressure at triple point.

TABLE 3.

Equation	Temperature range, °C	Reference
Solid UF_6		
$\log P_{mm}=\frac{2751}{T}-75.0e^{2560/T}-1.01\log T+13.797$	$-15-+65$	160
$\log P_{mm}=10.023-\frac{2486}{T}+0.0012\,T$	$0-+34.6$	159
$\log P_{mm}=6.38363+0.0075377\,t-942.76\,(t-183.416)$		158
$\log P_{mm}=-(3123.479/T)+21.87103-3.77962\log T$		157
Liquid UF_6		
$\log P_{mm}=-1946/T-0.00492T+0.934\log T+8.1$	65—100	160
$\log P_{mm}=6.99464-1126.288\,(t+221.963)$	64—116	158
$\log P_{mm}=7.69069-1683.165\,(t+302.148)$	>116	158
$\log P_{mm}=-(2065.679/T)+18.600033-3.72662\log T$		157

TABLE 4. Heats of sublimation and vaporisation of UF_6.

Temperature, °K	Heat, kcal mole^{-1}	Reference	Temperature, °K	Heat, kcal mole^{-1}	Reference
	Heat of sublimation			Heat of vaporisation	
223	12.145	128	337	6.820	126
253	12.075	128	338	6.920	128
273	12.220	125	340	6.859	129
273	11.980	128	343	6.890	128
273.16	12.023	129	348	6.487	125
293	11.870	128	350	6.671	129
298	11.970	125	363	6.670	128
298	11.800	126	370	6.404	129
298.16	11.872	129	383	6.310	128
313	11.730	128			
323	11.580	125			
329.56	11.500	126			
330	11.537	129			
333	11.530	128			
337	11.380	126			

C. Thermochemical Properties

The heat of formation:

$$U(\text{metal}) + 3F_2(\text{gas}) = UF_6(\text{gas})$$

is 505 ± 3 kcal mole^{-1}.

According to Llewellyn's data[128] the heat of sublimation of solid UF_6 is given by the equation

$$\lambda_T = 12\,600 - 875\,600e^{-2560/T} - 2T \text{ cal mole}^{-1}$$

and the heat of vaporisation of liquid UF_6 by the equation

$$\lambda_T = 8890 - 0.0225\,T^2 + 1.85\,T \text{ cal mole}^{-1}.$$

The author points out that the latter equation does not satisfy the condition $\lambda_T = 0$ at the critical temperature. The empirical equation

$$\lambda_T = 6920 - 5.3\,(t-65) - 0.134\,(t-65)^2 \text{ cal mole}^{-1}.$$

satisfying the condition $\lambda_T = 0$, has been put forward. Numerical values of the heat of sublimation and vaporisation[125,126,128,129] are given in Table 4. The heats of sublimation and vaporisation at the triple point are 11.38 kcal × mole^{-1} and 6.82 kcal mole^{-1} respectively, so that the heat of fusion is $\lambda_{fus} = \lambda_{sub} - \lambda_{vap} = 4.56$ kcal mole^{-1}.[125] Direct calorimetric determination of the heat of fusion gives the same value.

The heat of hydrolysis according to

$$UF_6(\text{solid}) + 2H_2O \longrightarrow (UO_2F_2 + 4HF)(\text{liquid})$$

was determined by Popov *et al.*[71] as 50.22 ± 0.051 kcal × mole^{-1}.

The thermal conductivity of gaseous UF_6 corresponds to the equation $k = (1.459 + 0.00614\,t) \times 10^{-5}$ cal cm^{-1} sec^{-1} × deg^{-1}, and individual values are 1.42×10^{-5} at 5° and 1.94×10^{-5} at 105°.[128] The thermal conductivity of liquid UF_6 is known for one temperature (72°), 3.83×10^{-4} (±3%) cal cm^{-1} sec^{-1} deg^{-1}.

D. Mechanical Properties

The density of liquid uranium hexafluoride at the triple point is 3.624 g cm^{-3},[128] which agrees with the value found earlier[130]. Determination of the density of gaseous UF_6 has confirmed that it consists of non-associated molecules. The viscosity of liquid and gaseous UF_6 has been measured in the range 0°–200°.[128]

The structure of UF_6. The problem of the structure of the uranium hexafluoride molecule has not yet been finally solved. Some authors[131,132] interpret the electron diffraction data for uranium hexafluoride on the basis of a rhombic bipyramid model, but others[133,134] suggest that the molecule may be an irregular octahedron with three short (1.87 Å) and three long (2.17 Å) bonds. The possibility of a molecule with an inversion centre and two short (1.87 Å), two intermediate (2.12 Å), and two long (2.22 Å) bonds is not excluded. It has been suggested[135] that the electronic configuration of uranium permits a regular octahedral structure and development of the theory of electron diffraction has shown that the uranium hexafluoride molecule corresponds more to this type[136]. The U–F distance in uranium hexafluoride is 1.994 Å.[121] From the number of active lines in the infra-red, Raman, and absorption spectra, it can be concluded that uranium hexafluoride has a completely symmetrical structure[137,138]. The dipole moment, equal to zero[139], is not consistent‡ with a regular octahedral model. A number of papers[123,140] have been devoted to study of the absorption spectra of uranium hexafluoride in the visible and ultra-violet.

Sheremet'ev[141] has shown that the absorption spectrum of gaseous and solid UF_6 in the visible and near ultra-violet consists of overlapping absorption bands. From this he concludes that the electronic vibrational energy levels of the UF_6 molecule are diffuse and change little

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‡ This should probably read *is consistent* (Ed. of Translation).

on passing from room temperature to 88°K. The structure of the 407–347 mμ absorption band is identical for gaseous and solid UF_6, confirming that uranium hexafluoride crystals are of the molecular type[141,142]. If we assume the point group symmetry O_h (regular octahedron) for the UF_6 molecule, its six fundamental vibrations are distributed as follows: three to the valency vibrations and three to the deformational vibrations[143,144]. Sheremet'ev's experimental data[141] do not agree completely with earlier calculations[138]. On the basis of the absorption spectra frequency data, the author suggests that the sturcture of the UF_6 molecule is not exactly a regular octahedron.

Weinstock and Malm[121] have reviewed the structures of a number of hexafluorides, including PuF_6 and NpF_6. From a study of the infra-red absorption spectrum, magnetic susceptibility, and electron diffraction, they concluded that the UF_6, and PuF_6 and NpF_6, molecules are regular octahedra (point group O_h). That being so, it is possible to explain the absence of association in UF_6.

E. Chemical Properties

Uranium hexafluoride is an extremely reactive substance. Its chemical properties are in many respects analogous to those of the higher fluorides of the actinides and of the chromium subgroup elements. Those hexafluorides can be arranged in the following order of stability towards dissociation into fluorine and lower fluorides[120]: PuF_6, NpF_6, UF_6, MoF_6, WF_6. Bromine trifluoride fluorinates compounds of uranium, molybdenum, and tungsten with formation of the hexafluorides, but plutonium hexafluoride acts towards BrF_3 as a fluorinating agent:

$$PuF_6 + BrF_3 = PuF_4 + BrF_5.$$

Plutonium hexafluoride is able to fluorinate the lower fluorides of all the elements standing to its right in the above series, giving the higher fluorides. For example, uranium tetrafluoride is fluorinated to UF_6:[121]

$$4UF_4 + PuF_6 = 2U_2F_9 + PuF_4,$$

$$U_2F_9 + 1.5PuF_6 = 2UF_6 + 1.5PuF_4.$$

Neptunium hexafluoride only partially fluorinates BrF_3 to BrF_5. The latest quantitative studies suggest two possible (but not certain) ionisation processes for the hexafluorides:

$$2MF_6 \rightleftarrows MF_5^{+} + MF_7^{-},$$

and

$$2MF_6 \rightleftarrows MF_4^{2+} + MF_8^{2-}.$$

Both processes produce ions, which may, to a certain degree, be stable. Proof that ionisation of this type is possible is provided by preparation of salts containing these ions. At present, however, such salts have been obtained only for uranium: $2RbF.UF_6$, $3AgF.UF_6$, $3NaF.UF_6$, and $3KF.UF_6$.

Uranium hexafluoride reacts with highly-dispersed sodium fluoride at 100° to yield the complex $3NaF.UF_6$;[5,145-147] between 80° and 320° the dissociation pressure of this complex (to UF_6 and NaF) is given by $\log P_{mm} = 10.88 - 50.90/T$, and $\Delta H = -23.2$ kcal $mole^{-1}$. The vapour pressure reaches 760 mm Hg at 363°. When $3NaF.UF_6$ is heated to 400° in a current of nitrogen or fluorine, almost all the uranium hexafluoride present is liberated. When it is heated to 245°–345° under an excess pressure of UF_6 the reaction

$$3NaF.UF_6 = UF_5.3NaF + 0.5F_2$$

takes place. Further reduction to the tetravalent state takes place on heating under excess UF_6 pressure to 550°.

A fundamental property of UF_6 is its tendency to undergo hydrolysis to uranyl fluoride and hydrogen fluoride:

$$UF_6 + 2H_2O = UO_2^{2+} + 2F^- + 4HF_{aq}.$$

The UF_6–HF system has been studied[148,149] by the polythermal method and the equilibrium diagram has been constructed (Fig. 5). Pressure was measured, so that it was possible to plot isobars on the equilibrium diagram. The system has a region corresponding to the formation of immiscible solutions, starting at 61.2°, in the concentration range 10 ± 5 formula % UF_6 to 80 ± 3 formula % UF_6. The highest temperature of separation into layers (101°) occurs at 40–50 formula %. In the low-temperature region a eutectic is formed at -85° and less than 0.5 formula % UF_6. No chemical compound of UF_6 and HF was detected. in the system, so they can be separated by simple distillation. Hydrogen fluoride dissolves up to 10 formula % of the hexafluoride, and the hexafluoride up to 20% hydrogen fluoride (the concentration limits for separation into layers).

Reduction reactions are characteristic. According to Ruff and Heinzelman's observations[2], uranium hexafluoride is reduced to UF_4 at room temperature by gaseous hydrogen. These observations have not been confirmed, however; attempts to reduce UF_6 with gaseous hydrogen between -78° and +100° using traces of water and technical UF_4 as catalysts did not give positive results[58]. Dawson *et al.* studied the reaction between uranium hexafluoride and hydrogen in detail, and concluded, from thermodynamic calculations, that the reduction of uranium hexafluoride by hydrogen should be complete, but that its extent depends on the temperature. Similar calculations for the reaction $UF_4 + 2H_2 = U + 4HF$ showed, however, that at 25° the equilibrium is displaced to the left, while near 1000° it is

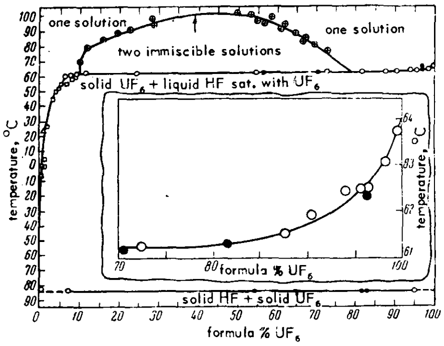

Fig. 5. Equilibrium diagram for the UF_6–HF system[149].

in the opposite direction. The authors confirmed experimentally the reaction between uranium hexafluoride and gaseous hydrogen for various temperatures, duration of reaction, and $H_2 : UF_6$ ratios in the gas mixture. It was established that at 430° the reduction of uranium hexafluoride is fairly complete; below 350° pure UF_4 was not obtained. The use of various catalysts for the reduction did not give positive results, only chlorides showing a significant effect.

Hydrogen halides are reductants for uranium hexafluoride[59,60]. The reaction between HCl and UF_6 at 200° yields a mixture of brown, green, and black products; owing to an incomplete reaction, both the tetrafluoride and intermediate uranium fluorides are formed. Hydrogen bromide reacts with uranium hexafluoride at 80° to yield pale green, friable uranium tetrafluoride powder. The use of carbon tetrachloride as reducing agent is of considerable interest. Nairn *et al.*[61] showed that the reduction of UF_6 by carbon tetrachloride takes place at 100°–200°. Other reducing agents include amorphous carbon[150], which reacts with UF_6 to form UF_4, CF_4, and other fluorocarbons, and also silicon, phosphorus, and sulphur. In the liquid phase UF_6 is reduced by PCl_3 and $SOCl_2$.

Systems based on uranium hexafluoride. A knowledge of systems in which UF_6 is a component is important for various technological reasons. UF_6–halogen fluoride–HF systems have been studied with the aim of setting up processes for fluorination of the metallic blocks obtained in the technology of irradiated uranium.

A study of the UF_6–ClF_3 system (liquid–solid equilibrium) was made by Wendolkowski and Barber[151] (Fig. 6) over a wide range of concentrations (0–100 mole % UF_6), ensuring experimentally that equilibrium was established while the melting and solidification curves were being recorded. With chlorine trifluoride, uranium hexafluoride forms a simple system with a eutectic point at -77.4°, 0.4 mole % UF_6. Enantiotropy was observed at -83.1°. The system shows positive deviation from ideal behaviour. The eutectic point could not be determined experimentally, since the heat of crystallisation of small quantities of uranium hexafluoride is insufficient for the accurate reproduction of the heating and cooling curves at a uranium hexafluoride content of ~0.4 mole %. The composition of the eutectic can be calculated, however, from the solubility data for ideal solutions and the experimental activity coefficients. Calculations carried out by the authors gave 0.4 mole % UF_6. The phase equilibrium in this system was also studied with allowance for pressure[152]. The liquid–vapour equilibrium diagram (Fig. 7) shows the absence of an azeotropic mixture. At 67° the components are completely miscible, but at 75° there exists a range of partial miscibility at 0.3–0.5 mole % UF_6.

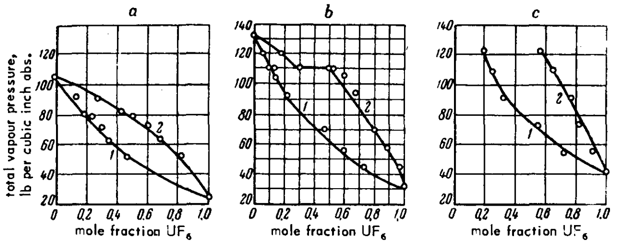

Fig. 7. ClF_3–UF_6 liquid–vapour equilibrium diagrams at various temperatures[152]:
a) 67°; *b*) 75°; *c*) 84°; 1) vapour; 2) liquid.

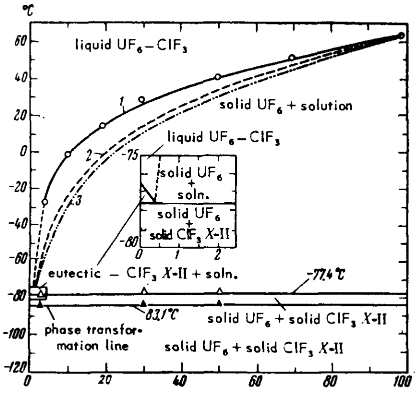

Fig. 6. Equilibrium diagram for the UF_6–ClF_3 system[151]:
1) experimental curve; 2) theoretical curve; 3) ideal curve.

The equilibrium diagram of the ternary HF–UF_6–ClF_3 system is given by Rutledge and Davis[153] for the temperature range -100° to +100° (Fig. 8), from studies of the three binary systems HF–ClF_3,[154] UF_6–ClF_3,[151] and UF_6–HF.[149]

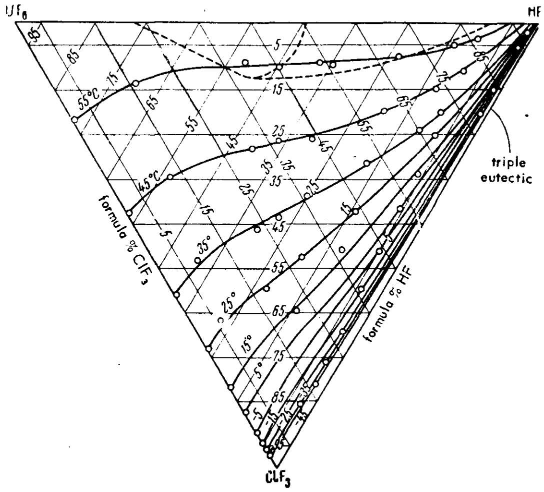

Fig. 8. The UF_6–ClF_3–HF system[153].

It was established that the ternary system, of simple eutectic type, contains pure components as solid phase. The ternary eutectic point of the $HF-UF_6-ClF_3$ system has the composition (formula %) 0.0–0.2 UF_6, 19.5 ClF_3, and 80.5 HF at -91°. The lower temperature limit at which two immiscible liquids saturated with solid uranium hexafluoride exist is 53° [composition (formula %) 49 UF_6, 13 ClF_3, and 38 HF]. Association of the components of the system and change in their association with temperature, pressure, and concentration made a theoretical discussion of this system, similar to that for the above binary system, difficult.

Study of the solid–liquid phase equilibrium in the condensed Br_2-UF_6 system[155] showed that this is a simple eutectic system. The solid phases are the pure components. The system shows positive deviation from ideal behaviour at concentrations $>$ 15 mole % Br_2. The eutectic is at 99–100 mole % bromine, melting point -7.4° ± 0.1°.

The UF_6-BrF_3 and UF_6-BrF_5 systems[156] have been studied to obtain data on the solubility of uranium hexafluoride as a function of temperature and to determine the solid phases existing in equilibrium with the saturated solution. They are simple eutectic systems (Figs. 9 and 10). The solid in equilibrium with the saturated solution contains the pure component. Both solidification and fusion curves were recorded for the UF_6-BrF_3 system. The curves were identical, indicating that equilibrium was attained. The eutectic point is at 6.4° and 4.1 mole % UF_6.

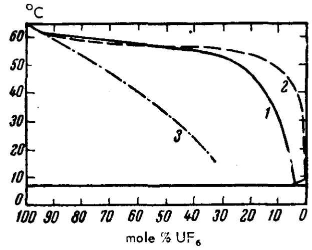

Fig. 9. Solubility curve for the UF_6-BrF_3 system[156]. 1) Experimental curve; 2) curve calculated according to Hildebrand; 3) ideal curve.

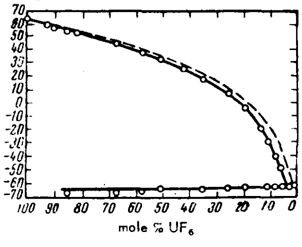

Fig. 10. Phase changes in the UF_6-BrF_5 system[156].

For the UF_6-BrF_5 system (Fig. 10), good agreement was obtained between the solidification and fusion curves. Because of the supercooling effect observed close to the eutectic point (-63.5°), the composition of the eutectic (3.2 ± 0.5 mole % UF_6) was obtained by extrapolation. The vapour pressure of BrF_5[152] was measured at 68° and 80° under conditions of complete miscibility of the components. These systems were also studied by the refraction method[157].

The data obtained in these studies have been used in the separation of uranium hexafluoride by distillation. Work has been carried out on the separation of binary mixtures of UF_6 with ClF_3, HF, Br_2, BrF_3, and BrF_5 and of the ternary mixture of UF_6 with ClF_3 and HF. For the $HF-UF_6$ system, a linear relationship between the composition of the azeotropic mixture and pressure was observed. The UF_6-Br_2 system could not be separated, but a UF_6-BrF_3 mixture is readily separated. The compositions of the azeotropic mixtures in the binary systems formed by HF with Br_2, BrF_3, and BrF_5 have been determined.

7. URANYL FLUORIDE

The fluorine compounds of uranium(VI) include uranium oxide fluorides containing the uranyl group, of which the simplest is uranyl fluoride UO_2F_2. Characteristic features of uranyl fluoride are its high solubility in water and its tendency to undergo reduction and to form various complex compounds.

Uranyl fluoride plays an important part in the technology of nuclear materials, as a product of the hydrolysis of uranium hexafluoride. Hydrolysis may be undesirable in gas-diffusion processes for separating uranium isotopes, since it yields solid components in the gas stream, leading to breakdown of the normal operation of the filtration assemblies. Hydrolysis of UF_6 with the production of uranyl fluoride solution is carried out to isolate uranium from the hexafluoride in a non-volatile form, as a stage in the technological preparation of metallic uranium. A uranyl fluoride solution can be used to prepare the tetrafluoride by reduction, either electrochemically or chemically.

In view of its high solubility and low effective cross-section for thermal neutrons, uranyl fluoride in solution has been suggested as a uranium-containing material for homogeneous nuclear reactors[158].

Uranyl fluoride was one of the first uranium compounds to be described. Methods for its preparation and its composition were reported as early as the beginning of last century by Berzelius[159], and later by Bolton[1]. Their syntheses were based on the reaction between uranium trioxide and hydrofluoric acid or on double decomposition reactions involving repeated treatment of other uranyl salts, for example uranyl acetate, with hydrofluoric acid. Evaporation of the solutions yielded the hydrate $UO_2F_2.nH_2O$.

Most work on the dissolution of uranium trioxide in HF solution has been done only recently, in collecting data on the UO_3-HF-H_2O system[160]. The reaction between uranium trioxide and hydrogen fluoride can also be carried out with gaseous HF at 300° – 500°; anhydrous uranyl fluoride is then obtained. This can also be prepared from uranium ammonium phosphate, which lost first water and then ammonia at 60° and 450° respectively and was then treated with hydrogen fluoride at 500°. Pure UO_2F_2 was left as a non-volatile product[161].

The hydrolysis of uranium hexafluoride is another method of preparing uranyl fluoride. This has been studied in connection with the diffusion method for separating uranium isotopes. Thus Googin[162] hydrolysed liquid UF_6 by adding it to water in a closed vessel, the reaction mixture being cooled. The reverse process (addition of water to solid uranium hexafluoride) has also been used. The solid salt isolated was anhydrous uranyl fluoride. It is reported that hydrolysis of uranium hexafluoride by sulphuric acid solution (1 part of UF_6 to 2 parts of 70% H_2SO_4) yields uranyl sulphate.

A. Physical Properties

Anhydrous uranyl fluoride has a rhombohedral structure[163] with one molecule in the unit cell: $a = 5.755 \pm 0.003$ Å, $\alpha = 42°47' \pm 3'$, space group $R\bar{3}m$.

The heat of formation of uranyl fluoride

$$U(\text{solid}) + O_2(\text{gas}) + F_2(\text{gas}) = UO_2F_2(\text{solid})$$

was calculated by Popov *et al.*[71], who obtained 391.4 ± 3.6 kcal at 32°. The heat of solution of uranyl fluoride in aqueous HF has also been determined. The specimen of uranyl fluoride was prepared by dissolving uranium trioxide in the stoichiometric quantity of aqueous HF with subsequent evaporation to dryness. The dry residue was heated *in vacuo* to constant weight with gradual increase in temperature from 100° to 150°. The product contained 77.17 ± 0.09% uranium. The heat of solution of UO_2F_2 at 32° for component ratios $HF : H_2O = 1 : 400$, $UO_2F_2 : HF = 1 : 4$ is 8.10 ± 0.01 kcal mole^{-1}.

The specific heat of uranyl fluoride has been measured[164] over the range 13° to 418 °K by means of an adiabatic vacuum-type calorimeter. The specific heat, enthalpy, entropy, and free energy of uranyl fluoride in this temperature range have been given. The enthalpy and entropy at 298.16 °K are 63.96 internat. J g^{-1} and 0.4400 internat. J g^{-1}deg^{-1}. No phase changes were observed.

B. Chemical Properties

The most important chemical properties of uranyl fluoride are its solubility and tendency to undergo hydrolysis and complex-formation.

The phase states of sexivalent uranium in aqueous solutions are described by the $HF-UO_3-H_2O$ system, which Marshall *et al.* studied at a constant $UO_3 : F$ ratio of 1 : 2 over the temperature range from the ice eutectic (-13°) to the critical saturation temperature (+377°)[160] (Fig. 11).

The electrical conductivity of aqueous solutions of UO_2F_2 various concentrations (0.0001–6.0 *N*) has been measured at 0°, 25°, 50°, and 90°.[165] The conductance values and the form of the Λ *vs.* $C^{\frac{1}{2}}$ curves show that uranyl fluoride is a very weak electrolyte, whose dissociation shows almost no increase with change in temperature from 0° to 90°. The values of Λ for 25° were corrected for the conductivity of H^+ ions formed by hydrolysis. Extrapolation of the results gave $\Lambda = 87\ \Omega^{-1}\text{cm}^2$ from which $\lambda^0_{UO_2^{2+}} = 32\ \Omega^{-1}\text{cm}^2$ was calculated. Values of the dissociation constant for the reaction:

$$UO_2F_2 \rightleftarrows UO_2F^+ + F^-,$$

were calculated. Although at uranyl fluoride concentrations up to 0.01 *N* the dissociation constant remains almost unchanged (4.34×10^{-5}–4.85×10^{-5}), the authors suggest that the dissociation is more complex than this.

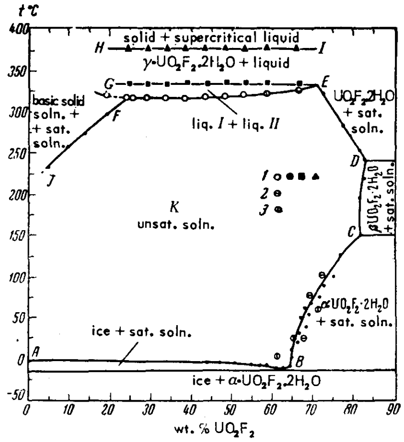

Fig. 11. Equilibrium diagram for the UO_3-HF-H_2O system, constructed from the data of various authors[160].
1) Marshall *et al.*; 2) *Dean; 3) *Kunin.

Johnson and Kraus[166] have measured the density and refractive index of aqueous solutions of uranyl fluoride in the range 1 to 62 wt.% at temperatures close to 25° and 30°. The results were extrapolated to 25.0° and 30.0°. Most of the density determinations were made by the pyknometric method and some with a gradient tube. The refractive indices were determined using an immersion refractometer (reproducibility ± 0.0004). The values found for the density can be expressed by:

$$1/d = 1/d_0 + aF_2 + bF_2^2,$$

where d and d_0 are the densities of the solution and pure solvent, F_2 the weight fraction of UO_2F_2 in the solution, and a and b are constants (at 25° a = -0.9120, b = 0.0567; at 30° a = -0.9126, b = 0.0569). The apparent molal volume of uranyl fluoride in solutions of different concentrations has been calculated: $\Phi_v = 28.0 + 17.5F_2$. The refractive index values can be expressed by:

$$n_D^t = n_D^{t^0} + \alpha c + \beta c^{3/2},$$

where n_D^t and $n_D^{t^0}$ are the refractive indices of the solution and water at temperature t, c the molar concentration of the solution, and α and β are constants (at 25° α = 0.02055, β = -0.00185; at 30° α = 0.02049, β = -0.00183). The n_D values were used to calculate the molar refraction of uranyl fluoride, $R = 17.1 \pm 0.1$ cm^3; this is independent of concentration.

The activity coefficients of uranyl fluoride have been determined from the freezing point depression[167]. They indicate that uranyl fluoride is essentially undissociated in

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* See J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium", Part 1, First Edn., National Nuclear Energy Series, McGraw Hill, New York, 1951, p.569 (Ed. of Translation).

the range 0.1–5 mole % UO_2F_2. The activity coefficients were also determined by Johnson *et al.*[168] using an ultracentrifuge at 30°. The values obtained are close to those calculated from freezing point data, and indicate the existence of a dimerisation equilibrium in uranyl fluoride solutions. For dimerisation, $\Delta H \simeq 5$ kcal and $\Delta S \simeq 19$ e.u. Addition of KF to uranyl fluoride solution considerably increase the stability of the dimer.

When uranyl fluoride dissolves in hydrofluoric acid, fluoro-complexes $UO_2F_n^{(2-n)+}$ are formed. The number of fluoride ions coordinated around the UO_2^{2+} has been calculated[169] by the method of successive approximations from potentiometric measurements (with a quinhydrone electrode) in fluoride-containing buffer solutions in the presence and absence of UO_2^{2+}. The limiting value of the formation function found for the fluoride complex is four, that is, $[UO_2F_4]^{2-}$ is the highest member of the series of complexes formed at a fluoride concentration of 0.3 M. The formation functions of the complexes when the fluoride concentrations are not too high are found from the concentration equilibrium constants for the reactions

$$HF \rightleftarrows H^+ + F^-,$$

$$HF_2 \rightleftarrows H^+ + 2F^-,$$

which are calculated from the pH values. The fact that the formation functions are independent of the UO_2^{2+} concentration shows that in the concentration range studied (up to 0.025 M) the UO_2^{2+} ion does not form polynuclear complexes. The formation constants of the mono-, di-, tri-, and tetra-fluoro-complexes are (litre mole^{-1}): 3.9×10^4, 2.2×10^3, 3.6×10^2, and 23 respectively.

The polarographic behaviour of UO_2^{2+} in a hundredfold excess of fluoride ions has been studied[170] using as base electrolytes 0.1 M KCl and 0.1–0.2 M $NaClO_4$ at pH 1–7. The results were used to calculate the concentration of complex ions $UO_2F_n^{(2-n)+}$ ($n = 1-4$) and it was found that UO_2F^+ and UO_2F_2 are either reversibly reduced or dissociate rapidly to UO_2^{2+} ions, which are reversibly reduced.

The rate constants for the pick-up of electrons and the transfer coefficient α have been calculated. It is suggested that the reaction:

$$UO_2F_n^{(2-n)+} + e = UO_2^+ + nF^-.$$

takes place at the electrode. The rate of disproportionation of U^V depends on the F : U concentration ratio.

Complex aquo-compounds formed from uranyl fluoride and an alkali fluoride can be represented as a genetic series[171] (Table 5). Of the twelve theoretically possible types of fluoro-compound in the series, ten have been obtained. In complex compounds based on the uranyl ion, the fluoride ion may occupy either one or two coordination positions (the latter in binuclear compounds). Three types of binuclear complex in which fluorine acts as a bridging group have been discovered (Table 5). There are no indications of compounds containing more than two uranium nuclei[171].

TABLE 5. Genetic series of complex aquo-compounds derived from uranyl fluoride and an alkali fluoride[171].

Compound type	Moles U / Moles F	Example	Reference
$[(UO_2)_2F]^{3+}$	1 : 0.5	none obtained	
$[UO_2F]^+$	1 : 1.0	Na $[UO_2F(C_2O_4)_2(H_2O)]$	172
$[(UO_2)_2F_3]^+$	1 : 1.5	K_2 $[(UO_2)_2F_3(O_2)(OOH)(H_2O)_4]$	173
$[UO_2F_2]^0$	1 : 2.0	$[UO_2F_2](H_2O)_2$	
$[(UO_2)_2F_5]^-$	1 : 2.5	Na $[(UO_2)_2F_5(H_2O)_4]$	
$[UO_2F_3]^-$	1 : 3.0	Na $[UO_2F_3(H_2O)_3].H_2O$	1
$[(UO_2)_2F_7]^{3-}$	1 : 3.5	K_3 $[(UO_2)_2F_7(H_2O_2)]$	174
$[UO_2F_4]^{2-}$	1 : 4.0	exists in aqueous solution as the ion $[UO_2F_4]^{2-}$	169
$[(UO_2)_2F_9]^{5-}$	1 : 4.5	K_5 $[(UO_2)_2F_9]$	174
$[UO_2F_5]^{3-}$	1 : 5.0	Ba_3 $[UO_2F_5(H_2O)]_2$	1
$[UO_2]_2F_{11}]^{7-}$	1 : 5.5	non obtained	
$[UO_2F_6]^{4-}$	1 : 6.0	Na_4 $[UO_2F_6]$	175

Note. The square brackets are placed arbitrarily, irrespective of other ligands in the coordination sphere of the complexes.

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