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MECHANISMS OF THE HYDROLYSIS OF AROMATIC SULPHONYL CHLORIDES AND OF ALKYL AND ARYL ARENESULPHONATES

R. V Vizgert

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INTRODUCTION

The reactions of esters involving the carbonyl group, *i.e.* hydrolysis [1-7], alcoholysis [8,9], and ammonolysis [10,11], have been widely discussed in the literature, but considerably less work has been done on the corresponding reactions involving the sulphonyl group: those with sulphonyl chlorides and the esters of aromatic sulphonic acids.

The significance of these reactions in organic chemistry is not limited to the production of dyes [12], drugs [13], surface-active agents [14], insecticides [15], etc. [16] They occupy an important position in the general theory of solvolytic processes. In the present review an attempt will be made to summarise and systematise published information on the hydrolysis of aromatic sulphonyl chlorides and aryl and alkyl sulphonates, and also to compare the specific features of reactions involving the sulphonyl group with the corresponding reactions in which the carbonyl group takes part.

1. SUBSTITUTION IN COMPOUNDS CONTAINING SULPHONYL OR CARBONYL GROUPS

In the carbonyl group an octet is formed by the carbon–oxygen double bond in the

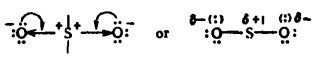


group and by the two covalent bonds linking the carbon with oxygen and with the radical R. Owing to the presence of mobile π electrons and also the great electronegativity of oxygen, the double bond is readily polarised in the direction of the oxygen, so that the electron density is diminished on the carbonyl carbon and increased on the oxygen, which thus forms the negative pole, while the carbon is the positive pole, of the molecular dipole. The electrophilic character of the carbon creates favourable conditions for its attack by nucleophilic reagents; hence most nucleophilic substitution and addition reactions in compounds containing a carbonyl group involve the nucleophilic reagent attacking the carbonyl carbon [17,18].

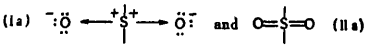
In compounds containing a sulphonyl group the octet rule can be maintained provided that, if two oxygen atoms are linked with the sulphur atom in a sulpho-group by semipolar bonds



the other two bonds (linking the sulphur with oxygen and with the radical R) are covalent. With this distribution of electrons the sulphur is positively charged, which would seemingly facilitate attack by nucleophilic reagents. Actually, the presence of a complete octet hinders this attack. Nevertheless, when it is remembered that the octet rule does not extend to elements of the third and higher periods in the Periodic System, and the sulphur atom can enlarge its octet, the following interpretation is possible for the structure of the $>SO_2$ group



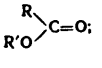
Adoption of the two extreme formulae (Ia) and (IIa):



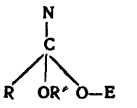
does not, of course, represent the actual distribution of electrons, and is useless for predicting reactivity.

Recently the presence of a semipolar bond in these compounds has been denied on the basis of the following results. The S–O interatomic distances in the $>SO_2$ group have been found to be 1.432 Å, which approximates to the length of a double bond, while those of an S–O single bond in the group S–O–R are 1.7 Å; this is attributed[19] to the formation of a π bond by the 3*d* orbitals of the sulphur atom. On the other hand, the Hammett constant σ for the *p*-SO_3 group is similar to the values obtained for other *para*-substituents (the p*K* relates to the ionisation of a proton in the substituent groups, not the SO_3H, in substituted benzenesulphonic acids), which suggests that conjugation occurs also in sulphonate ions, and that the sulphur atom in sulphonic acids can expand its octet to a decet or a dodecet[20,21]. However, the tendency to such expansion is slight, since compounds containing the $>SO_2$ group do not yield enolic forms[22]. Consequently the sulphur in the SO_2 group is positively charged, its shell of valence electrons contains vacant orbitals, and like carbonyl carbon it can undergo nucleophilic attack, although to a considerably smaller extent. Thus, whereas the carbonyl group readily adds on anions or molecules having lone pairs of electrons, such reactions are difficult with the sulphonyl group.

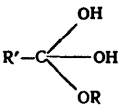
The second difference lies in peculiarities associated with the formation of the transition state. A reactant carboxylic ester molecule has a planar structure of the type:



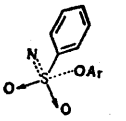
as the nucleophilic reagent approaches, all three substituent groups move closer and, at the instant of formation of the intermediate, yield a tetrahedral structure, with electrophilic reagents adding on to the oxygen, and nucleophilic reagents to the carbon



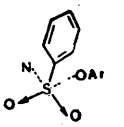
If the resultant splits off a simple molecule and gives a functional group with a double bond, this does not affect the kinetics, since the slowest process is the addition. Bender showed that the intermediate product is tetrahedral[23] in alkaline and in acid hydrolysis:



The sulphur in a sulphonyl group is coordinatively saturated, and it is therefore difficult to imagine the formation of an intermediate product by addition of a nucleophilic species to the sulphur atom. If, however, reactions involving the sulphonyl group are accomplished in a single transition state, the bonds can probably be distributed in two possible ways: (*a*) the attacking and the eliminated groups are in the same plane as the sulphur and oxygen atoms:



or (*b*) the attacking and the eliminated groups are in a plane perpendicular to the O ← S → O plane



Changes in bond angle then require considerable amounts of energy.

Finally, the third difference between compounds containing sulphonyl and carbonyl groups consists in the different polarities of the S–Cl and C–Cl bonds in sulphonyl and acyl chlorides respectively, of the S–OAr and C–OAr bonds in aryl sulphonates and benzoates, and of S–OAlk and C–OAlk bonds in alkyl sulphonates and benzoates. All these factors should produce differences with respect to catalysts, and in the steric effects of substituents, in the influence of the polarity of the solvent and the nucleophilic character of reagents on the rate of hydrolysis, and hence should be shown also in reaction mechanisms.

2. SITE OF BOND RUPTURE ON HYDROLYSIS

The hydrolysis of esters may take place either by an acyl–oxygen[24-27] or by an alkyl–oxygen[28-34] mechanism, more rarely by both mechanisms at the same time[35-38]. The mechanism of hydrolysis is substantially affected by the electronegativity of R and R′ in the ester R.COOR′, and

also by the presence of substituents which cause steric hindrance at the point where reaction occurs[29,39,40]. Esters formed by carboxylic acids with primary aliphatic alcohols, substituted benzyl alcohols, and phenols are hydrolysed by an acyl–oxygen mechanism[41–44]. An alkyl–oxygen mechanism is favoured by increasing the strength of the acid[36] and by introducing electron-donor groups into R′, which increase the stability of its ionic carbonium form, as is the case with the esters of tertiary alcohols[45]. The question of the site of bond rupture is settled unambiguously by isotopic and stereochemical methods.

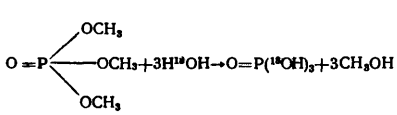
Use of water containing heavy oxygen in the study of the hydrolysis of alkyl and aryl sulphonates has enabled the site of bond rupture to be established with certainty: in the former case it is the alkyl–oxygen bond which is broken[46], and in the latter case the bond linking sulphur with the oxygen of the phenoxy-group[47,48]. Investigation of the reactivities of alkyl and aryl sulphonates in other nucleophilic substitutions, such as their reactions with amines, alkoxides, etc., also indicates the presence not only of different labile bonds but also of different reactive centres, in the first type of compound the carbon atom of the alkyl group, and in the second the sulphur atom of the sulpho-group[49–56].

3. INFLUENCE OF CATALYST ON THE MECHANISM OF HYDROLYSIS

The kinetics of the saponification of esters by acid hydrolysis is complicated by the effect of the acid formed during hydrolysis[57,58]. In hydrolysis in acid medium it is the cation of the protonated form of the ester $RCOOHR^+$ which reacts[59,60]. This is supported by the presence of an *ortho*-effect in the hydrolysis of substituted phenyl acetates in the presence of an acid catalyst[61]. Bender was able to show that, in the acid hydrolysis of ethyl benzoates in the presence of $H_2{}^{18}O$, the rate of oxygen exchange is 20% of that of hydrolysis, and hence that a true intermediate, not a transition complex, is formed[23]. In several cases, however, no strict proportionality is observed between $\log k$ and the Hammett acidity function, the reaction velocity being proportional to the acid concentration, which indicates that the intermediate compound is very complex. The reaction is probably bimolecular, rapid addition of H^+ to the oxygen of the ester first taking place, followed by the rate-determining stage of the reaction in which the carbon atom is attacked by water molecules.

Alkyl–oxygen and acyl–oxygen bonds are not affected in the same manner by the use of acid and alkaline catalysts. In saponification with alkalis it is mainly the latter type of bond which is cleaved; hydrolysis in neutral and acid media favours rupture of the alkyl–oxygen bond.

It has been shown by an isotopic method that the alkaline hydrolysis of trimethyl phosphate involves fission almost exclusively of P–O bonds:



$$O{=}P(OCH_3)_3 + 3H^{18}OH \rightarrow O{=}P(^{18}OH)_3 + 3CH_3OH\ .$$

In contrast, the acid-catalysed or autocatalytic hydrolysis of trimethyl phosphate is accompanied by bond cleavage in both the possible ways, 30% at the expense of P–O and 70% at the expense of C–O bonds[62,63].

The effect of substituents in the acid hydrolysis of carboxylic esters is slight and shows little regularity[27].

With esters of strong acids, in contrast to those of carboxylic acids, the rate of hydrolysis does not increase in the presence of acid catalysts[36,64–66]. This is probably because the basicity of carboxylic esters is substantially greater than that of sulphonic esters or sulphonyl chlorides. As a result, the concentration of the protonated form of the latter is vanishingly small at low acidities; this is responsible for the absence of acid catalysis. In the vicinity of 100% H_2SO_4, in oleum, and in an H_2SO_4–HSO_3Cl mixture, acid solvolysis of $ArSO_2Cl$ occurs and involves preliminary addition of two protons to the SO_2Cl group[67]. The rate of hydrolysis of ethyl benzenesulphonate is constant at pH 1.4–6.4 and at low alkali concentrations, but increases in proportion to the alkali concentration when this exceeds 0.1 *N*.[68] Therefore the kinetics of the hydrolysis of alkyl sulphonates in acid, neutral, and feebly alkaline solutions obeys a first-order equation.

The hydrolysis of benzenesulphonyl chlorides occurs in a similar manner to that of alkyl benzenesulphonates. The reaction velocity remains constant from pH 1 to 8, and increases sharply at pH 9. In neutral and acid media hydrolysis is produced almost exclusively by unionised water molecules[69,70]. Substituted phenyl esters of benzenesulphonic acid, other than mono- and di-nitrophenyl benzenesulphonates, are not hydrolysed at all in neutral and weakly acidic media[71]. Thus, phenyl benzenesulphonate does not yield even traces of phenol when heated in 60% aqueous dioxan at 120° for 3 weeks[72]. Hence, whereas the hydrolysis of carboxylic esters is accelerated by acid and alkaline catalysts, the rate of hydrolysis of alkyl and aryl sulphonates is independent of the hydrogen-ion concentration.

In spite of the apparent similarity between alkyl and aryl sulphonates, they differ fundamentally in their behaviour in neutral and weakly alkaline media. Whereas the rate of hydrolysis of alkyl sulphonates increases slowly and progressively with increase in alkalinity of the medium, the rate of hydrolysis of aryl sulphonates increases sharply under these conditions.

In the absence of bases, the hydrolysis of alkyl benzenesulphonates occurs according to the equation[49]

$$RSO_2OAlk + H_2O \rightarrow RSO_2OH + AlkOH$$

and obeys the first-order law:

$$\frac{dx}{dt} = k(a-x),$$

where $a-x$ is the concentration of the ester.

In the presence of bases, the hydrolysis of alkyl benzenesulphonates occurs according to the equation[73]:

$$RSO_2OAlk + OH^- \rightarrow RSO_2O^- + AlkOH\ , \quad (R = C_6H_5)$$

and obeys the kinetic equation:

$$\frac{dx}{dt} = k_1(a-x) + k_2(a-x)(b-x),$$

where $a-x$ is the ester concentration, $b-x$ the hydroxide-ion concentration, k_1 the first-order rate constant, and k_2 the rate constant of the bimolecular reaction. If relatively high alkali concentrations are used, the neutral hydrolysis can be neglected. Thus for ethyl benzenesulphonate in 0.01 *N* NaOH, $k_2 = 0.0730$ litre mole^{-1} sec^{-1}, and at this temperature $k_1 = 0.000482$ sec^{-1} (in aqueous–alcoholic medium). The activation energies of alkaline and neutral

hydrolysis differ little from one another (21 120 and 22 030 cal mole^{-1}). For ethyl *m*-nitrobenzenesulphonate in 0.033 *N* NaOH $k_2 = 5.7 \times 10^{-3}$ litre mole^{-1} sec^{-1} and $k_1 = 5.23 \times 10^{-5}$ sec. The activation energies for neutral and alkaline hydrolysis of this ester are also quite close to one another, 19 570 and 18 270 cal mole^{-1}.[74] The values given here for k_2 and k_1 were calculated independently of one another, and therefore k_2 includes both alkaline and neutral "aqueous" hydrolysis. In order to calculate k_2 for alkaline hydrolysis alone, a method of graphical differentiation can be used, where

$$k_2^1 = \frac{dx/dt - k_1(a-x)}{(a-x)(b-x)},$$

for ethyl *m*-nitrobenzenesulphonate $k_2^1 = 0.00081$ and $k_2 = 0.00114$ litre mole^{-1} min^{-1}. A graph of the variation of x with t shows that under these conditions the "aqueous" hydrolysis accounts for 30% of the total change in concentration of the compound.

Tommila and Lindholm[49] note also that, in the solvolysis of ethyl benzenesulphonate (in water, methanol, or ethanol), the activation energy is constant (~ 22 000 cal) and the differences in reaction velocities are produced solely by a change in the frequency factor, the logarithm of which varies between 11.22 and 9.5. This can probably be attributed to the absence of any displacement of electrons in the SO_2 group under the influence of the field of the hydroxide ion or the water dipoles, since the corresponding carboxylic esters show an appreciable difference in activation energy with change in polarity of the medium or in the nature of the catalyst.

Aryl sulphonates are hydrolysed only in the presence of alkaline catalysts, according to the equation[74]

$$ArSO_2OAr' + 2OH^- \rightarrow ArSO_3O^- + Ar'O^- + H_2O,$$

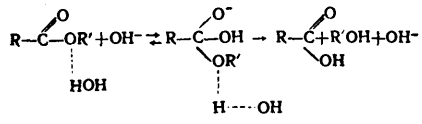
the reaction following a second-order expression which takes into account the double consumption of alkali

$$\frac{dx}{dt} = k(a-x)(b-2x).$$

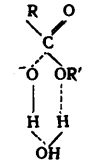
The activation energy E and the frequency factor A for hydrolysis in alkaline aqueous dioxan solution are lower with phenyl benzenesulphonate than with the corresponding ethyl ester (17 860 cal mole^{-1} and log A = 8.66 compared with 19 070 cal mole^{-1} and 9.65), providing a further indication of different mechanisms of hydrolysis with these esters.

According to Hinshelwood *et al.*[2] the activation energy is affected by two factors, the necessity for (1) overcoming the repulsion between the ester molecule and the OH^- ion, and (2) weakening the original bonds (deflecting them from the normal position to the configuration in the transition state).

In the alkaline hydrolysis of carboxylic esters repulsion is least at the carbonyl carbon, and the hydroxide ion attacks this atom, since repulsion is weak, and the activation energy comparatively low. A diminution in activation energy is also favoured by addition of water molecules and formation of an intermediate complex, which probably precedes addition of the OH^- ion[2-4]:



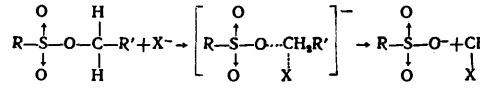
It has recently been suggested that in the transition state an ester molecule, a water molecule, and a hydroxide ion form a six-membered ring. Such an active complex, in which bonds which are being broken alternate with bonds which are being formed, is produced more easily if an alternation of charges on the ions and on the polar bonds is achieved. This additional electrostatic effect lowers the energy of repulsion and favours the formation of cyclic transition complexes[75,76]:



Nucleophilic substitution occurs quite differently in benzenesulphonic esters. Nucleophilic attack on the sulphur atom in the $>SO_2$ group is difficult, although the atom is positively charged. The latter tends to draw off the electrons in the chain towards itself: S ← O ← C; as a result, the alkyl carbon acquires a weak positive charge, and the hydroxide ion adds on to this atom. However, the attraction between the negative ion and the carbon atom is weak, and consequently the activation energy and the frequency factor for the hydrolysis of alkyl sulphonates are far higher than for the corresponding carboxylic esters. In the alkaline hydrolysis of ethyl benzoate in water, for example, E = 12 700 cal and log A = 7.76, while with ethyl benzenesulphonate in water E = 21 100 cal and log A = 12.70.[61] On the other hand, the entropy of activation is less negative with alkyl sulphonates (-10 cal deg^{-1} mole^{-1}) than with ethyl benzoate (-24.9 cal), indicating different degrees of strain in the structures in the transition state.

Whereas in the alkyl sulphonates the transition state has a free, unstrained structure, in the carboxylic esters there is a rigid structure, associated with a redistribution of electron density in the carboxyl group in the transition state.

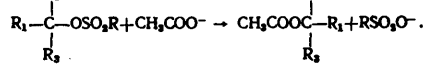
The hydrolysis of alkyl benzenesulphonates is bimolecular, takes place in one step, and, in conformity with Hughes and Ingold's terminology, is an S_N2 reaction[77]



where X = OH^-, $C_2H_5O^-$, or other nucleophilic reagent.

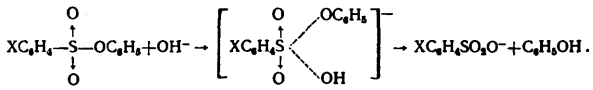
It is probable that solvolysis takes place by the same mechanism[78,79].

Reaction of alkyl sulphonates with alkali-metal carboxylates occurs by an S_N2 mechanism with Walden inversion[80,81]:



With phenyl benzenesulphonates the difficulty of nucleophilic attack by the OH^- ion on the phenyl group results in

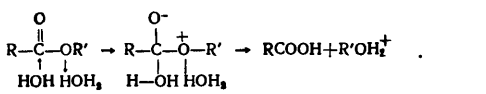
hydrolysis occurring by its attack on the sulphur atom, and perhaps corresponding to the transition state[71,72]



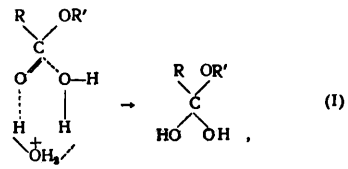
In contrast to the alkyl sulphonates, the reaction occurs here by an "acyl"–oxygen mechanism. Whereas with carboxylic esters such a mechanism of hydrolysis depends on the electrophilic character of the carbonyl carbon and the polarity causing rupture of the C–O bond, with benzenesulphonic esters it depends on the electrophilic character of the sulphur and on the polarity of the S–O bond, which, incidentally, is greater in the aryl sulphonates than in the alkyl sulphonates. Aryl sulphonates provide convenient subjects for studying the mechanism of hydrolysis, since both of these factors can be varied by varying the nuclear substituents in the phenol and in the benzenesulphonic acid. Rupture of the S–O bond was established in an isotopic investigation[48] of the alkaline hydrolysis of phenyl *p*-nitrobenzenesulphonate, nitrophenyl benzenesulphonate, 2,4-dinitrophenyl *o*-nitrobenzenesulphonate, and 2,4-dinitrophenyl toluene-*p*-sulphonate and of the neutral hydrolysis of the latter two esters and also of 2,4-dinitrophenyl benzenesulphonate.

In the alkaline hydrolysis of phenyl benzenesulphonate (on being heated with KOH in a dioxan–$H_2{}^{18}O$ mixture at 90° for 1 h) no exchange of ^{18}O with the oxygen atoms in the ester takes place. These results indicate that the reactions under investigation do not involve the intermediate addition of the OH^- ion to the sulphur atom, but are reactions of type S_N2 occurring by a synchronous one-step mechanism[48]. In this respect the phenyl benzenesulphonates resemble the phenyl benzoates. Whereas when the OH^- ion attacks the carbonyl carbon in ethyl benzoate an intermediate product is formed with a life corresponding to the molecule and a period of existence comparable with the collision period[28], with phenyl benzoate no isotopic oxygen is detected in the unchanged molecule, and the reaction probably takes place by a synchronous mechanism, which facilitates an increase in polarity of the C–O bond[82].

In the acid hydrolysis of carboxylic esters, the proton combines with the ethereal oxygen, and the second step results in addition to the carbonyl carbon of an OH^- ion from the water[57]:

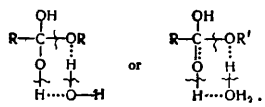


Syrkin gives convincing arguments against the above scheme for acid hydrolysis. It is not clear how the desolvation of H_3O^+ aq, which requires much energy, is compensated for, and it is difficult to understand why the proton adds on to the ethereal and not the carbonyl oxygen, which has a larger negative charge. The possibility of redistributing the *p*-electrons of the oxygen gives the carbonyl oxygen a partial negative charge, while the ether oxygen has a partial positive charge, so that the proton probably adds on to the former, while the hydroxyl from water adds on to the more positive carbonyl carbon[75] according to the scheme:



(I)

with subsequent addition of a water molecule or H_3O^+



Such a six-membered mechanism is, in the opinion of its authors, free from the defects of earlier schemes.

The presence of the intermediate compound (I) was demonstrated by the work of Bender[28].

The absence of double bonds in benzenesulphonic esters makes impossible the displacement of electrons necessary for both the above processes; therefore the hydrogen ion has no catalytic effect on the hydrolysis of alkyl and aryl sulphonates.

4. INFLUENCE OF THE POLAR EFFECTS OF SUBSTITUENTS ON THE RATE OF ALKALINE HYDROLYSIS OF ESTERS

(*a*) Influence of the Nature of the Acid Component and of Substituents in the Acid Component

The influence of substituents, transmitted through the benzene ring[74] to the sulpho-group, follows, according to results obtained for the alkaline hydrolysis of alkyl and aryl sulphonates[74] and also the "aqueous" hydrolysis of aromatic sulphonyl chlorides[83], the general rules. Electrophilic substituents increase, whereas electron-donor substituents decrease, the rates of hydrolysis of alkyl and aryl sulphonates and of aromatic sulphonyl chlorides[50,83] (see Table 1).

TABLE 1. Rate of hydrolysis of alkyl and aryl sulphonates and of aromatic sulphonyl chlorides (70% dioxan–water solution).

Substituent X	Aryl sulphonates $XC_6H_4SO_3OC_6H_5$			Ethyl sulphonates $XC_6H_4SO_2OC_2H_5$			Aromatic sulphonyl chlorides $XC_6H_4SO_2Cl$		
	10^3k_{20}	E	$\log P_z$	10^3k_{20}	E	$\log P_z$	10^3k_{20}	E	$\log P_z$
4-CH_3O	0.076	19260	8.92	0.248	20880	10.49	22.6	14550	6.20
4-CH_3	0.145	18650	8.78	0.291	20150	10.10	24.5	13810	5.74
H	0.374	17860	8.66	0.596	19070	9.65	34.3	13430	5.30
4-Cl	1.120	17190	8.72	1.445	18800	9.88	49.7	12310	5.02
4-Br	1.128	17060	8.60	1.440	18270	9.52	49.1	12310	5.05
4-NO_2	26.3	13160	7.40	6.52	17710	9.80	$k_{20=123.3}$	10350	4.56
3-NO_2	11.44	15200	8.35	5.45	18270	10.10	128.7	11000	4.55
2-NO_2	7.34	16340	8.92	14.08	18580	10.72	45.3	13580	5.87
2.5-Cl_2	2.97	17030	9.00	5.92	18240	10.12	34.17	12870	5.25

A similar order for the effect of substituents is observed in the hydrolysis of esters formed by bishydroxyphenyl sulphone with substituted benzenesulphonic acids [72,84,85] (see Table 2).

The units of the rate constants for the alkaline hydrolysis of alkyl and aryl sulphonates are litres $mole^{-1}$ sec^{-1}; the rate constants for the hydrolysis of aromatic sulphonyl chlorides are measured in sec^{-1}.

In the bimolecular reaction the substituents increase the activation energy in the same sequence ($4\text{-}NO_2 < 4\text{-}Cl <$ $< 4\text{-}Br < 4\text{-}CH_3 < 4\text{-}CH_3O$) as that in which they increase the electron density at the point of reaction.

However, although the effects of different substituents on the rates of hydrolysis of ethyl and aryl sulphonates and of benzenesulphonyl chlorides are in the same order, their relative magnitudes differ for the two reactions. Phenyl benzenesulphonate is saponified more slowly than the corresponding ethyl ester. Introduction of chlorine or bromine in the *para*-position has some effect in levelling out the rates of hydrolysis of esters formed by the two types of alcohol. Introduction of a *p*-methoxy-group diminishes the rates of hydrolysis of the ethyl and phenyl esters by factors of 2.3 and 5 respectively. When a nitro-group is introduced into the *meta*- and especially the *para*-position, the rate of hydrolysis of the phenyl esters begins to exceed that of the ethyl esters (introduction of NO_2 in the *para*-position increases the rates of hydrolysis by factors of 70 and 11.5 respectively). With two nitro-groups, in positions 3 and 5, the phenyl ester is saponified six times as rapidly as the corresponding ethyl ester. These results show that substituents in the acid component exert a greater influence on the rate of hydrolysis of phenyl esters than of ethyl esters.

The variation in the activation energy and the preexponential factor support the above suggestion. Their values are lower, and vary within wider limits, with the phenyl than with the ethyl esters. The lowest values are obtained with the *p*-nitro-derivatives, 13 160 and 7.4 respectively for the aryl sulphonates, and 17 710 and 9.8 for the ethyl sulphonates; the highest values are observed with the methoxy-derivatives, 19 260 and 8.92 for the aryl sulphonates, and 20 880 and 10.49 for the ethyl sulphonates. The wide variations in activation energies and preexponential factors with the aryl sulphonates are a consequence of the greater influence of the nature of substituents in the acid component on the rate of hydrolysis in the case of aryl sulphonates compared with ethyl sulphonates.

The difference in the influence of the orientation of substituents on the rates of hydrolysis of ethyl and aryl sulphonates is especially marked with *ortho*-substituents. Ethyl *o*-nitrobenzenesulphonate is saponified twice as rapidly as the corresponding *para*-derivative, while phenyl *o*-nitrobenzenesulphonate is saponified at one-quarter of the rate for the corresponding *p*-nitrobenzenesulphonic ester. The effect of the position of the nitro-group on the rate of hydrolysis of the ethyl esters can be represented by the following sequence:

$$o\text{-}NO_2 > p\text{-}NO_2 > m\text{-}NO_2 > H;$$

for the phenyl esters the sequence is different:

$$p\text{-}NO_2 > m\text{-}NO_2 > o\text{-}NO_2 > H.$$

2,5-Dichlorobenzenesulphonic esters are saponified more rapidly than the corresponding unsubstituted esters, the increase in rate of hydrolysis being particularly great with the ethyl ester, and ethyl 2,5-dichlorobenzenesulphonate being saponified twice as rapidly as the corresponding phenyl ester. Thus introduction of substituents into the *ortho*-position, compared with the *meta*- and *para*-positions, facilitates hydrolysis of ethyl sulphonates and hinders that of aryl sulphonates.

It is interesting that the effect of *ortho*-substituents on rate of hydrolysis shows the same trend with aryl sulphonates as with aromatic sulphonyl chlorides and carboxylic esters, as is evident from Table 3. Ethyl *o*-nitrobenzoate and phenyl *o*-nitrobenzenesulphonate are saponified more rapidly than the unsubstituted esters, but considerably more slowly than the *m*- and especially the *p*-nitro derivatives (see Table 3).

The effect of *meta*- and *para*-substituents in benzenesulphonic acid on the rate of alkaline hydrolysis of the aryl sulphonates is in the same order as with the benzoic esters [86,87] (see Table 4).

Thus aryl sulphonates exhibit greater resemblances to carboxylic esters than to ethyl sulphonates, which confirms the different mechanisms of hydrolysis with alkyl and with aryl sulphonates. In the former case the reactive centre is the carbon of the alcohol radical, and in the latter the

TABLE 2.

Acid $p\text{-}XC_6H_4SO_2OH$	10^3k_{20}	10^3k_{50}	E	log P_z
H	3.10	15.45	15420	8.64
p-Cl	4.42	21.70	15400	8.80
p-Br	3.84	16.19	15100	8.49
m-NO_2	38.8	171.20	14000	9.33

TABLE 3. Effect of the position of the nitro-group in the benzene nucleus on the rate of hydrolysis of aromatic sulphonyl chlorides, aryl sulphonates, and ethyl carboxylates and sulphonates (values of 10^5k_{50}).

Substituent X	H	*m*-NO_2	*p*-NO_2	*o*-NO_2
$C_6H_4SO_2Cl$ [80]	34.2	128.7	—	45.3
$C_6H_4SO_2OC_6H_5$	37.4	1144.0	2630.0	734.0
$C_6H_4CO_2C_2H_5$	55.0	3110.0	5090.0	334.0
$C_6H_4SO_2OC_2H_5$	56.9	545.0	652.0	1408.0

TABLE 4. Effect of orientation of substituents in benzenesulphonic acid on rate of alkaline hydrolysis of aryl sulphonates (10^3k_{50}, litre $mole^{-1}$ min^{-1}).

Substituent X	$p\text{-}XC_6H_4SO_2OC_6H_5$	$m\text{-}XC_6H_4SO_2OC_6H_5$
NH_2	0.0027	0.034
CH_3O	0.015	0.142
CH_3	0.030	0.055
H	0.078	0.078
Cl	0.233	0.525
NO_2	5.50	2.27

sulphur atom of the sulpho-group. In the aryl sulphonates the substituent in the benzene ring will be considerably closer to the reactive centre, the sulphur atom of the sulpho-group, and therefore its effect on the rate constant of hydrolysis, the activation energy, and the preexponential factor will also be more strongly developed than in the alkyl sulphonates. The shift in the reactive centre from the carbon of the alcoholic radical (in alkyl sulphonates) to the sulphur of the sulpho-group (in aryl sulphonates) also explains the difference in the effect of substituents in the *ortho*-position. *ortho*-Substituents exert a retarding influence on the hydrolysis of aryl sulphonates, aromatic sulphonyl chlorides, and carboxylic esters, where the reactive centre, the sulphur of the sulpho-group and the carbon of the carboxyl group, are directly linked to the benzene ring; and they increase the rate of hydrolysis of ethyl sulphonates, in which the reactive centre is somewhat remote. The decrease in rate of hydrolysis observed in the former case is due to the presence of an *ortho* effect, whereas in the latter case the *ortho* effect is absent.

Although in the case of alkyl and aryl sulphonates and aromatic sulphonyl chlorides a parallelism is observed between rate of hydrolysis and strength of acid (Figs.1 and 2), such parallelism is not observed with esters of acids belonging to different classes of organic acids and differing in strength — acetic, benzoic, and benzenesulphonic acids[72,88] (see Table 5).

In the above series of acid components, the greatest rate of hydrolysis is shown by acetic esters, and the lowest by benzenesulphonic esters

$$CH_3COOH > C_6H_5COOH > C_6H_5SO_2OH.$$

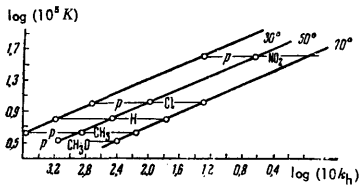


Fig. 1. Linear relations between dissociation constants of substituted benzoic acids and hydrolysis constants of the phenyl esters of the substituted benzenesulphonic acids.

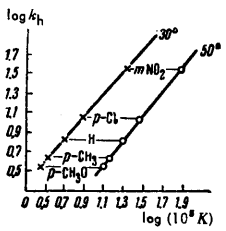


Fig. 2. Linear relations between hydrolysis constants of sulphonyl chlorides and dissociation constants of the corresponding acids.

TABLE 5. Alkaline hydrolysis of ethyl esters.

Acid component	$10^3 k_{18}^*$	$10^3 k_{30}$	$10^3 k_{80}$	E
Acetic	13.2	46.3	—	14450
Benzoic	1.47	5.52	—	15400
Benzenesulphonic	—	0.213	1.09	1600

* k in litre mole^{-1} sec^{-1}.

Within each series, there is a linear relation between hydrolysis rate constant and dissociation constant[42,88] (see Table 6).

The ionisation constants of the acids form to some extent a basis for assessing polar effects on the hydrolysis rate constant. An increase in strength of the acid forming the ester should diminish the stability of its ether bond.

The absence of a correlation between acid strength and rate of hydrolysis in benzoic and benzenesulphonic esters is due to the different mechanisms of hydrolysis and especially to different reactive centres, the carbonyl carbon in the first case and the alkyl carbon in the second.

Let us examine the reasons for deviations from this rule in acetic and benzoic esters. Conjugation between the π electrons of the benzene ring and of the carbonyl group, $\pi\pi$ conjugation, tends to stabilise the carboxylate ion, and thereby facilitates the splitting off of a proton from benzoic acid. Since in the alkaline hydrolysis of carboxylic esters the transition state is saturated, and there is no considerable conjugation with the functional group, the activation energy of hydrolysis for benzoic esters can be expected to exceed that for acetic esters by the stabilisation energy due to the conjugation



in the former esters. It is the presence of this conjugation which diminishes the susceptibility of the carbonyl carbon to nucleophilic attack.

Although, therefore, the phenyl group represents a system of conjugated σ and π bonds, is electron-accepting, and should tend to weaken the C–O bond, *i.e.* favour hydrolysis, benzoic esters are hydrolysed by alkalis more slowly than the corresponding acetic esters. Exactly the same situation occurs with cinnamic and crotonic esters[89]. The

TABLE 6. Effect of acid strength on rate of hydrolysis of esters $RCOOC_6H_5$.

R	Hydrolysis rate constant[42], $10^3 k_{18}$	Acid dissociation constant[42], $10^6 K_{25}$
H	rapidly saponified	214.2
CH_3	245.4	18.0
C_2H_5	150.0	13.4
C_6H_5	22.3	63.0
$C_6H_5CH_2$	605.0	56.6
$C_6H_5CH_2CH_2$	165.0	22.7

steric effect of the phenyl ring is slight, and therefore the appreciably lower rates cannot be due to this cause. Removal of the benzene ring from the carbonyl carbon destroys the conjugation, and an increase in rate of hydrolysis is observed in phenylacetic and phenylpropionic esters owing to the favourable inductive effect[42].

The effect of remoteness of the phenyl radical from the carbonyl carbon on rate of hydrolysis can be determined by calculating the transfer factor of the effect.

From the ratio of the rate constants for the hydrolysis of

$$C_6H_5COOC_6H_5\ (k_1),\quad C_6H_5CH_2COOC_6H_5\ (k_2),\quad C_6H_5CH_2CH_2COOC_6H_5\ (k_3),$$

to the rate of hydrolysis of phenyl acetate k_4 we have k_1: k_4 = = 0.09. The ratio is less than unity owing to conjugation; the transfer factor of the effect is 2.47 for phenylacetic acid, and 1.27 for phenylpropionic acid.

When conjugation between the benzene ring and the carbonyl group of the ester is impossible, as with a phenylacetic, alkaline hydrolysis is more rapid than with the corresponding acetic ester (Table 6). This result can be regarded as evidence of the great capacity of the phenyl group for withdrawing electrons. The phenylpropionic ester shows a decrease in the transfer factor owing to weakening of the inductive effect of the benzene ring. The inductive effect of a substituent is approximately halved by the introduction of the methylene group.

Esters of substituted benzoic acids show complete parallelism between the dissociation constants of the acids and the reactivity of the ester link[90,91].

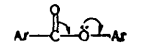
Comparison of the rate constants for the alkaline hydrolysis of phenyl methanesulphonate[82] $k_1 = 0.555$ litre mole^{-1} × × sec^{-1} and phenyl toluene-*p*-sulphonate $k_2 = 0.191$ litre × × mole^{-1} sec^{-1} shows no great decrease in rate of hydrolysis due to introduction of the benzene ring. The ratio of the rate constants k_1: $k_2 = 3$, whereas the corresponding ratio for phenyl acetate and benzoate is 14. The small difference between the rates of hydrolysis of the sulphonic esters shows either that the benzene ring is not conjugated with the sulphonyl group or that the initial and transition states have the same structure. The slight decrease in rate of hydrolysis can be attributed to the steric effect of the ring. The hydrolysis rate constants of the chlorides of carboxylic acids (acetyl and benzoyl chlorides) vary in conformity with the same rules as were observed with carboxylic esters. Different relations are observed with the sulphonyl chlorides: the hydrolysis rate constant of benzenesulphonyl chloride is $10^4 k_{30} = 4.33$, while the value for methanesulphonyl chloride[92] is $10^4 k_{30} = 1.5$ sec^{-1}: here introduction of a benzene ring does not diminish but increases the rate of hydrolysis, probably owing to the predominant influence of the polarity of the S–Cl bond, not of the nucleophilic character of the sulphur, on the rate of hydrolysis of aromatic sulphonyl chlorides.

(*b*) Influence of the Nature of the Alcoholic Component and of Substituents in the Alcoholic Component

The rate of hydrolysis of carboxylic esters is governed mainly by the electrophilic character of the carbonyl carbon. Increase in the electronegativity or acidic properties of the alcohol radical as a result of the inductive effect enhances the electrophilic character of the carbonyl carbon in the ester and thereby facilitates the addition of OH^- ions[42,93,94].

The alcoholic components arrange themselves in the following sequence with respect to their effect on the rate of alkaline hydrolysis of the acetic and benzoic esters: $C_2H_5OH < C_6H_5CH_2CH_2OH < C_6H_5CH_2OH < C_6H_5OH <$ $< HOC_6H_4SO_2C_6H_4ONa < HOC_6H_4SO_2C_6H_5$.

The difference in the rates of hydrolysis of ethyl benzoate (k_4) and phenyl benzoate (k_1) can be attributed to the electronic effect of the phenyl radical. The ratio is $k_1 : k_4 = 22.3 : 1.47 = 15$. With the benzyl ester this ratio is 1.67, while with the phenethyl ester it approaches unity: *i.e.* the electronic effect of the phenyl ring on the carbonyl carbon is almost completely extinguished when they are separated by two methylene groups. The large transfer factor for the phenyl radical is probably due to the influence of the inductive effect and the conjugation effect:



In the benzyl and phenethyl esters the alcoholic components are not involved in the conjugation, and only a slight inductive effect is developed.

A change in the nature of the alcoholic component in esters formed by benzenesulphonic acid with aliphatic alcohols affects not only the rate but also the mechanism of the reaction. If R in the ester $XC_6H_4SO_2OR$ is derived from a primary alcohol, reaction takes place by an S_N2 mechanism[49,74]; if R represents the radical of a benzyl[95], cycloalkyl[96], or a secondary or tertiary aliphatic alcohol, hydrolysis takes place by an ionic mechanism[97]. Alkyl benzenesulphonates in some respects resemble alkyl halides. The alkaline hydrolysis of methyl and ethyl halides in aqueous acetone or alcohol is mainly an S_N2 reaction, whereas isopropyl and t-butyl halides undergo hydrolysis in two steps by an S_N1 mechanism[20,21,98–100].

A study of the kinetics of the hydrolysis of methyl, ethyl, n-propyl, and isopropyl benzenesulphonates in aqueous solution showed that reaction velocity increases in the series[49]

$$\text{n-propyl} < \text{methyl} = \text{ethyl} < \text{isopropyl}.$$

The rate of hydrolysis of isopropyl benzenesulphonate in aqueous acetone or in aqueous dioxan is independent of the concentration of OH^- ions, and remains constant in alkaline, neutral, and acid media. The reaction velocity is governed by fission of the C–O bond:

$$RSO_2OCH(CH_3)_2 \rightarrow [RSO_2O^{-\delta} \ldots CH^{+\delta}(CH_3)_2] \rightarrow$$

$$\rightarrow RSO_2O + \overset{+}{C}H(CH_3)_2 \quad \text{(slow)},$$

$$(CH_3)_2\overset{+}{C}H + HOH \rightarrow (CH_3)_2CHOH + H^+ \rightarrow \text{(rapid)}.$$

s-Butyl benzenesulphonate behaves similarly.

The activation energy in the hydrolysis of sulphonic esters RSO_2OCH_2R' is determined mainly by the repulsion between the attacking reagent (OH^- or H_2O) and the alkyl carbon atom.

When R' = H, repulsion is insignificant, and reaction occurs by an S_N2 scheme. When, however, the energy of repulsion is significant, reaction takes place by an S_N1 mechanism. In conformity with this, the S_N1 mechanism

usually requires a greater activation energy than does S_N2 for similar molecules. The frequency factor is greater for the former than for the latter type of process. Introduction into the alkyl radical of substituents which increase the negative charge on carbon favours the unimolecular and hinders the bimolecular mechanism.

If R′ is an aryl radical, as in the hydrolysis of substituted benzyl toluene-*p*-sulphonates [101] $CH_3C_6H_4SO_2OCH_2C_6H_4X$ in 76.6% aqueous acetone (values of 10^5k_{25} in sec^{-1} for various substituents X are: *p*-NO_2 0.224, *m*-Br 0.880, *p*-Br 4.30, *m*-CH_3O 6.50, H 11.0, *m*-CH_3 19.7, *p*-CH_3 310.0, *p*-CH_3O 480.0), reaction occurs by the S_N1 mechanism and obeys a first-order equation.

The influence of the electronic nature of the substituents and the polarity of the medium on the rate of hydrolysis of benzyl toluene-*p*-sulphonates confirms the presence of an S_N1 ionic mechanism, in which the polarity of the C–O bond plays the decisive part. Therefore substituents which increase the electron density at the site of the reaction accelerate the reaction, while those which diminish the electron density retard the reaction.

The value of ρ for solvolysis is -2.2. The minus sign indicates a more complete intermediate dissociation of the C–O bond than in the solvolysis of $C_6H_5CH_2Cl$ (ρ = -1.33), which is probably linked with the greater solvation of the toluene-*p*-sulphonate ion compared with the chloride ion. Values of σ for all substituents other than *p*-CH_3 and *p*-CH_3O (σ = -0.65 and -2.5 respectively) coincide with those calculated earlier. The discrepancies are due to stabilisation of the $ArCH_2^+$ ion in the intermediate state by the supply of electrons from the *p*-CH_3 and *p*-CH_3O groups.

The solvolysis of cycloalkyl toluenesulphonates containing rings of different sizes (n = 4–15) also passes through a stage of slow ionisation of the toluene-*p*-sulpho-group [96].

Replacement of an alkyl by an aryl radical in the alcoholic component of benzenesulphonic esters fundamentally changes not only the reaction mechanism but also the point of attack. The sulphur atom in the sulpho-group then becomes the reactive centre, and the reaction becomes bimolecular with an S_N2 mechanism (see Table 7).

Alcoholic components arrange themselves in the following sequence according to rate of hydrolysis: C_6H_5OH < < C_2H_5OH < *pp′*-$HOC_6H_4SO_2C_6H_4ONa$ < *p*-$HOC_6H_4SO_2C_6H_5$.

This sequence corresponds to increasing acidity of the reactants with the exception of phenyl benzenesulphonate, which, because of the change in reaction mechanism on passing from alkyl to aryl sulphonates, does not fit into this order. The esters of the di- and mono-hydroxy derivatives of diphenyl sulphone show a further diminution in the stability of the ester link to hydrolysis.

The alcoholic components arrange themselves in the following sequence with respect to the rate of hydrolysis of the carboxylic esters (acetates and benzoates): C_2H_5OH < < C_6H_5OH < $HOC_6H_4SO_2C_6H_4ONa$ < $HOC_6H_4SO_2C_6H_5$, *i.e.* in order of increasing acidic properties. The phenyl esters showed no deviation from this sequence, in conformity with the common mechanism of hydrolysis of these esters.

Substituted phenyl benzenesulphonates show a complete parallelism between the acidity of the alcoholic components and the rate of hydrolysis.

Electrophilic and nucleophilic substituents affect the rate of hydrolysis in the same sense, independently of their orientation in the benzene ring of the phenol or of the benzenesulphonic acid (Table 8 collates the rate constants for the hydrolysis of aryl sulphonates with the dissociation constants of the substituted phenols).

Although the order of the effect of different substituents is the same, the relative magnitude of the effect for each substituent depends on whether it is located in the benzene ring of the acid or of the alcoholic component. Electrophilic substituents (*p*-Cl, *p*-NO_2) exert a greater influence on the rate of hydrolysis of aryl sulphonates when they are located in the phenolic ring (see Table 8). The influence of electron-donor substituents transmitted through the benzene ring of the phenol is weaker than that of the same substituents in the benzenesulphonic acid. If it is assumed that the reactive centre in the hydrolysis of aryl sulphonates is the sulphur atom in the sulpho-group, the greater effect of electrophilic substituents in the benzene ring of the phenol can be explained either by the presence on the oxygen of two pairs of *p*-electrons conjugated with the electrons of the benzene ring or by a considerable increase in polarity of the S–O bond. The variation in the activation energy and the frequency factor corresponds to the changes observed in the rate constant. The influence of substituents in the *ortho*-, *meta*-, and *para*-positions develops differently depending on whether the benzene ring is in the acid or the alcoholic component.

In esters formed by benzenesulphonic acid and a substituted phenol the influence of a nitro-group on the rate of

TABLE 7. Alkaline hydrolysis of benzenesulphonic esters $C_6H_5SO_2OR$, having different phenolic components, in 70% dioxan–water solution [85].

R	$10^3k_{20}^*$	10^3k_{30}	log P_z	E
C_2H_5	0.213	1.09	7.88	16000
C_6H_5	—	0.43	—	—
$C_6H_4SO_2C_6H_4OH$	3.10	15.45	8.64	16500
$C_6H_5SO_2C_6H_4$	4.92	23.25	8.10	15100

* k in litre $mole^{-1}$ sec^{-1}.

TABLE 8. Effect of the nature of the substituents in the phenyl ring on the rate of alkaline hydrolysis of aryl sulphonates [71] $C_6H_5SO_2OC_6H_4X$.

Substituent X	$10^3k_{20}^*$	log P_z	E	Dissociation constant K
2-CH_3	0.129	10.24	20900	$6.3\cdot10^{-11}$**
4-CH_3	0.184	8.78	18500	$6.7\cdot10^{-11}$
3-CH_3	0.263	8.82	18300	$9.8\cdot10^{-11}$
H	0.374	8.66	17900	$1.0\cdot10^{-11}$
4-Cl	2.47	8.77	16700	
3-NO_2	31.50	8.95	15400	$5.3\cdot10^{-9}$
4-NO_2	76.65	9.23	15300	$9.6\cdot10^{-9}$
2-NO_2	134.90	8.95	1000	$7.5\cdot10^{-8}$

* k in litre $mole^{-1}$ sec^{-1}.

** See Ref. 102.

hydrolysis varies in the following sequence: o-NO_2 > > p-NO_2 > m-NO_2; whereas a different order is found in esters of phenol with a substituted benzenesulphonic acid: p-NO_2 > m-NO_2 > o-NO_2. Thus a nitro-group in the *ortho*-position in the benzenesulphonic acid diminishes the rate of hydrolysis of aryl sulphonates and aromatic sulphonyl chlorides, whereas a nitro-group in the *ortho*-position in phenol has a favourable influence, exhibiting only its electronic effect, and producing no steric hindrance.

The influence of substituents, transmitted through the benzene ring of benzoic acid, on the rate of hydrolysis of ethyl and phenyl benzoates is far greater than their influence in the benzene ring of phenol: *i.e.* the observed regularity is opposite to that found for aryl benzensulphonates (see Table 9).

Introduction of a p-NO_2 group into benzoic acid increases the rate of hydrolysis of a benzoate by a factor of 85, but a p-NO_2 group in phenol increases the rate of hydrolysis of the phenyl ester by a factor of only 15. Yet introduction of this group into a benzenesulphonic acid increases the rate of hydrolysis of a phenyl benzenesulphonate by a factor of 70, while the corresponding factor for its introduction into the phenol is 205.

Such a difference in the effect of substituents in the alcoholic component on the rates of hydrolysis of carboxylic and of benzenesulphonic esters results from the difference in the mechanism of their hydrolysis. The reactivity of carboxylic esters is influenced by the electrophilic character of the carbon, which facilitates the approach of the OH^- ion and increases the polarity of the C–O bond undergoing rupture. The reactivity of sulphonic esters depends on the electrophilic properties of the sulpho-group and the polarity of the S–O bond undergoing rupture. Since substituents have a greater effect when present in the acid component than in the alcoholic component of carboxylic esters, the main factor influencing the rate and activation energy of the hydrolysis of such esters is the electrophilic character of the carbon. In benzenesulphonic esters the greater effect of substituents in the phenolic moiety indicates that it is the polarity of the S–O bond which governs the reaction velocity. The more polar the bond, the more readily is it ruptured, which also facilitates a synchronous mechanism of S_N2 type.

Thus the hydrolysis of carboxylic esters can be regarded as a nucleophilic addition, since the reaction velocity will be governed by addition to the carbonyl carbon; whereas the hydrolysis of benzenesulphonic esters is rather a nucleophilic substitution, since the rate depends mainly on the stability of the S–O bond under synchronous reaction conditions.

TABLE 9. Rate of alkaline hydrolysis of phenyl acetates and ethyl benzoates[90].

Substituent X	$XC_6H_4OCOCH_3$ 10^2k_{25}	$C_2H_5OCOC_6H_4X$ 10^2k_{25}
H	53.7	0.2891
m-CH_3	38.83	0.1686
p-CH	31.91	0.1142
m-NO_2	549.00	13.65
p-NO_2	805.0	24.63
p-NH_2	28.15	0.0864

Introduction of more than one nitro-group, whether in the acid or in the alcoholic component, gives a considerable increase in rate of alkaline hydrolysis compared with the mononitrated esters[58,66,103]. The increase in rate of hydrolysis is especially noticeable when two nitro-groups are introduced into the phenolic component (see Table 10).

In order to compare the effect of two nitro-groups in the benzenesulphonic acid with the effect of the same groups in the phenol, it is useful to calculate the transfer factor of the electronic effect of substituents at different ends of the system, from the ratios of the hydrolysis rate constant of phenyl 2,4-dinitrobenzenesulphonate (k_2) to that of the unsubstituted phenyl benzenesulphonate (k_1) and the ratio of that of 2,4-dinitrophenyl benzenesulphonate (k_3) to k_1

$$f_1 = \frac{k_2}{k_1} = \frac{183}{0.06} = 3050;\quad f_2 = \frac{k_3}{k_1} = \frac{880}{0.06} = 14\,300;\quad f_2 : f_1 = 4.7\,.$$

Similarly, for the p-mononitro-derivatives

$$f_3 = \frac{k_4}{k_1} = \frac{6.79}{0.06} = 113;\quad f_4 = \frac{k_5}{k_1} = \frac{15.9}{0.06} = 265;\quad f_4 : f_3 = 2.3\,.$$

The relatively high value of f_2 compared with f_1 is due to the operation of two factors, firstly the increase in polarity of the S–O bond, and secondly the presence of an *ortho* effect in phenyl 2,4-dinitrobenzenesulphonate. The latter effect is confirmed also by the considerably higher activation energy of hydrolysis (by 5000 cal) in phenyl 2,4-dinitrobenzenesulphonate compared with 2,4-dinitrophenyl benzenesulphonate.

With regard to the effect of orientation on the rate of hydrolysis of aryl sulphonates, the following sequence is obtained for the dinitro-compounds: 2,6 > 2,4 > 2,5 > 3,4. In this case, too, the greatest accelerating effect is exerted by two o-nitro-groups. Thus such groups exert no steric hindrance, which is consistent with an acyl–oxygen mechanism for the hydrolysis of these esters.

TABLE 10. Alkaline hydrolysis of nitro-substituted aryl sulphonates.

Ester	$10^3k_0^*$	10^3k_{15}	E	log P_z	ΔS
$C_6H_5SO_2OC_6H_3(NO_2)_2$-2,4	318.0	996.0	11900	9.02	—19.88
2,4-$(NO_2)_2C_6H_3SO_2OC_6H_5$	38.0	183.0	16400	11.68	
3,5-$(NO_2)_2C_6H_3SO_2OC_6H_5$	1.45	5.8	14400	8.67	
2-$NO_2C_6H_4SO_2OC_6H_3(NO_2)_2$-2,4	2450	—	—	—	—
2,4-$(NO_2)_2C_6H_3SO_2OC_6H_4NO_2$-2					
4-$ClC_6H_4SO_2OC_6H_3(NO_2)_2$-2,6	1980	—	—	—	—
4-$ClC_6H_4SO_2OC_6H_3(NO_2)_2$-2,4	1170	—	—	—	—
4-$ClC_6H_4SO_2OC_6H_3(NO_2)_2$-2,5	702	2310	12400	9.77	—16.41
4-$ClC_6H_4SO_2OC_6H_3(NO_2)_2$-3,4	178	560	11990	8.85	—20.67
4-$ClC_6H_4SO_2OC_6H_3$—2-NO_2-4-Cl	44.2	183	14800	10.49	—13.14
4-$ClC_6H_4SO_2OC_6H_3$—2-Cl-4-NO_2	36.7	144	14200	9.97	—15.56
4-$ClC_6H_4SO_2OC_6H_3$—2-Cl-3-NO_2	12.6	63.5	16800	11.53	— 8.43
$C_6H_5SO_2OC_6H_3(NO_2)_2$-2,6	737	2200	11400	8.98	—20.05
2,4,6-$(CH_3)_3C_6H_2SO_2OC_6H_3(NO_2)_2$-2,6	168	631	13800	10.27	—14.17
4-$CH_3C_6H_4SO_2OC_6H_3(NO_2)_2$-2,4	182	382	12800	9.28	—18.75
2,4,6-$(CH_3)_3C_6H_2SO_2OC_6H_3(NO_2)_2$-2,4	84.2	306	13600	9.82	—16.19

* k in litre $mole^{-1}$ sec^{-1}.

The influence of several different substituents on k, E, and P_z does not show the strict regularity characteristic of single *para*-substituents. In this case relations are complicated by variation not only in the nature of the substituents but also in their position. With each individual ester, however, variation in the rate constant depends on the activation energy, the reaction velocity increasing when the latter decreases. The temperature-independent factor P_z increases with increase in activation energy.

The entropy of activation is very negative, fluctuating between -13 and -20 cal deg^{-1} mole^{-1}, which approaches the entropy of activation for the hydrolysis of benzoic esters (-24.9) and differs from the corresponding value for ethyl benzenesulphonates (-10 cal deg^{-1} mole^{-1}). Such a difference in entropy of activation is caused by differences in the electron distribution on formation of the transition structures. The more negative the entropy of activation, the more polar is the active complex. With aryl sulphonates there is a rigid structure, associated with the electron distribution and with a change in solvation on formation of the transition state.

Introduction of methyl groups into benzenesulphonic acid, which decrease the positive charge on the sulphur, diminishes the rate of hydrolysis (Table 10). The introduction of three methyl groups in the 2,4,6-positions, which produce steric hindrance to the hydrolysis of esters, slows down the hydrolysis of sulphonates far less than could have been expected.

5. INFLUENCE OF SOLVENTS

With most nucleophilic substitutions, increasing the polarity of the medium increases the rate of hydrolysis, since it tends to increase the charge at the site of reaction.

The total activation energy includes the energy of bond rupture E_B and the repulsion energy E_x. If the dielectric constant ϵ is infinite, E_x falls to zero.

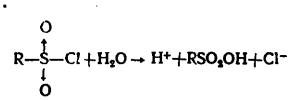
The relation between activation energy and dielectric constant can be expressed by the equation:

$$\epsilon = E_B + (E_x/E_{\epsilon_0}).$$

Thus the hydrolysis of esters is most rapid in water; organic solvents, such as ethanol, acetone, dioxan, etc., diminish the reaction velocity to a greater or lesser extent[39,104-110]. At the same time, the rate constant depends on the molecular structure of the solvent and not on its macroscopic properties[96]. As a result, the empirical relation established between activation energy and dielectric constant of the solvent represents a special case[80]. However, interaction no doubt occurs between the reactants and the solvent, resulting in the formation of either cyclic complexes[75,76] or solvates[111].

The hydrolysis of sulphonyl chlorides is accelerated by an increase in polarity of the solvent[92,112-114].

Data available on the influence of the nature and position of substituents[74] (Table 1) and also of the polarity of the solvent on rate of hydrolysis indicate that the uncatalysed hydrolysis of substituted benzenesulphonyl chlorides occurs by an S_N2 mechanism, being represented by a pseudounimolecular expression where the solvent molecule is a direct reactant[70]:



and reaction is accomplished by nucleophilic attack on the positively charged sulphur atom.

Whereas for hydrolysis in 70% dioxan–water medium substituents are arranged in the following sequence with respect to their accelerating influence: 4-NO_2 > 2,4,6-$(CH_3)_3$ > H > 2,4-$(CH_3)_2$ > 4-CH_3 > 4-CH_3O, the change in polarity of the medium on passing to 40% dioxan–water solution gives a different sequence[115]: 2,4,6-$(CH_3)_3$ > 4-NO_2 > > H > 2,4-$(CH_3)_2$ > 4-CH_3O > 4-CH_3; the sequence in water is 4-CH_3O > 4-CH_3 > 4-NO_2 > 4-Cl (Fig. 3).

The inductive effect of substituents on the rate of hydrolysis of aromatic sulphonyl chlorides can be estimated by means of Taft's equation: $\log k/k_0 = \rho^\circ\sigma^\circ$,[117] where k and k_0 are the hydrolysis rate constants for the substituted and unsubstituted benzenesulphonyl chlorides respectively, σ° is the inductive constant of the substituents (C_6H_5 being taken as standard, for which $\sigma^\circ = 0$), and ρ° is a constant indicating the sensitivity of the given reaction series to the inductive effect of the substituents. The graph of $\log k$ plotted against the σ° constants is shown in Fig. 4. All the substituents other than 2,4,6-$(CH_3)_3$ and 2,4-$(CH_3)_2$ fit well on the same straight line.

The value of ρ° in Taft's equation is positive and diminishes with increasing proportion of water: for 70, 60, 50, and 40% dioxan–water solutions the reaction constant is 1.33, 1.13, 0.93, and 0.80 respectively. In the cases of 2,4-$(CH_3)_2$ and 2,4,6-$(CH_3)_3$ the reaction constant is negative (-3.44). A large negative value of ρ° indicates a change in mechanism.

Thus the polar and steric effects of these substituents continuously decrease the absolute reaction velocity by the S_N2 mechanism, while the rate by the S_N1 mechanism increases starting from 2,4-$(CH_3)_2$.

Increasing the polarity of the medium (on passing from a 70% dioxan–water solution to water, with a change in dielectric constant from 18 to 80) increases the rate of hydrolysis of all benzenesulphonyl chlorides, but not to the same extent, the factor being 3 in the case of p-NO_2 and 175 for p-CH_3O.

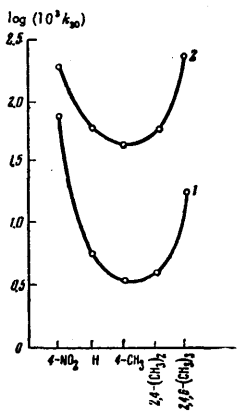


Fig. 3. Effect of the nature and orientation of substituents on the hydrolysis rate constant of substituted benzenesulphonyl chlorides in dioxan–water solutions: 1) 70%; 2) 40%.

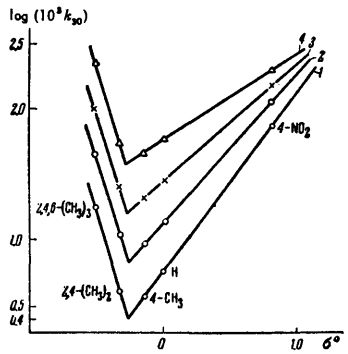


Fig. 4. Dependence of the hydrolysis rate constants of substituted benzenesulphonyl chlorides on σ° in dioxan–water solutions: 1) 70%; 2) 60%; 3) 50%; 4) 40%.

The dependence of log k on the ionising power of the solvent in the Grunwald–Winstein equation is linear, the straight lines lying close together and that for p-nitrobenzenesulphonyl chloride having the lowest slope (Fig. 5).

The Grunwald–Winstein equation is [118]:

$$\log k_{ij}/k_{0i} = m_i \log k_{0j}/k_{00},$$

where k_{ij} represents the rate constant for the hydrolysis of substituted benzenesulphonyl chlorides in different dioxan–water solutions, k_{0i} the corresponding rate constant for hydrolysis in the standard solvent (80% ethanol by volume), k_{0j} the rate constant for the hydrolysis of t-butyl chloride in the given solvent, and k_{00} the corresponding rate constant in 80% aqueous alcohol. The ratio log k_{0j}/k_{00} is denoted by Y and is termed the "ionising power of the solvent". The equation is abbreviated log $k_{ij}/k_{00} = m_i Y$, m_i being a constant depending solely on the nature of the substance. Values of Y can be calculated for any solvent by means of the formula

$$Y = a + bN + cN^2 + dN^3 + eN^4, \qquad (1)$$

where N is the mole fraction of water and a, b, c, ... are correction factors, their values under our conditions being: a = -5.641; b = 15.837; c = 20.374, and d = 13.885. Values of Y calculated by means of Eqn. (1) are listed in Table 11.

The presence of linear relations (Fig. 5) and the increase in the value of m indicate that the hydrolysis of benzenesulphonyl chlorides takes place partly by an S_N1 mechanism, except in the case of the p-nitro-derivative.

The existence of two mechanisms, S_N2–S_N1, in the hydrolysis of aromatic sulphonyl chlorides follows also from a calculation of the number of water molecules associated with the chlorides in the transition state [78]. If the reaction velocity is assumed to be proportional to the nth power of the molar concentration of water, the rate equation will be of the form

$$\frac{dx}{dt} = k\,[a - x]\,[H_2O]^n,$$

whence

$$\log k = \log k_i + n \log C_{H_2O},$$

$$\log k = n \log [H_2O] + \text{const.}$$

TABLE 11.

Concn. of dioxan–water soln., vol. %	N_{H_2O}	Y
40	0.88	+1.99
50	0.82	+1.33
60	0.75	+0.65
70	0.65	−0.13

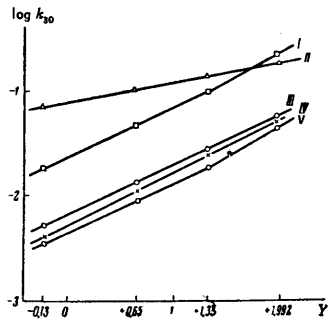


Fig. 5. Dependence of the hydrolysis rate constants on the ionising power Y of the solvent: I) 2,4,6-$(CH_3)_3$; II) 4-NO_2; III) H; IV) 2,4-$(CH_3)_2$; V) 4-CH_3.

The value of n was found from the slope of the plot of log k against the molar concentration of water (Fig. 6).

The reaction is first order with respect to the sulphonyl chloride, but the reaction order with respect to water depends both on the nature of the substituent and on the concentration of dioxan. With p-NO_2 in 70–40% dioxan–water solutions the reaction is first order with respect to water; with the other chlorides in 70–50% dioxan–water solutions the reaction is third order with respect to water, and in 50–40% dioxan–water solutions the reaction order is 4–5.

From these results it follows that, at all dioxan concentrations between 40 and 70%, p-nitrobenzenesulphonyl chloride entraps one molecule of water and is hydrolysed by a bimolecular S_N2 mechanism, which involves nucleophilic attack by the water.

All other sulphonyl chlorides at dioxan concentrations of 60–70% associate with about three water molecules, while in 40% solution four water molecules are closely involved in formation of the transition complex. This last fact indicates the tendency of sulphonyl chloride to react by a mixed S_N2–S_N1 mechanism with the latter predominating in 40% solution.

Values close to three are greater than are required for reaction by an S_N2 mechanism. It is probable that solvation of the sulphonyl chloride molecules by a few water molecules is sufficient to produce the energy required to split the S–Cl bond, and after sufficient extension, one of the water molecules of the solvate layer can react with the sulphonyl group. The transition state is probably formed within a cell made up of four molecules of water and an outer layer of oriented water molecules. Variation in the

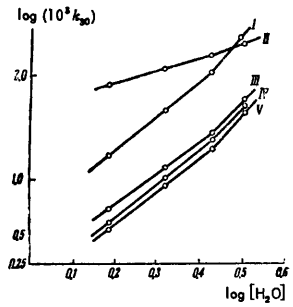


Fig. 6. Relation between log k and log $[H_2O]$: I) 2,4,6-$(CH_3)_3$; II) 4-NO_2; III) H; IV) 2,4-$(CH_3)_2$; V) 4-CH_3.

TABLE 12. Effect of the polarity of the solvent on the rate of alkaline hydrolysis of p-nitrophenyl benzenesulphonate[115].

Content of solvent	$10^3 k^*_{25}$	$10^3 k_{20}$	log P_z	E
vol. %	A. Aqueous dioxan solution			
40	12.80	52.70	8.033	13760
50	13.05	54.00	8.104	13850
60	13.60	57.30	8.225	13990
70	14.00	60.00	8.356	14150
80	17.30	76.60	8.67	14460
wt. %	B. Aqueous acetone solution			
40	9.1	36.5	7.70	13500
50	9.7	40.5	8.01	13900
60	10.1	41.8	8.00	13860
70	12.0	51.6	8.32	12400

* k in litre mole^{-1} sec^{-1}.

nucleophilic character of the reagent shows that trimethylbenzenesulphonyl chloride is very insensitive to change in alkalinity of the medium, which in turn confirms the S_N1 mechanism in this case, involving ionisation according to the scheme:

$$(CH_3)_3C_6H_2SO_2Cl \rightarrow (CH_3)_3C_6H_2SO_2^+ + Cl^- \quad \text{(slow)},$$

$$(CH_3)_3C_6H_2SO_2^+ + H_2O \rightarrow (CH_3)_3C_6H_2SO_2OH + H^+ \quad \text{(rapid)}.$$

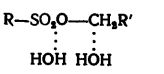
Alkyl benzenesulphonates exhibit a tendency to react more rapidly by the S_N2–S_N1 mechanisms than by either of them separately[74,78,119]. The transition from an S_N2 to an S_N1 mechanism becomes more marked with increasing polarity of the solvent. The effect of the solvent on the uncatalysed hydrolysis of alkyl sulphonates shows a great similarity to the hydrolysis of alkyl halides. The reaction velocity by the S_N1 mechanism increases with increase in the ionising properties of the solvent. With bimolecular reactions the transition from the initial to the intermediate state is linked with the magnitude of the charges, and therefore it depends, nevertheless, on the ionising properties of the solvent, although to a smaller extent. These points have been verified for the alkyl halides and the solvolysis of alkyl sulphonates[34,120–122]. The rate of hydrolysis of isopropyl benzenesulphonate increases steadily with increasing content of water in the solvent: 50° the rate in pure water is 4.3 times that in 17.8% aqueous acetone, and 1000, 10000, and 73000 times those in 80, 92.5, and 98% aqueous acetone, respectively.

The influence of the polarity of the medium is considerably less marked in the hydrolysis of ethyl and n-propyl benzenesulphonates. The corresponding factors for the former ester are 2.3, 86, 500, and 1080 respectively. The relation log $k = n \log [H_2O]$ remains linear when the concentration of acetone in water varies between 0 and 60–70%. The slope of the curve indicates that seven molecules of water are involved in formation of the transition state in the case of t-butyl chloride, six with the corresponding bromide, but only two with ethyl bromide.

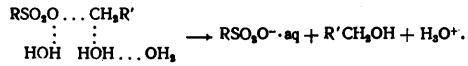
The number of molecules of water involved in the transition state with the alkyl sulphonates is as follows:

Isopropyl benzenesulphonate in	0–50% dioxan	6.0	molecules (n)
	50–90% "	2.6	"
Ethyl benzenesulphonate in	0–50% "	3.6	"
	50–95% "	2.1	"

The value $n = 6$ is characteristic of the S_N1 mechanism in the range 0–50%. Values of 2.1–1.7 for alkyl benzenesulphonates correspond to a medium containing < 50% of water and represent the S_N2 mechanism. In the rate-determining stage of the reaction, one molecule of water forms a bond with the alkyl carbon, while the other forms a hydrogen bond with the oxygen of the O–C group. The transition state can be represented by the scheme:



or



In the case of the S_N1 reaction, experiment shows that six molecules of water are required. They determine the activation energy required to split the C–O bond. A carbonium ion is formed without the participation of the aqueous solvent, and then reacts with one of the water molecules.

The values of 3.6 and 3.8 for an n-alkyl benzenesulphonate are larger than are required for the S_N2 reaction. They show, moreover, that four molecules of water are involved in forming the transition state.

These results can be summarised by stating that ethyl and n-propyl benzenesulphonates react by an intermediate mechanism in solvents having a high water content, and by the S_N2 bimolecular mechanism in solvents containing less than 50% of water. Isopropyl benzenesulphonates undergo hydrolysis by a unimolecular mechanism, but this becomes difficult in solvents containing a small quantity of water.

The influence of the polarity of the medium on the rate and mechanism of the alkaline hydrolysis of aryl sulphonates corresponds to a typical S_N2 mechanism[71,74,115]. Increasing the polarity of the solvent — changing from 80 to 40% dioxan in water solution, and from 70 to 40% acetone in water solution — decreases the rate of alkaline hydrolysis to 1/1.35–1/1.3 of its value. The comparatively slight decrease in rate of hydrolysis of aryl sulphonates with increasing polarity of the medium may be explained (in conformity with Ingold's views) by a decrease in polarity of the reactants in the transition state (compared with the initial state) due to dispersal of the charges[108] (see Table 12).

With each class of compounds a transition from an S_N2 to an S_N1 mechanism can probably be traced for change in polarity of the substituent, in the nucleophilic character of the reagent, and in the ionising properties of the solvent.

6. INFLUENCE OF STERIC FACTORS ON THE RATE AND MECHANISM OF THE HYDROLYSIS OF THE CHLORIDES OF CARBOXYLIC AND SULPHONIC ACIDS

It is of interest to study steric effects in the hydrolysis and solvolysis of benzenesulphonyl chlorides and aryl sulphonates, since this provides an independent approach to establishing the mechanism of hydrolysis with this class of compounds. Depending on the reaction mechanism, the spatial factor may produce either steric hindrance or steric promotion [74,83,115]

Experimental results on the influence of the structure of the initial benzenesulphonyl chloride, the ionising properties of the solvent, and the nature of the reagents on the rate of hydrolysis indicate that trimethylbenzenesulphonyl chloride is hydrolysed by an S_N1 mechanism, whereas the dimethylated compound hydrolyses partly by an S_N2 and partly by an S_N1 mechanism.

Comparison of the relative rates of hydrolysis of substituted benzenesulphonyl chlorides with those of alkyl benzenesulphonates [121] and alkyl halides (Table 13) [20,123,124] shows that aromatic sulphonyl chlorides are similar in some respects to alkyl halides and the alkyl sulphonates. Independently of whether the Alk–Br, Alk–O–S, or $ArSO_2$–Cl bond is broken, the accumulation of electron-donor groups, by creating steric hindrance at the reaction site, in all cases diminishes the reaction velocity by the S_N2 mechanism and favours the S_N1 mechanism.

A change in the nature of the group which is eliminated (Br^-, $C_6H_5SO_2O^-$, Cl^-) has a considerable effect on the absolute rate of substitution, but an insignificant effect on the reaction mechanism. The latter is understandable, since the group which is eliminated completely removes at the same time the previously delocalised electrons, independently of the reaction mechanism. With the alkyl sulphonates and alkyl bromides the minimum rate is shown by the ethyl derivative, but with the alkylated benzenesulphonyl chlorides by the methyl compound (see Table 13).

TABLE 13. Comparison of the relative rate of hydrolysis of substituted benezenesulphonyl chlorides (A) with methyl, ethyl, and isopropyl benezenesulphonates and with the corresponding bromides (B).

A			B	
R	$C_6H_5SO_2Cl$*	R	$C_6H_5SO_2OR$**	RBr***
H	1	CH_3	1	1
$CH_3C_6H_4$	0.76	C_2H_5	0.43	0.76
$(CH_3)_2C_6H_3$	0.98	$(CH_3)_2CH$	4.17	1.46
$(CH_3)_3C_6H_2$	3.80	s-butyl	6.00	

* 50% dioxan–water solution.
** 56% acetone–water solution [70].
*** 50% ethanol–water solution [97].

TABLE 14. Reactions of substituted benzoyl chlorides XC_6H_4COCl with alcohols [126,127].

Substituent X	$\frac{k_{XC_6H_4COCl}}{k_{C_6H_5COCl}}$
H	1.00
o-OCH_3	66.0
o-CH_3	5.2
p-CH_3	0.68
o-NO_2	1.8
p-NO_2	15.6
2,4,6-$(NO_2)_3$	very slow
2,4,6-$(CH_3)_3$	very rapid

Substituted benzenesulphonyl chlorides show greater variations in relative rate constants with change in the nature of the substituent than is the case with alkyl bromides, and smaller than with substituted alkyl sulphonates. It is very probable that the C–O bond in these sulphonates is the most ionic in character, then follows the S–Cl bond in the sulphonyl chlorides, and the least polarised bond is the C–Br linkage in the bromides. Thus nucleophilic substitution at the S atom in benzenesulphonyl chlorides can be effected by S_N2–S_N1 mechanisms, as occurs at a saturated carbon atom [3,4,20,21,57,98,99,108,109,123,124].

Carboxylic acid chlorides are readily hydrolysed, since chlorine has a higher electron affinity than has hydroxyl (or the OR′ group in esters), and the conjugation of the carbonyl which normally occurs in acids and in esters breaks down.

Most reactions of acid halides could occur in two possible ways: (1) addition at the carbonyl carbon, and (2) ionisation [125]:

$$R{-}COCl + CH_3OH \rightarrow R{-}\underset{\displaystyle OCH_3}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}{-}Cl \rightarrow RCOOCH_3 + HCl\,, \qquad (1)$$

$$RCOCl \rightarrow RCO^+ + Cl^- \xrightarrow{CH_3OH} RCOOCH_3 + HCl\,. \qquad (2)$$

Reactions occurring according to Eqn. (1) are confirmed by the steric effects observed in both the hydrolysis and the alcoholysis of acid halides. In substituted benzoyl chlorides all groups (other than *p*-methyl) increase the rate of reaction with alcohols (see Table 14).

In the cases of the methyl and methoxy-compounds, the *ortho*-isomers show considerably higher reaction velocities than do the *meta*- and *para*-isomers. Steric hindrance appears in reactions taking place by an ionic mechanism, and reaches a maximum with 2,4,6-trimethylbenzoyl chloride, which at 0° reacts with methanol too rapidly for the reaction velocity to be measured [126]. Study of the kinetics of the hydrolysis of substituted and unsubstituted benzoyl chlorides in the presence of different amounts of the hydroxide ion in a water–acetone mixture supports still more strongly the possibility of S_N2 and S_N1 mechanisms [128,129]. The latter mechanism is favoured by an increase in the water content of the mixture. 2,4,6-Trinitrobenzoyl chloride hydrolyses mainly by the S_N2 mechanism, whereas 2,4,6-trimethylbenzoyl chloride hydrolyses mainly *via* an ionic stage. Thus whether steric factors impede hydrolysis depends on the mechanism of the latter.

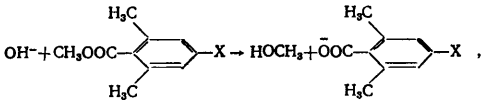
7. INFLUENCE OF STERIC FACTORS ON THE RATE AND MECHANISM OF THE ALKALINE AND AQUEOUS HYDROLYSIS OF ARYL SULPHONATES

The considerable influence of polar effects on the rate of alkaline hydrolysis of substituted phenyl benzenesulphonates shows that movement of electrons from the attacking agent to the displaceable phenoxy-group is not complete in the transition state. Therefore a change in polarity of the replaceable group should affect the reaction velocity[71]. The influence of the polar substituents (Tables 1 and 8) and of the polarity of the medium (Table 12) on the alkaline hydrolysis of aryl sulphonates indicates that such reactions are effected by an S_N2 mechanism[48] and are accompanied by fission of the S–OAr bond.

Investigation of the alkaline hydrolysis of 2,4- and 2,6--dinitrophenyl mesitylenesulphonates in the presence of $H_2{}^{18}O$ also indicates an acyl–oxygen mechanism. With such a mechanism of hydrolysis it is quite obscure why phenyl mesitylenesulphonate is hydrolysed by alkalis only slightly more slowly than is phenyl toluene-*p*-sulphonate, whereas the corresponding mesitylenecarboxylic ester is very difficult to hydrolyse owing to the difficulty of nucleophilic attack on the carbonyl carbon[130].

Although the rate constant for the alkaline hydrolysis of methyl benzoate at 25° is 5.02, the corresponding value for methyl 2,4,6-trimethylbenzoate at 25° is 1.35. Introduction of activating substituents into the *para*-position has little effect on the rate constant.

Alkaline hydrolysis of a methyl 2,6-dimethyl-4-X-benzoate involves attack on the alkyl carbon of the ester group[130]:



the presence of considerable steric hindrance results in a different bond being broken.

Measurement of the dissociation constants of a series of 4-substituted 2,6-dimethylbenzoic acids[131] (in 20 vol.% aqueous dioxan and in 50% aqueous ethanol)[130] shows that the polar effect of the 4-substituent is fundamentally equal to the corresponding effect on the dissociation of the *para*--substituted benzoic acid under the same conditions[132,133]. Thus the dissociation of both series of acids obeys the Hammett equation, the values of ρ being very similar. This shows that dissociation of sterically hindered benzoic acids, in contrast to their hydrolysis, does not disturb the conjugated of the substituted groups with the reactive centre.

The steric effect of methyl groups in the 2,6- and 2,4,6--positions of benzoic esters on their rate of hydrolysis is readily visualised from the structure of the transition complex, in which three substituent groups move to give a tetrahedral structure, the presence of three methyl groups in the benzene ring undoubtedly impeding formation of the intermediate.

It is considerably more difficult to produce a spatial representation for the effect of steric factors on reactions at an unsaturated sulphur atom. In the initial $ArSO_2OAr'$ molecule the valence bonds are probably arranged tetrahedrally, but sulphur, in contrast to carbonyl carbon, is coordinatively saturated, and attack by a nucleophilic reagent can occur in two possible ways, the sulphonyl group being arranged in a plane either coplanar with or perpendicular to that containing the attacking and eliminated groups (see Section 1); this determines whether the sulphonyl group will or will not be conjugated with the benzene ring, and hence whether or not steric hindrance may occur.

Experimentally, introduction of an NO_2 group into phenyl benzenesulphonate *ortho* to the sulpho-group has a retarding influence compared with *para*- or *meta*-substitution, showing that in this case the benzene ring remains coplanar and the *o*-NO_2 group sterically hinders the approach of reagents. The introduction of methyl groups in the 2,4,6--positions of the benzene ring of the acid part in substituted phenyl benzenesulphonates can be expected not only to force the ring out of planarity but also to change the mechanism of hydrolysis.

In order to clear up the anomalous behaviour of the mesitylenesulphonic ester, let us examine the influence of the polarity of the medium and the accumulation of methyl groups in the acyl part of the ester on the rate of hydrolysis of methylated aryl sulphonates (see Tables 15 and 16).

Increasing the polarity of the solvent — on passing from a 70 to a 50% dioxan–water solution — diminishes the rate of hydrolysis of dinitrophenyl and phenyl methylated benzenesulphonates by a factor of 1.7–1.8. The comparatively small decrease in rate of hydrolysis of aryl sulphonates with increase in polarity of the medium may be explained by a diminished polarity of the reactants in the transition state compared with the initial state, due to dispersion of the charges. Furthermore, an increase in polarity of the medium in the alkaline hydrolysis of aryl sulphonates is accompanied by a decrease in activation energy and in the preexponential factor. The dispersion of the charge probably weakens electrophilic character of the sulphur atom, and at the same time the increase in polarity of the solvent increases the polarity of the S–O bond undergoing rupture, thereby diminishing the activation energy.

TABLE 15. Alkaline hydrolysis of dinitrophenyl benzenesulphonates $XC_6H_4SO_2OC_6H_3(NO_2)_2$-2,4 in 70 and 50% dioxan–water medium[115].

Substituent X	70%			50%		
	$10^3 k_{15}$	log P_z	E	$10^3 k_{15}$	log P_z	E
H	996	9.02	11900	560	8.26	11200
4-CH_3	382	9.28	12800	247	8.76	12300
2,4-$(CH_3)_2$	270	9.72	13600	148	9.31	13400
2,4,6-$(CH_3)_3$	301	9.46	13200	176	9.18	13100

TABLE 16. Alkaline hydrolysis of phenyl benzenesulphonates $XC_6H_4SO_2OC_6H_5$ in 70 and 50% dioxan–water medium.

Substituent X	70%	50%
	$10^4 k_{70}$	$10^4 k_{70}$
H	18.97	10.1
4-CH_3	8.0	4.6
2,4-$(CH_3)_2$	7.0	4.1
2,4,6-$(CH_3)_3$	8.0	4.9

Study of the effect of electron-donor groups on the rate of alkaline hydrolysis confirms the presence of an S_N2 mechanism. Aryl methylated sulphonates arranged themselves in the following sequence of decreasing reaction velocity:

$$H > 4\text{-}CH_3 > 2,4,6\text{-}(CH_3)_3 > 2,4\text{-}(CH_3)_2 .$$

The mesitylenesulphonic ester behaves somewhat anomalously (Fig. 7).

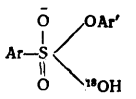
Introduction of three methyl groups, by causing steric hindrance at the site of reaction, gives a slight increase, instead of the expected decrease, in the rate of hydrolysis, which can be explained by the trimethylated benzene ring being forced out of coplanarity, so that nucleophilic attack on the sulphur atom is facilitated.

Introduction of a nitro-group into the phenyl part of the ester has a substantial effect on the rate of alkaline hydrolysis (Tables 15 and 16): phenyl benzenesulphonate is saponified at a rate which is only 1/15 000 of that of the corresponding 2,4-dinitrophenyl ester, providing evidence of the great effect of two nitro-groups on the polarity of the S–O bond.

Of the mono- and di-nitro-substituted phenyl benzenesulphonates only those with a nitro-group in the phenolic part undergo uncatalysed hydrolysis with water. Thus the amounts of 2,4-dinitrophenyl benzenesulphonate and phenyl 2,4-dinitrobenzenesulphonate hydrolysed in a given time are 46 and 4% respectively. An analogous phenomenon is observed when a third nitro-group is introduced into the phenol or into the benzenesulphonic acid. *o*-Nitrophenyl 2,4-dinitrobenzenesulphonate also is not hydrolysed by water, whereas 2,4-dinitrophenyl *o*-nitrobenzenesulphonate is hydrolysed rapidly.

The rate of aqueous hydrolysis of aryl sulphonates is considerably lower than that of the corresponding ethyl sulphonates [$k_{50} = 3.14 \times 10^{-3}$ min^{-1} for m-$NO_2C_6H_4SO_2OC_2H_5$, while $k_{70} = 0.54 \times 10^{-4}$ min^{-1} for $C_6H_5SO_2OC_6H_3(NO_2)_2$-2,4].

Among the dinitrated aryl sulphonates the 3,4-dinitrophenyl esters show the lowest rate of hydrolysis. Chloronitro-derivatives other than the 4-chloro-2-nitrophenyl ester are not hydrolysed by water. Dinitro-substituted esters containing methyl groups in the benzenesulphonic acid are hydrolysed more rapidly than the corresponding non-methylated esters, whereas the opposite order is observed in alkaline hydrolysis. Investigation of the neutral hydrolysis of 2,4-dinitrophenyl mesitylenesulphonate in the presence of $H_2{}^{18}O$ points to an acyl–oxygen mechanism alone[48]. The phenols isolated after hydrolysis contain no heavy oxygen isotope. Unchanged 2,4-dinitrophenyl toluenesulphonate recovered after neutral hydrolysis in the presence of $H_2{}^{18}O$ contained no ^{18}O. This suggests that the intermediate complex



is formed reversibly during the hydrolysis or not at all. The proton has insufficient time to move from one oxygen atom to another before the complex decomposes, and thus the oxygen atoms do not lose their identity. The reaction has a synchronous bimolecular mechanism. On the basis of an acyl–oxygen mechanism of neutral hydrolysis and its occurrence only with mono- and di-nitrophenyl esters, and also in view of the absence of steric effects in the presence of two *o*-methyl groups, the main factor influencing the neutral hydrolysis of aryl sulphonates can be assumed to be the polarity of the S–O bond.

Examination of the kinetics of the neutral hydrolysis of dinitrophenyl benzenesulphonates containing nucleophilic substituents enables an approach to be made to an interpretation of the mechanism of neutral hydrolysis[115] (see Table 17).

In this case an increase in polarity of the medium — the change from a 70 to a 50% dioxan–water solution — does not diminish the rate of hydrolysis of dinitrophenyl benzenesulphonates, but increases it by a factor of 3.1. The opposite influence of solvent polarity on the rates of alkaline and of neutral hydrolysis of aryl sulphonates is evidence of different reaction mechanisms. In the former case the S_N2 mechanism predominates, whereas in the latter an S_N1 mechanism may develop.

The activation energy for neutral hydrolysis is high, 21 200 as compared with 11 900 for alkaline hydrolysis, and approximates to that for the hydrolysis of alkyl sulphonates (19 100). In this case increase in solvent polarity produces an increase in activation energy and in the preexponential factor for H, 4-CH_3, and 2,4-$(CH_3)_2$. With 2,4,6-$(CH_3)_3$ there is a fall in activation energy accompanied by an increase in the preexponential factor.

The rate of neutral hydrolysis gives the following sequence for methylated aryl sulphonates:

$$2,4,6\text{-}(CH_3)_3 > H > 4\text{-}CH_3 > 2,4\text{-}(CH_3)_2 .$$

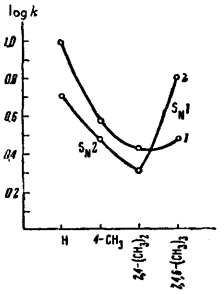


Fig. 7. Rate of alkaline hydrolysis of aryl sulphonates in 70% solution: 1) alkaline, log ($10^3 k_{15}$); 2) neutral, log ($10^5 k_{70}$).

TABLE 17. Neutral hydrolysis of dinitrophenyl benzenesulphonates $XC_6H_4SO_2OC_6H_3(NO_2)_2$-2,4 in 70 and 50% dioxan–water medium.

Substituent X	70%			50%		
	$10^4 k_{70}$	log P_z	E	$10^4 k_{70}$	log P_z	E
H	0.53	9.22	21 200	1.64	9.86	21 500
4-CH_3	0.304	9.25	21 600	1.19	9.90	21 800
2,4-$(CH_3)_2$	0.206	9.36	22 050	1.06	10.42	22 100
2,4,6-$(CH_3)_3$	0.64	8.88	20 500	2.20	9.20	20 200

The fact that in this case the activation energy and the pre-exponential factor are changed in opposite senses may indicate a different mechanism of hydrolysis for the trimethylbenzenesulphonate compared with the other arenesulphonates. Replacement of H by 4-CH_3 and by 2,4-$(CH_3)_2$ produces a successive decrease in rate of hydrolysis; introduction of three methyl groups is accompanied by an increase in rate of hydrolysis ($k_{70} = 1.64 \times 10^{-4}$ for 2,4-dinitrophenyl benzenesulphonate, $k_{70} = 2.2 \times 10^{-4}$ for the corresponding methylated compound), which may be explained by a change in mechanism from S_N2 to S_N1 resulting from the accumulation of methyl groups causing steric hindrance to nucleophilic attack at the site of reaction (Fig. 7).

The effect of all the above factors on the rate of the aqueous hydrolysis of aryl sulphonates suggests that 2,4-dinitrophenyl benzenesulphonates can react in the more polar solvents by an S_N1 mechanism. This can be regarded as proved in the case of the trimethylated ester.

The fact that aqueous hydrolysis occurs only when two nitro-groups are present in the phenol, and not when they are present in the benzenesulphonic acid, can be interpreted on the basis of two mechanisms S_N2 and S_N1 being present. Whereas the activation energy of alkaline hydrolysis is determined by the electrophilic character of the sulphur, and is employed mainly in overcoming the repulsion of the approaching reagent, in aqueous hydrolysis the activation energy is determined by the ease of rupture of the S–O bond, and therefore aqueous hydrolysis takes place only with aryl sulphonates containing electronegative substituents in the phenolic part of the ester.

8. CORRELATION OF RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF ARENESULPHONIC ESTERS WITH THEIR STRUCTURE [134]

Rate constants have been cited earlier for alkaline hydrolysis in the reaction series [50,66,71,72,74,83,103]: (1) $C_6H_5SO_2OAr$, (2) $ArSO_2OC_6H_5$, (3) $ArSO_2OAr'$, and (4) $ArSO_2OC_2H_5$. The symbols Ar and Ar′ denote mono- or poly-substituted phenyl groups. The experimental results can be evaluated quantitatively by means of the rule of linear relations between the free energy changes of activation for the standard substance and for substances containing different substituents within a given reaction series. The change in free energy can be measured by the expression $\log k_i/k_0$, *i.e.* the logarithm of the ratio of the rate constant for a substance containing a substituent i to that for the standard substance. The total change in free energy is the sum of the separate elementary changes due to the various structural factors affecting reactivity.

In general, the dependence on the nature of Ar of the reactivity of compounds of the type Ar–Y, where Y represents the reactive centre, can be expressed [67]:

$$\log k = \log k_0 + \rho_0\sigma^\circ + \psi + S, \qquad (1)$$

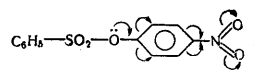
where k_0 is the rate constant for C_6H_5–Y, σ° the inductive constant of the substituent Ar with C_6H_5 as standard (for which $\sigma^\circ = 0$), ρ_0 is a constant representing the sensitivity of the given reaction to the inductive effect of the substituent Ar, ψ a term representing the quantitative effect of direct polar conjugation between the reactive centre and the substituent X in $X\text{-}C_6H_4$ = Ar, and S a measure of the steric factor in the case of *ortho*-substituents in Ar.

For all *meta*-substituents and those *para*-substituents which cannot undergo direct conjugation with the reactive centre, Eqn. (1) reduces to the Hammett equation [41,135] with σ replaced by σ°

$$\log k = \log k_0 + \rho_0\sigma^\circ. \qquad (2)$$

Fig. 8 illustrates the relations between log k and σ° for the reaction series (1)–(3). The straight lines are drawn through points corresponding to substituents for which ψ and S are put equal to zero.

(1) Alkaline hydrolysis of substituted phenyl benzenesulphonates in 70% aqueous dioxan (Table 8). In this case there are no deviations from a linear relation between log k and σ°, indicating practically complete absence of possible conjugation between *para*-substituents of type S† and the reactive centre:



Consequently the influence of substituents in the phenol ring on the reactive centre is transmitted only as an inductive effect. The electronegative group $>SO_2$ probably suppresses conjugation of the p-electrons of the oxygen with the benzene ring.

At 50° $\rho_0 = 2.747 \pm 0.041$, $\log k_{calc} = -3.36$, and $r = 0.9996$. The reaction constant for the hydrolysis of substituted phenyl benzenesulphonates is quite high, which indicates the great sensitivity of the hydrolysis rate constant to structural changes in the ester molecule. This

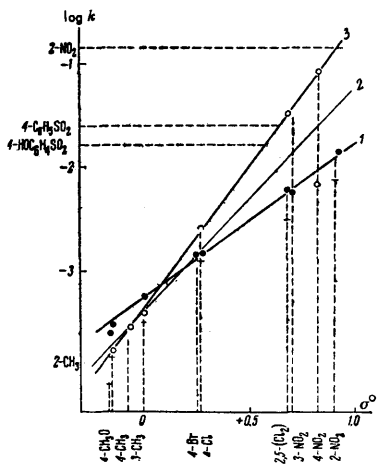


Fig. 8. Dependence of log k on inductive constants σ° of aromatic substituents in the hydrolysis of: 1) $ArSO_2OC_2H_5$; 2) $ArSO_2OC_6H_5$; 3) $C_6H_5SO_2OAr$.

† Substituents of type +S possess an unshared pair of electrons and are electron-donors; substituents of type -S are electron-acceptors by a mechanism of polar conjugation [67].

reaction series is extremely convenient for calculating new values of σ° by means of the formula $\sigma^\circ = (\log k + 3.36)/2.747$, the following having been obtained. 2-CH_3 - 0.19, 2-NO_2 + 0.91, 4-*p*-$HOC_6H_4SO_2$ + 0.56, and 4-$C_6H_5SO_2$ + 0.66. The value of σ° for *o*-NO_2 is somewhat greater than published values of σ-*ortho* for this substituent (+0.80 [117] and +0.65). This clearly indicates that in this case $S = 0$. This conclusion is not unexpected, since the sulphur atom undergoing attack by the OH^- ion is quite remote from the substituted benzene ring.

At 0° $\rho_0 = +3.09 \pm 0.059$, $\log k_{calc} = -5.63$, and $r = 0.999$. The temperature-dependence of ρ_0 is represented by the equation

$$\rho_0 = +0.20 + 3660/2.3\,RT.$$

(2) Alkaline hydrolysis of phenyl esters of substituted benzenesulphonic acids in 70% aqueous dioxan (Table 1). In this case *para*- and *ortho*-substituents of +S type can be directly conjugated with the reactive centre. Values of ρ_0' and ρ_C in the equation

$$\log k = \log k_0 + \rho_0\sigma^\circ + \rho_C\sigma_C^\circ$$

calculated by the method of least squares from experimental data for the substituents 4-CH_3O, 4-CH_3, H, 4-Cl, 4-Br, 3-NO_2, and 4-NO_2 at 50° are $\rho_0' = +2.24$, $\rho_C = +0.54$, and $\log k_0 = -3.43$. The reaction constant for the hydrolysis of aryl sulphonates, +2.24, is close to the value of +2.6 calculated by Hammett [41] for the hydrolysis of ethyl benzoates.

Since in this case the hydroxyl attacks a sulphur atom directly linked with a substituted phenyl group, steric hindrance is to be expected with *ortho*-substituents, and $S \neq 0$. The deviations of the experimental values of $\log k$ from the straight line

$$\log k = -3.43 + 2.24\sigma^\circ$$

yield in the case of the *ortho*-substituted phenyl esters values of $S = -0.75$ for 2-NO_2 and of $\psi + S = -0.65$ for 2-Cl.

(3) Alkaline hydrolysis of phenyl benzenesulphonates substituted in both benzene rings (Table 10). This reaction series (3) includes series (1) and (2) as well. In this case methods of "cross-correlation" (the superposition of several independent correlation equations) [138] must be employed to calculate the rate constants. In view of this, the following equation can be written down for this reaction series

$$\log k_{ij} = \log k_{00} + \rho_0\Sigma\sigma_i^\circ + \rho_0'\Sigma\sigma_j^\circ + \rho^*\Sigma\sigma_i^\circ\Sigma\sigma_j^\circ + \rho_C^+\sigma_{C_i}^{\circ+} + S\ldots, \quad (3)$$

where the subscript i refers to nuclear substituents in the benzenesulphonic acid, and j to substituents in the phenyl ring. The value of ρ^* is found from the relation

$$\rho^* = \frac{\rho_{0k} - \rho_0}{\sigma^\circ_k} = \frac{\rho'_{0k} - \rho_0}{\sigma'_k},$$

where ρ_{0k} and ρ'_{0k} relate to the hydrolysis reaction series $X^kC_6H_4SO_2OAr$ and $ArSO_2OC_6H_4X^k$, X^k being some constant substituent. The equality $\rho^* = 0$ means that substitution in one ring has no effect on the interaction between the reactive centre and substituents in the other ring, and conversely. The value of ρ^* calculated by the method of least squares from the values given for ρ_0, ρ_0', and ρ_C and experimental values of $\log k_{ij}$ at 0° is $\rho^* = -0.61 \pm 0.06$. Thus the quantity ρ^* cannot be neglected in the present case. The negative value of ρ^* indicates that the presence of electronegative substituents in one ring diminishes interaction between the reactive centre and electronegative substituents in the other ring, and conversely.

Neglecting the temperature-dependence of ρ_C, ρ^*, and S, we obtain the following equation for calculating rate constants when substituents are present in both aromatic rings

$$\log k_{ij} = 8.35 - 17\,400/2.3\,RT + (-0.20 + 3660/2.3\,RT)\Sigma\sigma_i^\circ + (0.20 + 3660/2.3\,RT)\Sigma\sigma_j^\circ - 0.61\,\Sigma\sigma_i^\circ\Sigma\sigma_j^\circ + 0.54\,\sigma_{C_i}^{\circ+} + S. \quad (4)$$

The precision of the equation is shown by the value $S = 0.185$ for a change in $\log k_{ij}$ by more than six orders of magnitude.

Calculation of the rate constants for 2,4,6-trimethylbenzenesulphonic esters gives satisfactory agreement with experimental results only if the term $0.54\sigma_{C_i}^{\circ+}$ in Eqn. (4) is omitted and it is assumed that $S = 0$. This proves that two *o*-methyl groups, without offering steric hindrance to attack by the hydroxide ion, nevertheless destroy the coplanarity of the system and "cut out" direct conjugation with the reactive centre.

(4) Alkaline hydrolysis of substituted ethyl benzenesulphonates in 70% aqueous dioxan (Table 1). Direct conjugation of +S-type substituents in *para*- and *ortho*-positions with the reactive centre is theoretically possible. However, the deviations from the straight line $\log k = \log k_0 + \rho_0\sigma^\circ$ are small with the 4-CH_3O and 4-CH_3 groups, and are altogether absent with the halogens. In the case of the latter, at least, the quantity ψ can be neglected.

At 50° $\rho_0 = +1.425 \pm 0.091$, $\log k_{calc} = -3.23$, and $r = 0.991$.

The absence of deviations when a nitro- or a chloro-group is present in the *ortho*-position shows that steric hindrance is absent ($S = 0$). This is because the hydroxide ion is then attacking the ethyl carbon [14]. Differences in the value of ρ for the hydrolysis of aryl and alkyl sulphonates confirm that these reactions have different mechanisms.

The above results show that the rule of the linear relation between changes in free energy and the principle of the independence and additivity of the effects of individual structural factors on reactivity can be successfully applied to these series of reactions.

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THE CHEMISTRY OF SOME 1-SUBSTITUTED ALKA-1,3-DIENES

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I. INTRODUCTION

There are now many publications on the chemistry of the diene hydrocarbons. They are concerned mainly with the order of addition of various nucleophilic and electrophilic reagents, and also with developing ideas on the ability of dienes to form polymers, especially the industrially important buta-1,3-diene and isoprene rubbers.

The most recent views on the properties of dienes, and in particular of butadiene, are inseparably linked with their stereochemistry. Establishment of the *cis*- and *trans*--configurations of dienes is a most important contemporary stage in the evolution of diene chemistry. Conformational analysis makes it possible to obtain a deeper understanding of the various reactions of dienes, and also the structure and properties of the diverse derivatives of these compounds.

The present paper represents an attempt to give a systematic account of the most important investigations associated with various syntheses, leading ultimately to hetero--substituted buta-1,3-dienes.

II. 1-ALKOXYBUTA-1,3-DIENES

This section describes methods of synthesis and some chemical properties of compounds having the general formula

$$ROCH{=}CH{-}CH{=}CH_2.$$

These α-substituted butadienes can exist also as a pair of geometrical *cis*-*trans*-isomers.

1. Methods of Preparation

Existing methods for the synthesis of 1-alkoxybuta-1,3-dienes are based on various reactions of the following classes of organic compounds: acetals of unsaturated aldehydes, aldehydes and ketones, alkoxylated acetals of aldehydes, halogenated acetals of aldehydes, butenyne (vinylacetylene), and butadiyne (diacetylene).

Meier[1] was the first to obtain 1-methoxybuta-1,3-diene from the acetal of crotonaldehyde:

$$CH_3{-}CH{=}CH{-}CH(OCH_3)_2 \xrightarrow{-CH_3OH} CH_2{=}CH{-}CH{=}CHOCH_3.$$

The reaction was carried out in the presence of NaH_2PO_4 at 350°.

A new method was subsequently proposed[2] for synthesising 1-alkoxybuta-1,3-dienes by passing acetals of vinylacetaldehyde in the vapour phase over acid catalysts in a vacuum at 300°. The yield of the final product was ~45%:

$$CH_2{=}CH{-}CH_2{-}CH_2(OR)_2 \xrightarrow{-ROH} CH_2{=}CH{-}CH{=}CHOR.$$

Nazarov *et al.*[3] synthesised 1-ethoxy-3-methylbuta-1,3-diene by passing the vapour of 1,1-diethoxy-3-methylbut-2-ene (the diethylacetal of 3-methylcrotonaldehyde) over NaH_2PO_4 at 320°. The reaction is represented by the following scheme:

$$(H_3C)_2CH{-}CH_2{-}CHO \xrightarrow{Br_2;\,C_2H_5OH} (H_3C)_2CH{-}CHBr{-}CH(OC_2H_5)_2 \rightarrow$$

$$\xrightarrow{KOH} (H_3C)_2C{=}CH{-}CH(OC_2H_5)_2 \rightarrow CH_2{=}C(CH_3){-}CH{=}CHOC_2H_5.$$

The same workers[3] obtained a 77% yield of an alkoxy-substituted isoprene by the catalytic cleavage of 1,1,3-triethoxy-3-methylbutane. The process of condensation and cleavage can be represented as follows:

$$(H_3C)_2C(OC_2H_5)_2 \xrightarrow{CH_2=CHOC_2H_5} (H_3C)_2C(OC_2H_5){-}CH_2{-}CH(OC_2H_5)_2 \xrightarrow[\text{catalyst}]{t^\circ} CH_2{=}C(CH_3){-}CH{=}CHOC_2H_5.$$

Condensation of the acetal with ethyl vinyl ether was effected at 0° in the presence of a catalytic quantity of the boron trifluoride–ether complex. The vapour of the resulting 1,1,3-triethoxy-3-methylbutane was passed over the contact catalyst $MgHPO_4$ at 350° and a pressure of 15–20 mm. A study of the efficiency of different catalysts for such cleavage reactions showed the best results to be obtained on $MgHPO_4.Na_2SiO_3$ catalysts deposited on activated charcoal. Several other 1-alkoxybuta-1,3-dienes have been obtained in a similar manner[1,4,5].

Alkoxy-dienes can be prepared also by other methods. Wichterle[6] observed that the acetal of chlorobutyraldehyde decomposes under the action of metallic potassium to yield 1-alkoxybuta-1,3-dienes

$$CH_3CHClCH_2CH(OR)_2 \xrightarrow[-HCl]{-ROH} CH_2{=}CH{-}CH{=}CHOR + CH_3CH{=}CH{-}CH(OR)_2.$$

Potassium alkoxides add on smoothly to the triple bond in butenyne[7] forming mainly 1- and 2-alkoxybuta-1,3-dienes and also a small amount of the 1,1-dialkoxybut-2-ene.

$$CH_2{=}CH{-}C{\equiv}CH + ROH \longrightarrow \begin{cases} CH_2{=}CH{-}C(OR){=}CH_2\ (10\%) \\ CH_2{=}CH{-}CH{=}CHOR\ \text{(main product)} \\ CH_3{\cdot}CH{=}CH{-}CH(OR)_2\ \text{(small amount)}. \end{cases}$$

Shostakovskii *et al.*[8,9] worked out a new method for the synthesis of alkoxybuta-1,3-dienes, consisting in the selective hydrogenation of alkyl but-1-en-3-ynyl ethers, which can be represented as follows:

$$HC{\equiv}C{-}C{\equiv}CH + ROH \rightarrow HC{\equiv}C{-}CH{=}CHOR \xrightarrow{H_2} CH_2{=}CH{-}CH{=}CHOR.$$

Hydrogenation of butenynyl ethers takes place in methanolic solution over palladium (on gypsum) at room temperature.

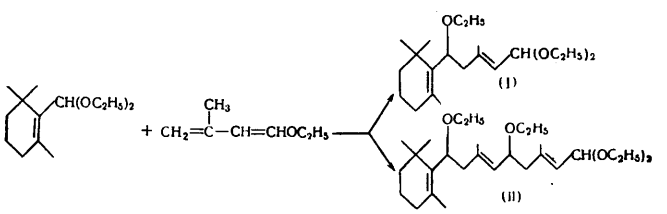
2. Some Chemical Reactions of 1-Alkoxybuta-1,3-dienes

(a) Condensation. Alkoxy-dienes, like other vinyl ethers, undergo condensation reactions. Nazarov and Krasnaya[10] were the first to effect the condensation of acetals with ethoxyisoprene and with ethoxybutadiene:

$$CH_3{-}C(R){=}CH + CH_2{=}CH{-}CH{=}CHOC_2H_5 \longrightarrow$$

$$\rightarrow \begin{cases} (H_3C)(R)C{=}CH{-}CH(OC_2H_5){-}CH_2CH{=}CH{-}CH(OC_2H_5)_2 \\ (H_3C)(R)C{=}CH(CHCH_2CH{=}CH)_2{-}CH(OC_2H_5)_2 \\ (H_3C)(R)C{=}CH(-CHCH{=}CH)_3{-}CH(OC_2H_5)_2. \end{cases}$$

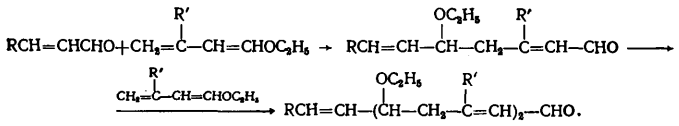
These reactions take place under the influence of boron trifluoride–ether at 0°–5°. Ethoxyisoprene undergoes condensation far more readily than does ethoxybutadiene, and gives a high yield of the final products. These workers were able to lengthen the carbon chain by 5–10 carbon atoms, and correspondingly increase the number of conjugated double bonds.



Considerable interest attaches to the condensation with ethoxyisoprene of the acetal of β-cyclo-citral[11], which opens up a path for the synthesis of several biologically active substances. This reaction takes place at 40°–65°. The corresponding reactions with (I) yield ethoxydihydro-β-ionylideneacetaldehyde and the corresponding alcohol,

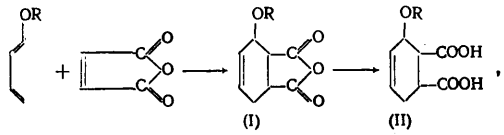
while from the substance (II) high yields of the diethoxybisdehydroaldehyde of Vitamin A and diethoxybisdehydrovitamin A have been synthesised.

Krasnaya and Kucherov[12] condensed various aldehydes with alkoxy-dienes



Formation of unsaturated alkoxy-aldehydes in this way goes well in the presence of boron trifluoride, zinc chloride, and boric acid.

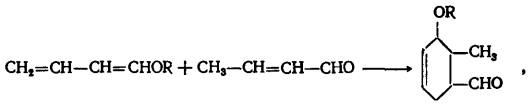
(b) Diene synthesis. 1-Alkoxybuta-1,3-dienes readily take part in diene synthesis with maleic anhydride[13-15]:



where R = C_2H_5. A similar condensation has been carried out with 1-methoxybuta-1,3-diene and 1,4-diethoxybuta-1,3-diene, giving the corresponding cyclic anhydrides, and also with 1-butyl- and 1-isopentyl-buta-1,3-diene[2].

Farmilo and Nicholls[4] undertook the condensation of a mixture of *cis*- and *trans*-1-methoxybuta-1,3-diene with maleic anhydride, and found that only the *trans*-isomer forms an adduct. In their view this reaction can be utilised for the separation of geometrical isomers.

Shostakovskii *et al.*[9] condensed 1-cyclohexyloxybuta-1,3-diene with maleic anhydride, and found that formation of the adduct was accompanied by copolymerisation of the anhydride with butadiene. As a result, a copolymer was isolated which probably had a regular structure. Condensation of 1-alkoxybuta-1,3-dienes with crotonaldehyde[9], however, gave aldehydes of methylalkoxycyclohexenes:



where R = C_4H_9, C_6H_{11}.

The above work shows that geometrical isomerism has a considerable influence in the diene condensation of 1-alkoxybuta-1,3-dienes, only the *trans*-isomers undergoing condensation. Diene condensations are accompanied by heteropolymerisation. The reason for this must obviously be sought in the behaviour of the *cis*-isomer of the original alkoxybuta-1,3-diene.

The polymerisation of 1-alkoxybuta-1,3-dienes has not been investigated systematically, and the literature contains only isolated and contradictory observations. Thus Wichterle[16] was the first to note that 1-ethoxybutadiene undergoes polymerisation on standing. Other workers[5] observed considerable polymerisation of 1-methoxybuta-1,3-diene even on distillation. Flaig[15] showed that 1-alkoxybutadienes are difficult to polymerise. This is fully consistent with the general rule that butadiene is more strongly activated by substituents in position 2 than in position 1. Thus in the absence of air, for example, pure 1-alkoxybutadienes take months to polymerise. In air or in the presence of peroxides, polymerisation takes place with the formation of products of high molecular weight.

III. SULPHUR-CONTAINING BUTA-1,3-DIENES

1. Methods of Synthesis

Existing methods for the synthesis of sulphur-containing buta-1,3-dienes are based on various reactions of butadiene and butadiyne, thiols, and also alcohols and phenols.

A study of the effect of various reaction conditions showed[17,18] that addition of the thiol takes place merely on gentle heating of a mixture containing butadiyne in the presence of potassium hydroxide:

$$HC{\equiv}C{-}C{\equiv}CH + RSH \longrightarrow HC{\equiv}C{-}CH{=}CHSR.$$

The resulting alkenyne can add on a further thiol molecule, giving 60–90% yields of 1,4-dialkylthiobuta-1,3-dienes:

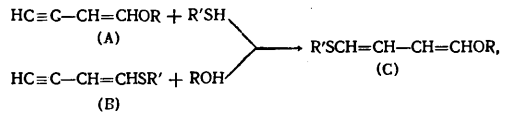
$$HC{\equiv}C{-}CH{=}CHSR + RSH \longrightarrow RSCH{=}CH{-}CH{=}CHSR.$$

Addition of the second thiol molecule takes place more readily on heating and under the influence of radical initiators.

Prilezhaeva *et al.*[19] made a detailed study of this reaction. They discovered also that, if two thiols are taken, formation of the mixed buta-1,3-diene sulphides is accompanied by a symmetrisation of the unsymmetrical dienes:

$$RSCH{=}CH{-}C{\equiv}CH + R'SH \longrightarrow RSCH{=}CH{-}CH{=}CHSR',$$
$$2RSCH{=}CH{-}CH{=}CHSR' \longrightarrow R'SCH{=}CH{-}CH{=}CHSR' + RSCH{=}CH{-}CH{=}CHSR,$$

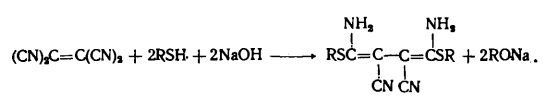
where R = CH_3, C_2H_5, C_4H_9; R' = C_4H_9. The yield of individual dialkylthiobutadienes reached 77%. Sulphur-containing dienes have been prepared also by the reaction of alkyl but-1-en-3-ynyl ethers with thiols and of alkyl but-1-en-3-ynyl sulphides with alcohols[20]:



where R = C_4H_9, C_6H_{11}, $C_6H_5CH_2$; R' = C_2H_5, C_6H_5.

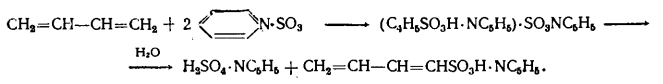
Thiols were found to add on smoothly to alkyl but-1-en-3-ynyl ethers (scheme A), converting the latter into alkyl (or aryl) thiobutadienyl ethers (product C). In the case of ethanethiol, addition to alkyl but-1-en-3-ynyl ethers is carried out in the presence of azodiisobutyronitrile at 75°–80°, and good yields of the corresponding alkylthiobutadienyl ethers are obtained. In several cases the yield was lower in the presence of KOH. This indicates that the reaction takes place by a radical mechanism. However, attempts to effect addition of the alcohol to the but-1-en-3-ynyl sulphide (scheme B) under the above conditions were unsuccessful.

Alkylthiobutadienes have been obtained also by the condensation of thiols with tetracyanoethylene[21]. Yields of up to 80% of 1,4-dialkylthio-1,4-diamino-2,3-dicyanobuta-1,3-dienes were synthesised in this case. The reaction can be represented by the general equation:

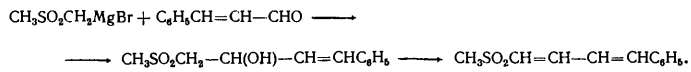


The work of Terent'ev and Dombrovskii[22-31] has shown that the pyridine–sulphur trioxide complex is an excellent sulphonating agent for monoalkenes and dienes containing an activated double bond. Sulphonation takes place when a mixture of the components in dichloroethane solution is heated at 100° – 120° for several hours.

These workers found[29] that, in the sulphonation of compounds containing conjugated double bonds, two molecules of this sulphonating agent first add on to one molecule of the initial compound, with subsequent elimination of a pyridinium sulphate molecule by hydrolysis. The mechanism of this reaction can be written, in the case of butadiene:

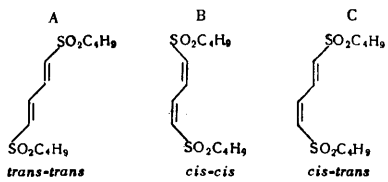


Dienes containing a sulphone grouping have been obtained[32] by organomagnesium synthesis, as follows:



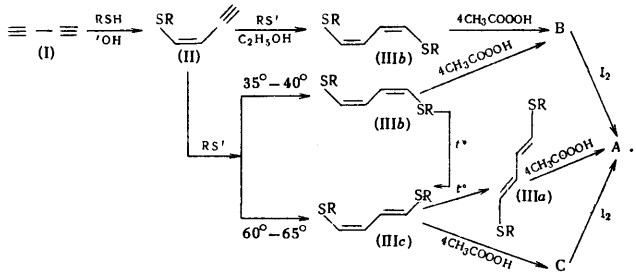
2. Some Chemical Reactions of Sulphur-Containing Buta-1,3-dienes

Prilezhaeva *et al.*[33] converted dibutylthiobuta-1,3-diene into a crystalline sulphone by oxidising it with acetyl hydroperoxide in ethereal solution at low temperatures. From the mixture of sulphones were isolated three possible geometrical isomers of dibutylsulphonylbuta-1,3-diene:



These workers effected in high yield the stereospecific ionic addition of a thiol to 1-butylthiobut-1-en-3-yne (II) with formation of the practically pure *cis* - *cis* isomer (III*b*). This takes place only with as complete removal as possible of air from the reaction medium, the use of inhibitors, and also, if the whole of the thiol is converted into a metal salt, on prolonged heating in ethanol.

When the reaction was carried out under conditions favouring a free-radical addition (with the free thiol, in the presence of air, and with an inert solvent as diluent), mixtures of III*b* and III*c* were obtained in which the latter predominated. On being heated in the presence of oxygen, III*b* partly isomerises into III*c*. Thus the free-radical addition of butanethiol to II is non-stereospecific. If conditions are such that there is competition between free-radical and ionic mechanisms (simultaneous presence of free thiol, a metal salt of the thiol, and air), reaction takes place slowly and mainly by the free-radical mechanism. Under these conditions III*a* appears in the reaction mixture, probably resulting from the isomerisation of III*c*. The stereochemical relations in this reaction are represented by the following scheme:



Oxidation of dialkyl(or aryl)thiobuta-1,3-dienes[34] yields the corresponding disulphones of general formula RSO_2CH : :CHCH : $CHSO_2R$. These disulphones have been isolated in good yield, and are stable crystalline substances, the structures of which have been demonstrated spectroscopically.

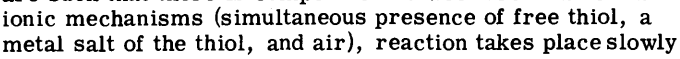
Stereochemical orientation in the synthesis of 1,4-dialkylthiobuta-1,3-dienes has been studied[35] with butadiyne and benzenethiol as components. The reaction was carried out under different conditions ensuring an ionic, a radical, or a mixed type of mechanism. Geometrical stereoisomers were isolated as crystalline substances, which were subjected to subsequent oxidation, isomerisation, and optical examination. In the case of 1,4-diethylthiobuta-1,3-diene with cyclopentadiene[36], diene synthesis takes place in stages and is accompanied by the formation of adducts containing different numbers of cyclopentadiene molecules per molecule of the diethylthiobutadiene. The proportions of the adducts obtained depend on those of the starting materials and on the duration of heating. In contrast to the analogous condensation with maleic anhydride, the adducts which are now formed do not split off ethylthio-groups. Elimination would obviously have led to aromatisation of the ring[17,20] and would have indicated that the cyclopentadiene, not the original diene, was acting as the dienophil.

IV. NITROGEN-CONTAINING BUTA-1,3-DIENES (METHODS OF SYNTHESIS)

The reactivity of buta-1,3-dienes containing nitrogen varies greatly with their composition and structure, and such compounds therefore exhibit great diversity. From our present point of view it is useful to discuss them in the order: amino-derivatives, nitro-derivatives, and cyano-derivatives of buta-1,3-diene.

1. Amino-Substituted Buta-1,3-dienes

Relatively little work has been done on the synthesis of monoamino-1,3-dienes. 1-Amino-4-phenylbutadiene was first synthesised by the action of sodamide (potassium) on 1-bromo-4-phenylbutadiene in liquid ammonia[37]:



Langenbeck *et al.*[38] found that piperidine reacts with crotonaldehyde to form 1,3-dipiperidinobut-2-ene, which

on being heated splits into piperidine and 1-piperidinobuta--1,3-diene:

$$CH_3CH{=}CH{-}CHO + 2HNC_5H_{10} \longrightarrow CH_3CH(NC_5H_{10})CH{=}CH(NC_5H_{10}) \xrightarrow{130^\circ}$$
$$\longrightarrow CH_2{=}CH{-}CH{=}CHNC_5H_{10} + HNC_5H_{10}.$$

The reaction is carried out in absolute ether in the presence of anhydrous potassium carbonate. Other monoaminated 1,3-dienes have been obtained by analogous methods in yields of 15–40%.

It is stated in a patent[39] that dialkylaminobuta-1,3-dienes are obtained by passing 1,4-bisdialkylaminobut-2-ynes in the vapour phase over various catalysts and finely dispersed metallic sodium. The reaction can be represented by the general equation:

$$R'_2NCH_2{-}C{\equiv}C{-}CH_2NR'_2 \xrightarrow[\text{catalyst, } t^\circ]{} R'_2NCH{=}CH{-}CH{=}CHNR'_2,$$

where R = CH_3 and R′ = C_2H_5.

This reaction goes at 250°–450° in the presence of chromium and aluminium oxides and other catalysts, giving yields up to 80%, and is accompanied by isomerisation, the mechanism of which has not yet been adequately studied. It may perhaps represent an acetylene–diene rearrangement, as has been shown in the case of 1,4-dichlorobut-2-yne[40].

1,4-Bisdialkylaminobuta-1,3-dienes having a more branched structure:

$$R_2N{-}\underset{\displaystyle R'}{\underset{|}{C}}{=}CH{-}CH{=}\underset{\displaystyle R''}{\underset{|}{C}}{-}NR_2$$

have also been obtained[41,42].

A new method has recently been worked out for the synthesis of 1,4-bisalkylaminobuta-1,3-dienes from butadiyne and various amines[43–45]:

$$2RNH_2 + HC{\equiv}C{-}C{\equiv}CH \longrightarrow RNHCH{=}CH{-}CH{=}CHNHR.$$

This method gives a high yield (80%) of the final product, and is simple to carry out experimentally, since reaction occurs very smoothly at room temperature.

With secondary amines stepwise addition takes place, 1-dialkylaminobut-1-en-3-ynes being first formed according to the equation:

$$R_2NH + HC{\equiv}C{-}C{\equiv}CH \longrightarrow R_2NCH{=}CH{-}C{\equiv}CH.$$

Addition of a second molecule of the amine to this product requires more severe conditions[45]. Thus n-pentylamine adds on to but-1-en-3-ynyldiethylamine at the boiling point of the alkenyne. The temperature can be lowered by carrying out the reaction under vacuum:

$$(C_2H_5)_2NCH{=}CH{-}C{\equiv}CH + H_2NC_5H_{11} \longrightarrow (C_2H_5)_2NCH{=}CH{-}CH{=}CHNHC_5H_{11}.$$

The main products and the direction of the reaction are governed by the nature of the initial amines.

2. Nitro-Substituted Buta-1,3-dienes

The literature contains only one reference[46] to the preparation of 1-nitrobuta-1,3-diene, which was obtained by the direct action of nitric acid on the diene:

$$CH_2{=}CH{-}CH{=}CH_2 + HONO_2 \longrightarrow CH_2{=}CH{-}CH{=}CHNO_2.$$

1,4-Dinitro-derivatives of 1,3-dienes have been obtained by other methods.

Perekalin and Lerner[47] obtained a 40% yield of 1,4-dinitrobuta-1,3-diene from dinitro-derivatives of ethylenic hydrocarbons:

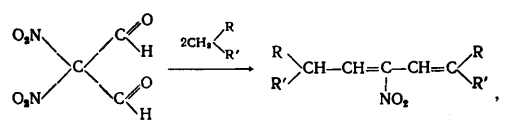
$$CH_2{-}CH{=}CH{-}CH_2 \xrightarrow{Cl_2} CH_2{-}CHCl{-}CHCl{-}CH_2 \xrightarrow{(CH_3COO)_4Pb} CH{=}CH{-}CH{=}CH.$$
$$\quad NO_2 \qquad\qquad NO_2 \qquad\qquad NO_2 \qquad\qquad NO_2 \qquad\qquad NO_2 \qquad\qquad NO_2$$

Novikov *et al.*[48] prepared the same product by condensing glyoxal with nitromethane, the yield being quantitative:

$$OCH{-}CHO \xrightarrow{CH_3NO_2} CH_2{-}\underset{\displaystyle NO_2}{\underset{|}{CH}}{-}\underset{\displaystyle NO_2}{\underset{|}{CH}}{-}CH_2 \xrightarrow{CH_3COCl}$$
$$\longrightarrow CH_2{-}\underset{\displaystyle NO_2}{\underset{|}{CH}}{-}\underset{\displaystyle NO_2}{\underset{|}{CH}}{-}CH_2 \xrightarrow{KHCO_3} CH{=}CH{-}CH{=}CH.$$
$$\quad NO_2 \qquad\qquad NO_2 \qquad\qquad NO_2 \qquad\qquad NO_2$$

Attempts at the direct synthesis of 1,2,3,4-tetranitrobuta-1,3-diene from butadiyne and dinitrogen tetroxide[49] have so far been unsuccessful, since the reaction has been accompanied by explosions. The only product which could then be isolated was oxalic acid.

Perekalin[50] has also worked out a method for synthesising several nitrobuta-1,3-diene derivatives based on the condensation of the sodium salt of nitromalonaldehyde with various substances containing reactive hydrogen atoms in methylene or methyl groups:



where R = C_2H_5COO, CN and R′ = CN, NO_2. In this way mono- and di-nitro-derivatives of 1,3-dienes have been obtained containing aromatic and heterocyclic radicals in the carbon chain.

Kochetkov and Dudykina[51] synthesised 1-nitro-4-phenylbuta-1,3-diene in yields up to 66% by the reaction of cinnamaldehyde with nitromethane

$$C_6H_5CH{=}CH{-}CHO + CH_3NO_2 \xrightarrow{-H_2O} C_6H_5CH{=}CH{-}CH{=}CHNO_2.$$

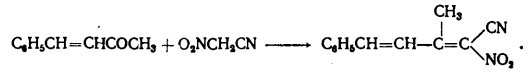
The action of N_2O_4 on phenylated dienes under various conditions gave good yields of the following dinitrobuta-1,3--dienes[52–54]:

(*a*) $C_6H_5CH{=}CH{-}CH{=}CHC_6H_5 \xrightarrow{N_2O_4} C_6H_5CH{-}CH{=}CH{-}CHC_6H_5 \longrightarrow$
$\quad NO_2 \qquad\qquad NO_2$

$$\xrightarrow[NH_4OH]{dil.} C_6H_5C{=}CH{-}CH{=}CHC_6H_5,$$
$$\quad NO_2$$

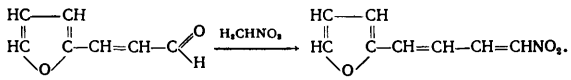
(*b*) $C_6H_5C{=}CH{-}CH{=}CC_6H_5 \xrightarrow[\text{abs. ether, cooled}]{N_2O_4} C_6H_5C{=}CH{-}CH{=}C\,C_6H_5$
$\quad NO_2 \qquad\quad H \qquad\qquad\qquad\qquad NO_2 \qquad\qquad NO_2$

Condensation of methyl phenylvinyl ketone with nitroacetonitrile gives a 65% yield of 2-methyl-1-nitro-4--phenylbuta-1,3-dienyl cyanide[55]:



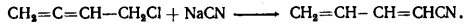
Methylamine and diethylamine act as catalysts for this reaction.

Condensation of furylacraldehyde with nitromethane provides a synthesis of 1-(2-furyl)-4-nitrobuta-1,3-diene[56]



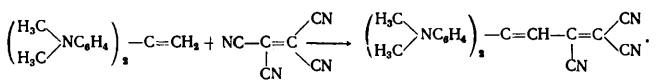
3. Cyano-Substituted Buta-1,3-dienes

Numerous papers have been published on methods of synthesising and the chemical properties of dienes containing one, two, or more cyano-groups. These methods and properties can differ greatly depending on the number of cyano-groups and their positions in the molecule, and also on the stereoisomerism of the diene system itself. Patent claims and several investigations[57-62] have been made on the synthesis of 1-cyanobuta-1,3-diene. According to Coffman[62], for example, this compound is obtained as follows:

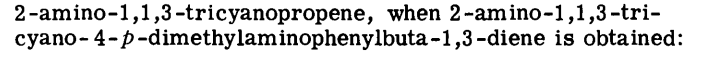


The reaction is carried out in methanol with gentle heating. In the light and also on standing, the reaction product polymerises, the resulting polymer resembling ω-polychloroprene.

Cyanobutadienes can be synthesised by the interaction of 1,1-bis-*p*-dimethylaminophenylethylene and tetracyanoethylene[63], which yield 3,4,4-tricyano-1,1-bis-*p*-dimethylaminophenylbuta-1,3-dienes. The principal reaction can be represented by the equation:



The same workers obtained a series of compounds of this type, differing in the numbers of dimethylaminophenyl and cyano-groups in the butadiene structure. There are also indications in patents[64,65] that such dienes can be obtained by the interaction of *p*-dimethylaminobenzaldehyde and 2-amino-1,1,3-tricyanopropene, when 2-amino-1,1,3-tricyano-4-*p*-dimethylaminophenylbuta-1,3-diene is obtained:

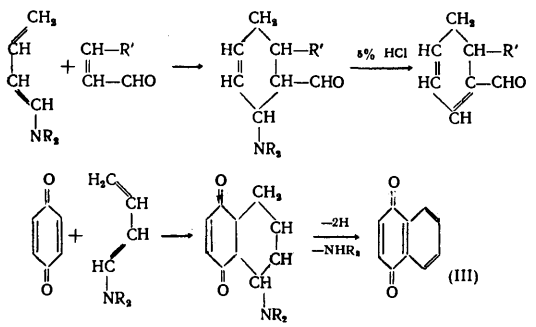


4. Some Chemical Reactions of Nitrogen-Containing Buta--1,3-dienes

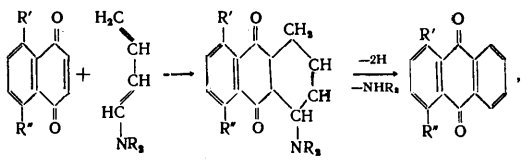
Among the typical reactions of compounds containing a system of conjugated double bonds is their ability to condense with various unsaturated compounds in which the multiple bond is activated by so-called electronegative groups such as C=O, C≡N, NO_2, etc.

In order to determine the effect of a nitro-group on the conjugated system of a diene, 1-nitrobuta-1,3-diene was prepared by the direct nitration of butadiene[66], and its reactivity with maleic anhydride was studied. It was concluded that the diene system in the nitrodiene had been deactivated, especially the αβ-double bond, as a result of which nitrobutadiene acts as a nitroalkene in additions.

Many investiations have been made on diene syntheses involving aminobuta-1,3-dienes and various dienophils[38,67]. Thus Langenbeck *et al.*[38] found that diene synthesis goes well with 1-aminobutadienes and compounds which are not acidic in character but contain a reactive double bond. Dienophils which are acidic in character result in rapid resinification of the aminobutadienes. Acraldehyde yields dihydrobenzaldehyde (I), crotonaldehyde gives dihydro-*o*-tolualdehyde (II), benzoquinone produces naphthaquinone (III), and from α-naphthaquinone is obtained anthraquinone (IV) and correspondingly naphthazarin passes into quinizarin (V).

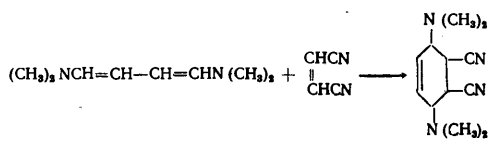


for (I), R′ = H; and (II) R′ = CH_3.

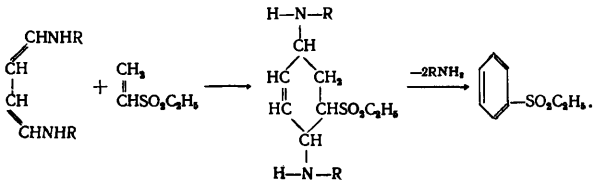


for (IV), R′ = R″ = H; and (V), R′ = R″ = OH.

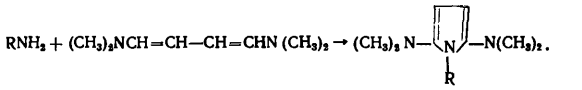
Some work has been done also on the chemistry of 1,4--diaminobuta-1,3-dienes. Thus Fegley *et al.*[68] studied the reaction of *cis-trans*- and *trans-trans*-isomers with dienophils containing electron-acceptor groups adjacent to the double bond. 1,4-Bisdimethylaminobuta-*cis*-1, *trans*-3--diene with fumaronitrile gives *cis-trans* (or *trans-cis*)--3,6-bisdimethylaminocyclohex-4-ene-*cis-trans*-1,2-dicarbonitrile. 1,4-Bisdimethylaminobuta-*trans*-1,*trans*-3--diene gives with the same dienophil *cis-cis*-3,6-bisdimethylaminocyclohex-4-ene-*cis-trans*-1,2-dicarbonitrile.



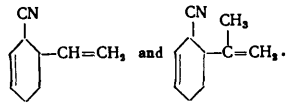
1,4-Diaminobutadienes undergo diene condensation also with ethyl vinyl sulphone[45]:



Among other chemical properties, the reactions of 1,4--diaminodienes with various amines have been studied. With primary amines *N*-substituted pyrroles are formed[69]:

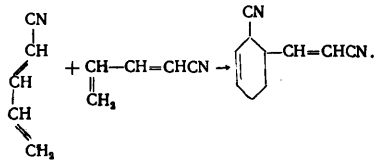


With 1-cyanodienes the general rule remains valid that the *cis*-isomer does not undergo condensation at all with maleic anhydride, whereas its *trans*-isomer gives an adduct in good yield[70]. With cyclopentadiene[71] as dienophil, both *cis*- and *trans*-isomers of the original cyanodiene give the corresponding adducts, in yields of 58 and 80% respectively under identical conditions. Butadiene and isoprene as dienophils[72] yield adducts having the structures:



A study of the dimerisation of monocyanodienes has shown[73] that *trans*-1-cyanobuta-1,3-diene is the main source of the dimer, whereas the *cis*-isomer is converted comparatively readily into a polymeric product.

Dimerisation of this diene can be represented in general as:



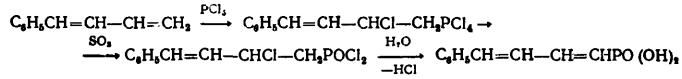
V. HETERO-SUBSTITUTED PHOSPHORUS-CONTAINING BUTA-1,3-DIENES

Under this name we are concerned with organic compounds having a butadiene carbon chain and containing other elements as well as phosphorus. Such compounds have been synthesised only during the past few years.

1. Methods of Preparation

One of the first papers on the synthesis of organophosphorus 1,3-dienes was that by Bergmann and Bondi[74], who obtained 4-phenylbuta-1,3-dienylphosphonic acid from 1-phenylbuta-1,3-diene and phosphorus pentachloride.

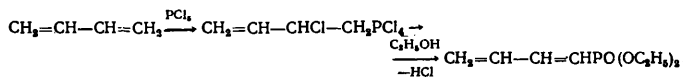
After appropriate treatment of the intermediate complex with dry sulphur dioxide followed by water, the organophosphorus diene was isolated:



However, the mechanism of the reaction and also the structure of the product have not been rigorously proved.

Papers by Kosolapoff and others[75,76] suggest that, when phosphorus pentachloride reacts with compounds containing double bonds, a chlorine atom adds on to the least hydrogenated carbon atom, while the PCl_4 group becomes attached to the most hydrogenated carbon atom.

Phosphorus pentachloride adds on in this way to butadiene, and the preparation of ethyl butadienylphosphonate in this way has been patented[77].



Dehydrochlorination of the intermediate product is effected with alcoholic potassium hydroxide.

Anisimov and others considerably extended the addition of phosphorus pentachloride to various unsaturated compounds, in particular to diene hydrocarbons[78,79].

Organophosphorus acid chlorides were converted into esters by reaction with alcohols in the presence of pyridine[80].

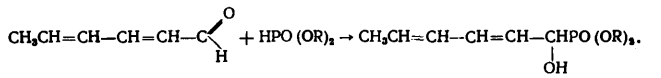
Organophosphorus dienes have been obtained also from alkynes. Zinov'ev *et al.*[81] studied the reaction of acetylenic hydrocarbons with phosphorus trichloride and oxygen, and found that a halogen atom and the $POCl_2$ group add on to the acetylenic bond with the formation of dienes.

Petrov *et al.*[82] added phosphorus pentachloride to hex--1-en-5-yne.

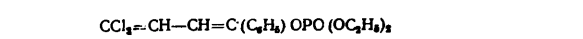
Vovsi *et al.*[83] first carried out the reaction of phosphorus pentachloride with 2-methylbut-1-en-3-yne.

Anisimov and his coworkers effected the addition of phosphorus pentachloride to ethynylcyclohexene[84] and to 2-methylbut-1-en-3-yne[85]. They also studied the properties of the resulting diene acid chlorides, which, as was to be expected, reacted readily with alcohols to yield the normal esters. Organophosphorus dienes have been obtained also by the addition of phosphoric esters to polyenes.

Pudovik and Kitaev[86] synthesised multifunctional phosphorus-containing 1,3-dienes by the reaction:



Allen and Johnson[87] prepared a diene containing phosphorus and an aromatic radical, and having the following structure:



Hetero-substituted organophosphorus dienes have been obtained also from alkyl but-1-en-3-ynyl ethers[88]:

$$ROCH{=}CH{-}C{\equiv}CH + 2PCl_5 \rightarrow [ROCHCl{-}CH(PCl_4{\cdot}PCl_5){-}C{\equiv}CH] \xrightarrow{2SO_2}$$
$$\rightarrow ROCH{=}C(POCl_3){-}CCl{=}CH_2 + POCl_3 + 2SOCl_2,$$

where R = CH_3, C_2H_5, C_3H_7, C_4H_9. The structures of the resulting compounds were proved from their Raman spectra[89]. Esters and amides of these acid chlorides have also been prepared[90].

A continuation of an investigation[88] which had been begun on this class of organic compounds was the synthesis[91] of 1-alkylthio-3-chloro-2-dichlorophosphinylbuta-1,3-dienes by the scheme:

$$RSCH{=}CH{-}C{\equiv}CH + 2PCl_5 \rightarrow [RSCHCl{-}CH(PCl_4{\cdot}PCl_5){-}C{\equiv}CH] \xrightarrow{\text{isomerisation}}$$
$$\rightarrow [RSCH{=}C(PCl_4{\cdot}PCl_5){-}CCl{=}CH_2] \xrightarrow{2SO_2} RSCH{=}C(POCl_3){-}CCl{=}CH_2 + 2SOCl_2 + POCl_3,$$

where R = CH_3, C_2H_5, C_3H_7, C_4H_9.

The structure of these derivatives was established from their infra-red spectra. Several of their chemical properties were also studied, and in particular their normal esters, amides, thiols, and other derivatives were synthesised[92-94].

2. Some Chemical Properties

Among the chemical properties of organophosphorus monomers, special significance attaches to their conversion into compounds of high molecular weight, many of which are widely used in various branches of the national economy. During recent years the chemistry of macromolecular organophosphorus compounds has been developed more intensively. Much research has been done on the polymerisation and copolymerisation of esters and amides of various phosphoric acids. It has been discovered that compounds of high molecular weight can be obtained comparatively easily from allyl and methylallyl esters of phosphonic acids.

In 1940 Warren[95] and Toy[96-97] discovered that allyl and methylallyl arylphosphonates could be polymerised to transparent, flameproof, vitreous materials. The formation of polymers was substantially affected by the structure and number of individual groups in the original monomer. Thus esters of phosphorus acids containing one allyl group form only products of low molecular weight at the best. Compounds containing two allyl groups are readily polymerised from the initial monomer[98-102].

It can be assumed from the work of several investigators[101,103-105] that the tendency to polymerisation of allyl and methylallyl esters of phosphorus acids, and the properties of the resulting polymers, will be influenced by the following factors: (a) the molecular weight of the monomer and the size of the substituents attached to the phosphorus atom, (b) the electronic character of these substituents, and (c) the presence or absence of inhibiting groups in the ester molecule.

Thus among compounds of the general formula

$$R{-}P(=O){-}(OCH_2{-}CH{=}CH_2)_2,$$

where the substituents (R) may be H, CH_3, C_2H_5, C_3H_7, iso-C_3H_7, or C_4H_9, those in which R is smallest in size will form a solid polymer, and as R becomes more bulky the hardness of the polymers will diminish until they become gelatinous. The hardness of the resulting polymer diminishes as the ester part of the monomer molecule becomes larger. Under such conditions the increase in molecular weight of the monomer probably has an effect, under otherwise identical conditions, of impeding polymerisation.

The hardness of the above polymers is substantially affected by the electronegativity of the substituent. Thus vitreous polymers are obtained from those allyl esters in which the electronegativity of the substituent directly combined with the phosphorus is greater than that of the methyl group (isobutenyl, aryl, benzyl, phenoxy, etc. group).

The presence of some atoms or groups in the allyl esters of phosphorus acid inhibits polymerisation, allowing at best viscous syrups or oils to be obtained, but not solid polymers. Among such inhibiting atoms or groups are sulphur and nitrogen located between the phosphorus and the allyl groups[106].

There are indications[99,101] that the presence of several double bonds in allyl arylphosphonates does not always make these substances capable of polymerisation. In spite of this, however, other investigators have obtained transparent solid polymers from diallyl arylphosphonates[100,106-108].

The ability of vinyl esters of phosphorus acids to form polymers has been investigated by Upson[109], Gefter and Kabachnik[110], and others[111,112]. Compounds of this type containing two or three double bonds yielded hard vitreous polymers on being heated in the presence of benzoyl peroxide. Esters containing only one double bond, however, either do not polymerise at all or else give viscous liquids or gelatinous masses.

VI. SILICON-CONTAINING BUTA-1,3-DIENES

In view of the vigorous development of the silicon industry, it is of particular importance to work out new methods for the synthesis and investigation of the chemical properties of organosilicon monomers, and among such monomers the silicon-substituted buta-1,3-dienes occupy a special position. It therefore seemed to us interesting to summarise the literature on this question.

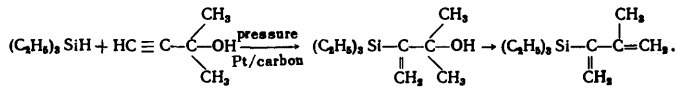
1. Methods of Preparation

Existing paths for the synthesis of silicon-substituted buta-1,3-dienes are based on various chemical reactions of the following organic starting materials: chloroprene and vinylacetylene (but-1-en-3-yne), trialkylsilanes, acetylenic alcohols containing silicon, and finally simple silanes.

Petrov and Sadykh-zade[113] synthesised triethylsilyl-1-butadiene by the selective hydrogenation of 4-triethylsilylbut-1-en-3-yne over palladium on $CaCO_3$:

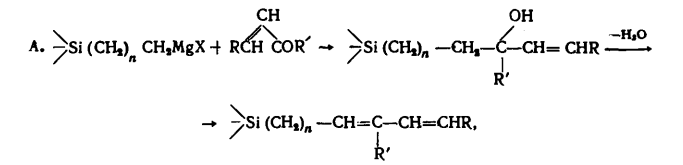
$$(C_2H_5)_3SiC{\equiv}C{-}CH{=}CH_2 \xrightarrow[Pd/CaCO_3]{H_2} (C_2H_5)_3SiCH{=}CH{-}CH{=}CH_2.$$

Shchukovskaya *et al.*[114] obtained a diene containing silicon by the dehydration of an unsaturated alcohol containing silicon:

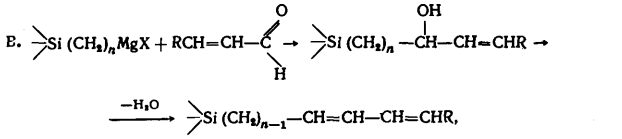


The organosilicon alcohol used as starting material was synthesised at elevated pressures and with platinum on activated charcoal as catalyst.

Sadykh-zade and Petrov[115,116] obtained various trialkylsilylbuta-1,3-dienes by a similar method:



where n = 2,6; R = H, CH_3, C_6H_5; R′ = H, CH_3.



where n = 1,3; R = H, CH_3, C_6H_5.

The alcohols were dehydrated by the action of $KHSO_4$.

It was subsequently shown[117] that silylbutadienes can be synthesised by the addition of silanes to but-1-en-3-yne at room temperature:

$$CH_3Cl_2SiH + HC\equiv C-CH=CH_2 \rightarrow CH_3Cl_2SiCH=CH-CH=CH_2,$$
$$Cl_3SiH + HC\equiv C-CH=CH_2 \rightarrow Cl_3SiCH=CH-CH=CH_2.$$

The best catalyst for such reactions proved to be a 0.01 N solution of chloroplatinic acid in isopropyl alcohol, *i.e.* the so-called Speier catalyst[118].

Several organosilicon dienes were obtained by Shostakovskii *et al.*[119]. These workers synthesised 1-butoxy-4-trimethylsilylbuta-1,3-diene by the selective hydrogenation of 1-butoxy-4-trimethylsilylbut-1-en-3-yne:

$$(CH_3)_3SiC\equiv C-CH=CHOR \xrightarrow{H_2} (CH_3)_3SiCH=CH-CH=CHOR.$$

The hydrogenation was catalysed with a mixture of 2% Pd on $CaCO_3$ and 5% Pt on carbon.

2. Some Chemical Reactions of Silicon-Containing Buta-1,3-dienes

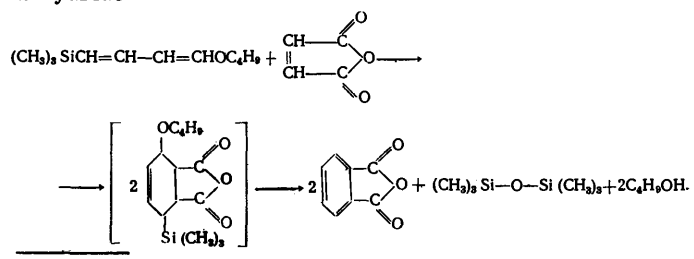
The literature on the synthesis and the properties of organosilicon dienes is very limited. This interesting branch of diene chemistry is in the initial stages of its development.

Alkylation of appropriate organosilicon butadienes can be achieved by replacing reactive chlorine atoms, for example, by methyl groups[120]:

$$CH_3Cl_2SiCH=CH-CH=CH_2+2CH_3MgI \rightarrow (CH_3)_2SiCH=CH-CH=CH_2+2MgICl,$$
$$Cl_3SiCH=CH-CH=CH_2+3CH_3MgI \rightarrow (CH_3)_3SiCH=CH-CH=CH_2+3MgICl.$$

A study was made of the tendency of the above silicon-containing diene hydrocarbons to undergo condensation and dimerisation[121]. Silylbutadienes were condensed with acraldehyde, methyl acrylate, and acrylonitrile. In all cases good yields of the corresponding cyclic adducts were obtained.

Shostakovskii *et al.*[119] have condensed 1-butoxy-4-trimethylsilylbuta-1,3-diene with maleic anhydride. The resulting cyclic adduct is unstable, and butanol is already eliminated under the reaction conditions. In the end it was possible to isolate only hexamethyldisiloxane and phthalic anhydride:



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FREE RADICAL REACTIONS IN THE ELECTROLYSIS OF ORGANIC COMPOUNDS

A. P. Tomilov and M. Ya. Fioshin

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1. INTRODUCTION

Electrolytic processes in aqueous and non-aqueous electrolytes often lead to the formation of free radicals. Free radical reactions during electrolysis do not appear to have attracted the attention they deserve, and very few published papers deal specifically with electrochemical methods of preparation of free radicals and with the characterisation of free radicals thus produced. Yet studies of the properties and behaviour of electrochemically generated free radicals offer great theoretical and practical possibilities.

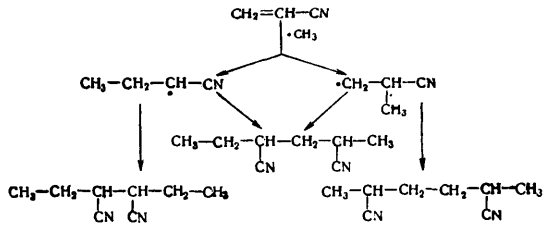
The present article discusses the electrochemical reactions of organic compounds in which free radicals are involved.

2. METHODS OF DETECTING FREE RADICALS IN THE ELECTROLYSIS OF ORGANIC COMPOUNDS

The formation of free radicals during electrolysis of organic compounds can be demonstrated by a number of methods.

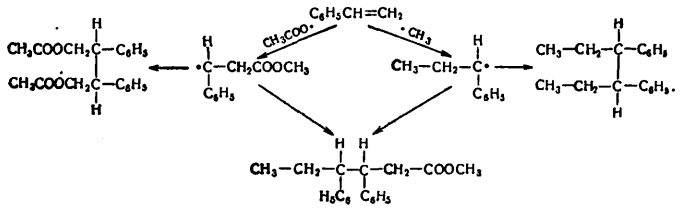
One can, for example, make a study of the products which appear when organic compounds are electrolysed in the presence of free radical acceptors, *i.e.*, of unsaturated compounds, which readily combine with free radicals. Styrene, acrylonitrile, butadiene, isoprene, and other similar compounds will readily accept free radicals.

The nature of the free radicals formed during electrolysis can often be inferred from the products obtained when organic compounds are electrolysed in the presence of such acceptors. The method was applied with success to the free radical reactions occurring during the Kolbe synthesis. Thus, electrolysis of a solution of potassium acetate in anhydrous acetic acid containing acrylonitrile gives a number of products [1] whose formation can be described by the following scheme if it is assumed that the anodic process generates methyl radicals which then react with molecules of acrylonitrile:



The electrolysis of sodium acetate solutions in acetic acid containing styrene [1,2], isoprene, or butadiene [3] yields

addition products of acetate radicals as well as of methyl radicals, thus:



An interesting reaction is observed when salts of dicarboxylic acid mono-esters are electrolysed in the presence of butadiene. For example, a salt of monoethyl maleate gives[3,4] substituted vinyl radicals at the anode:

$$2C_2H_5OOCH{=}CHCOO^- \xrightarrow{-2e} 2C_2H_5OOCCH{=}\dot{C}H{+}2CO_2,$$

which then react with butadiene:

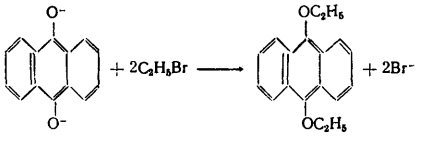
$$2C_2H_5OOCCH{=}\dot{C}H + CH_2{=}CHCH{=}CH_2 \rightarrow$$
$$\rightarrow C_2H_5OOCCH{=}CHCH_2CH{=}CHCH_2CH{=}CHCOOC_2H_5.$$

The resulting unsaturated compound gives sebacic acid upon saponification and hydrogenation. Electrolysis of the salt of monomethyl adipate in the presence of butadiene gives similar results[5].

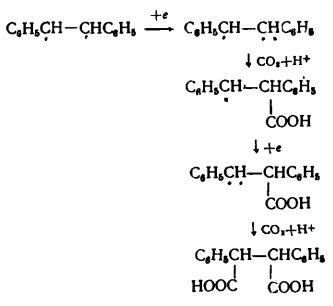
Certain other addition reactions between organic free radicals and organic compounds, which also can be used to detect the formation of free radicals during electrolysis, will be considered in Section 4d, "Interactions with the Solvent".

The free radicals formed during electrolysis are sometimes stable enough to cause observable changes in the colour and in the chemical properties of the solution. The following are a few examples:

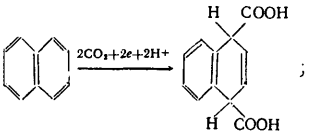
1. A solution of anthraquinone in acetonitrile develops new chemical properties during electrolysis. It reacts vigorously with ethyl bromide forming 9,10-diethoxyanthracene[6], probably *via* the electrolytically generated double anion:



2. The radical anions formed when a solution of stilbene in dimethylformamide is electrolysed can react with carbon dioxide, giving diphenylsuccinic acid[7]:



Addition of carbon dioxide to an organic radical with formation of a dicarboxylic acid has also been observed[8] with certain other hydrocarbons. Thus, naphthalene gives 1,4-dihydronaphthalene-1,4-dicarboxylic acid:

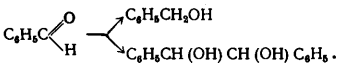


and phenanthrene gives 9,10-dihydrophenanthrene-9,10-dicarboxylic acid, whilst diphenylfumaric acid is obtained from diphenylacetylene.

3. The formation of free radicals during electrolytic reduction of naphthalene at a mercury cathode is also confirmed by the appearance of a green colour in the vicinity of the cathode. The same coloration is also observed during the reaction between naphthalene and metallic sodium[9], and is clearly due to free radicals.

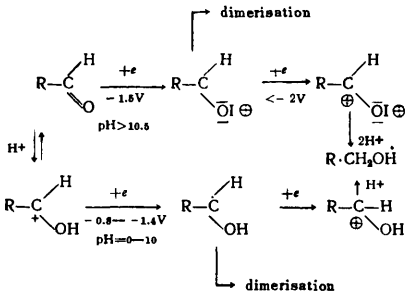
The chemical methods mentioned above can only detect free radicals which are sufficiently stable (and therefore long-lived) to diffuse into the solution. Physicochemical methods, above all polarographic analysis, are free from this limitation. By studying "current *vs.* potential" curves it is often possible to show that addition of electrons to an organic molecule at a dropping mercury cathode proceeds by a stepwise mechanism, which implies that the intermediate reduction product is a radical or a radical-ion. Polarographic data have proved very valuable for interpreting the mechanism of the electrolytic reduction of organic substances[10-12], and have shown that many electrochemical reactions proceed *via* free radical intermediates.

We shall consider, as an example, the electrolytic reduction of benzaldehyde[11,13], which can give two different products, benzyl alcohol or hydrobenzoin:



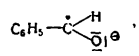
In an acid medium benzaldehyde gives two distinct one-electron waves, which merge into a single two-electron wave at pH 7. Further increase in pH gradually lowers the combined wave to one-half of its initial height, and a new wave appears whose height accounts for the decrease in height of the combined wave.

The following reaction mechanism[13] explains the behaviour of benzaldehyde during reduction:



In acid solution, a protonated molecule of aldehyde is reduced to the radical $C_6H_5\dot{C}HOH$, which then dimerises to hydrobenzoin. Further reduction of the radical (to benzyl

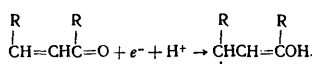
alcohol) is possible at sufficiently negative potentials (> -1.3 V). In strongly alkaline media the reduction follows a somewhat different path. An electron adds on to an unprotonated aldehyde molecule, giving the radical



which then dimerises. Further reduction of this radical occurs at potentials below -2 V, and appears to set in before protonation.

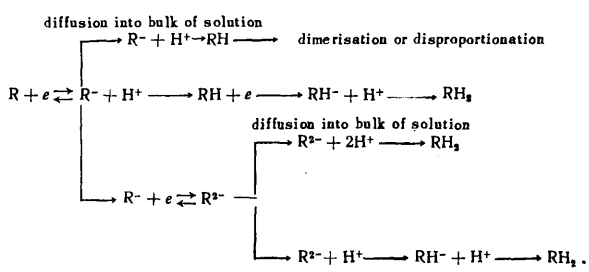
The above mechanism, originally put forward in connection with the electrolytic reduction of benzaldehyde, appears to be generally applicable to the reduction of other aromatic aldehydes and ketones [14-16], although some details of the electrode processes involved are still controversial.

The formation of free radicals has also been demonstrated during the electrolytic reduction of α,β-unsaturated aliphatic ketones, and the following mechanism has been suggested [12]:



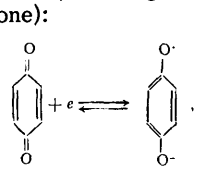
The structure of the resulting radical, however, has not yet been fully characterised.

Hoijtink *et al.*[17] made a careful polarographic study of the electrolytic reduction mechanism of many unsaturated hydrocarbons, and concluded that polycyclic aromatic hydrocarbons — and also aliphatic hydrocarbons containing conjugated double bonds, $(CH=CH)_n$ — are reduced through the intermediate stage of a radical anion, formed by addition of an electron:

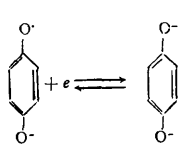


Polarographic studies [18] have also shown that free radicals are formed during the reduction of tropylium ions.

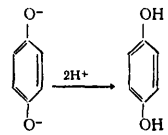
Some polarographic results [6] on the reduction of quinones are of considerable interest, because they confirm the above mechanism involving radical anions. The quinones investigated include the duroquinone of α-hydroxyphenazine [19], of *N*-methyl-α-hydroxyphenazine [20], and others [21,22]. Addition of one electron occurs, leading to the formation of radical ion (semiquinone):



which then adds on a second electron giving a di-anion:

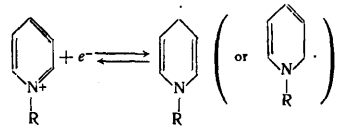


The di-anion captures protons from the solvent forming hydroquinone:



The reduction of anthraquinone, 2-methyl-1,4-naphthoquinone, and duroquinone proceeds according to this scheme.

The reduction of quaternary pyridinium ions has been shown, polarographically, to yield free radicals by a reversible one-electron step [23,24]:



N-ethylpyridinium salts with electron-acceptor substituents show a similar behaviour [25].

Holleck concluded, from a polarographic study of the reduction of aromatic nitro-compounds, that one-electron reactions can occur in alkaline media independently of hydrogen-ion concentration, giving rise to a radical anion [13,26]:

$$RNO_2 + e^- \rightarrow (RNO_2)^- .$$

Alternating-current, oscillographic voltammetry with a hanging-drop cathode [27-30] has given valuable indications of the formation of free radicals during electrolysis. Thus, the presence of free ketyl radicals during the reduction of benzophenone has been convincingly demonstrated by this polarographic technique [30]. Benzophenone and its reduction products are oxidised, at a mercury anode, at potentials more positive than -0.28 V. Using a.c. voltammetry, a well-defined peak is observed in the anodic branch at a potential of -1.34 V: this corresponds to the reversible oxidation of the ketyl radicals formed at the electrode during the cathodic polarisation.

Another successful technique for investigating the formation of free radicals during electrolysis is the method of paramagnetic resonance.

The method was first applied to solutions prepared by controlled-potential electrolysis and stabilised at liquid-nitrogen temperature. A qualitative proof was given of the formation of free radicals in the electrolysis of hydrocarbons and quinones, but no indication of the structure of the radicals was obtained because the EPR spectrum of frozen radicals has no hyperfine structure [31].

Some recent attempts have been made to place the electrolytic cell directly in the resonant cavity, thus enabling the structure and concentration of short-lived radicals to be studied. This improved technique has made it possible to demonstrate the presence of $ClO_4^{\cdot}$ radicals on the electrode in the electrolysis of 0.1 M solutions of lithium perchlorate in acetonitrile [32], and to prove that radical ions with single negative charges are formed during electrolytic oxidation of nitrobenzene [33], dinitrobenzene [34], phenothiazine [35], *p*-phenylenediamine [37], and various aliphatic nitro-compounds [36]. In these experiments the hyperfine structure of the EPR spectra was preserved, and the structure of the free radicals formed during electrolysis could be inferred from the results. Thus, it was shown that the

radical anion $(\dot{C}_6H_5NO_2)^-$ is present in the controlled-potential electrolytic reduction of nitrobenzene at a mercury cathode. Radicals of this type, it should be noted, had already been postulated by Holleck on the basis of his polarographic work [13,26].

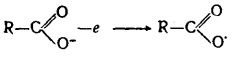
The structure $(NH_2C_6H_4NH_2)^+$, assigned by EPR to the positive radical ion formed during the controlled-potential oxidation of *p*-phenylenediamine at a mercury cathode [37], is also in full agreement with the conclusions of polarographic investigations of this compound [38-40].

3. CLASSIFICATION OF ELECTROCHEMICAL REACTIONS LEADING TO THE FORMATION OF FREE RADICALS

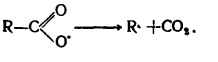
It has been shown, by the methods discussed in the previous section, that both anodic and cathodic electrochemical reactions can give rise to organic free radicals.

a. Anodic Reactions

Discharge of organic anions. The most typical reactions of this class take place when carboxylic acids or organometallic compounds are electrolysed. The salts of organic acids dissociate in aqueous solutions, to which they impart a high electrical conductivity. The same anions are formed also when these salts are dissolved in other solvents of high dielectric constant, such as methanol, organic acids, dimethylformamide, acetonitrile, etc. Electrolysis of these solutions, under suitable conditions, results in discharge of the anions at the anode with the formation of free radicals [41]:



The free radicals formed by the electrode reaction are unstable, and usually undergo further decomposition according to the equation:



The subsequent fate of these radicals is discussed below (see Section 4).

Solutions of mono- and dithio-acids [42-45], and also ether solutions of organomagnesium compounds [46] have a fair electrical conductivity due to their dissociation:

$$RMgX \rightleftarrows R^- + MgX^+.$$

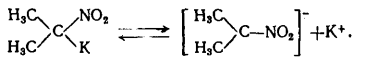
Only one anodic process is possible when such a solution is electrolysed: discharge of the anion and formation of the free radical R·.

Some other organometallic compounds (*e.g.* diethylzinc [47]), and certain organic compounds containing alkali metals, show a similar behaviour when their solutions are electrolysed. Thus, sodiomalonic ester dissociates in alcoholic solution according to the equation [48]:

$$NaHC(COOR)_2 \rightleftarrows Na^+ + HC(COOR)_2^-$$

and the anions can be discharged at the anode, giving the corresponding free radicals. This electrolysis scheme (dissociation followed by formation of free radicals) is also applicable to solutions of alkoxides [49] and mercaptides [50].

Some nitro-compounds form electrically conducting salts. For example, the dissociation of the potassium salt of nitroisopropane can be depicted as [51]:



Lastly, we should note that the salts of the oximido-derivatives of malonic acid can be electrolysed. Dissociation in this case proceeds [52] according to:

$$NaON{=}C(COOR)_2 \rightleftarrows Na^+ + ON{=}C(COOR)_2^-.$$

Oxidation of neutral organic molecules. The electrochemical oxidation of alcohols in sulphuric acid solution [53,54] is a reaction of this type. An alcohol molecule loses an electron at the electrode surface:

$$CH_3OH \xrightarrow{-e} [CH_3OH]^+ ,$$

and the resulting cation rapidly attacks water:

$$[CH_3OH]^+ + H_2O \longrightarrow CH_3O\cdot + H_3O^+ .$$

The methoxy radical now loses a second electron at the anode:

$$CH_3O\cdot \xrightarrow{-e} [CH_3O]^+ ,$$

and the $(CH_3O)^+$ ion gives up a proton to the solvent and is converted into formaldehyde:

$$[CH_3O]^+ + H_2O \longrightarrow HCHO + H_3O^+.$$

The electrochemical oxidations of aniline [55-57], *p*-phenylenediamine [37,39,40], and also of phenylthiourea [58], appear to follow a similar course.

Reaction of an organic compound with an inorganic free-radical primary anodic product. An organic free radical may be formed by a chemical reaction involving an inorganic free radical:

$$RH + X\cdot \longrightarrow R\cdot + HX,$$

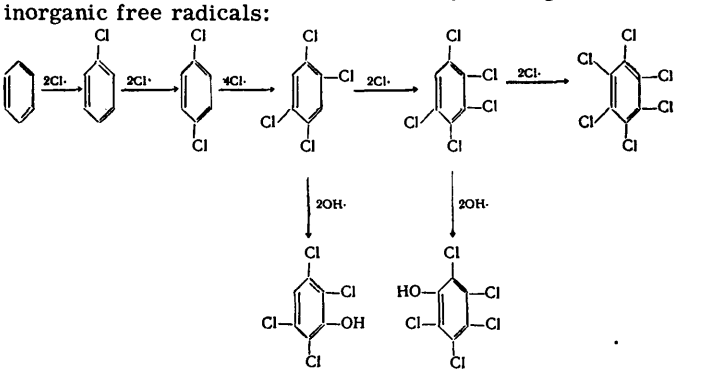
where X· is an inorganic free radical, formed as a primary product in an electrode reaction.

If the activity of the inorganic free radicals at the electrode surface is high enough, rapid combination with the R· radicals will take place:

$$R\cdot + X\cdot \longrightarrow RX .$$

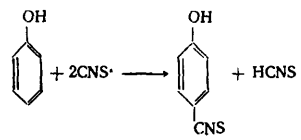
This sequence of events is usually termed "anodic substitution", and occurs in many electrochemical fluorinations, chlorinations, brominations, iodinations, hydroxylations, alkoxylations, thiocyanations, etc. [59]

The electrochemical chlorination of benzene, involving [60] the following scheme, is a good example of a reaction between an organic compound and electrolytically generated inorganic free radicals:

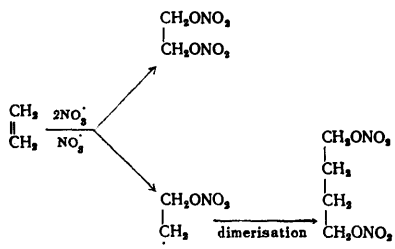


In addition to chlorination, hydroxylation occurs to some extent. A plausible explanation is an attack on the organic compound by anodically generated hydroxyl radicals.

Another typical reaction of this type takes place[61-65] between aromatic compounds and anodically generated thiocyanogen radicals. Thus, 4-thiocyanophenol can be obtained from phenol:



Ethylene reacts with the nitrate radicals formed in the electrolysis of aqueous solutions of nitrates[66]:



An interesting reaction has been reported[67] in the electrolysis of a solution of perchlorate in acetonitrile: the $ClO_4^{\cdot}$ radicals, formed at the anode, react with the acetonitrile, giving an organic free radical:

$$CH_3CN + ClO_4^{\cdot} \longrightarrow \dot{C}H_2CN + HClO_4.$$

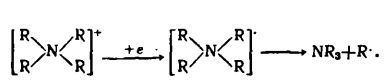
b. Cathodic Reactions

The following processes can give rise to free radicals at a cathode.

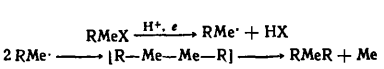
Discharge of organic cations. For example, tropyl radicals are formed[18] by discharge of tropylium ions:

$$C_7H_7^+ \xrightarrow{+e} C_7H_7^{\cdot}.$$

Free radicals also appear when quaternary ammonium cations are discharged[68]:



Fission of a halogen atom from an organic molecule. Many dehalogenation reactions[69-75], and symmetrisations of organometallic compounds, can be classified here. The symmetrisation process is described by the following general equations:



Addition of a proton and an electron to the double bond of an organic compound. Reactions of this type are fairly common. They can be visualised as

The cathodic reduction of hydrocarbons containing conjugated double bonds[7-9,82-84], and of many of their derivatives, and also the reduction of carbonyl compounds[14-16,85-88], involve this type of reaction.

4. FREE RADICAL REACTIONS

It is well established that free radicals can undergo the following reactions in solution[89,90].

1. Dimerisation. For example, ethane is formed from two methyl radicals:

$$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6.$$

2. Disproportionation, such as the formation of ethane and ethylene from ethyl radicals:

$$C_2H_5\cdot + C_2H_5\cdot \rightarrow C_2H_6 + C_2H_4.$$

3. Addition to unsaturated compounds present in solution, or reaction with the electrode metal.

4. Solvent interaction. For example, the primary phenyl radicals, formed in the electrolysis of a solution of phenylmagnesium bromide in dry ether react with the ether almost quantitatively.

Some of the most typical examples of these four reaction types will now be discussed.

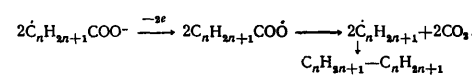
a. Dimerisation Reactions

Dimerisation is by far the commonest reaction of electrolytically generated free radicals.

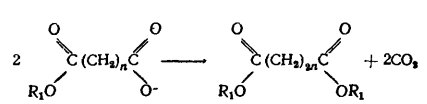
Anodic dimerisation. Nearly all cases of anodic dimerisation involve free radicals produced by the discharge of organic anions.

Aliphatic hydrocarbon radicals which appear when the salts of carboxylic acids or organometallic compounds are electrolysed invariably show some tendency to dimerise.

The dimerisation of hydrocarbon radicals formed during electrolysis of carboxylates is generally known as Kolbe's electrosynthesis, and is usually represented as:

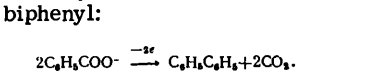


Practically all aliphatic acids with a normal carbon chain, and many of their derivatives such as the mono-esters of dicarboxylic acids, undergo the Kolbe reaction[91,92]:



A recent review[41] deals exhaustively with the dimerisation of radicals formed in the electrolysis of carboxylic acids and their derivatives.

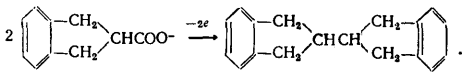
It was long believed that aromatic acids do not give dimeric products at the anode. Fichter[93] showed, however, that electrolysis of a solution of benzoic acid in pyridine yields biphenyl:



If, instead of benzoic acid, a solution of phenylacetic acid in pyridine is electrolysed, the yield of dibenzyl by the reaction

$$2C_6H_5CH_2COO^- \xrightarrow{-2e} C_6H_5CH_2CH_2C_6H_5+2CO_2,$$

is 50% of theoretical. This is due to the relatively high stability of the benzyl radical $C_6H_5\dot{C}H_2$, which favours dimerisation. Similar results are obtained when β-phenylpropionic acid is electrolysed. Electrolysis of a solution of indane-2-carboxylic acid in methanol gives a low yield of 2,2′-bi-indanyl at the anode[94]:



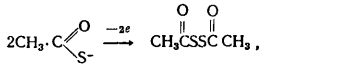
Dimerisation of hydrocarbon radicals has been observed in the electrolysis of n-butyl-, isobutyl-, and n-hexylmagnesium bromides[95].

The free radicals formed from anodically discharged xanthate anions undergo interesting dimerisation reactions at the anode. Thus, potassium methylxanthate reacts to give dimethylxanthogen[44]:

$$2CH_3OCSS^- \xrightarrow{-2e} CH_3OCSSSCOCH_3 .$$

Other xanthogenates show an analogous behaviour.

Thioacetic acid gives diacetyl disulphide on electrolysis[42]:

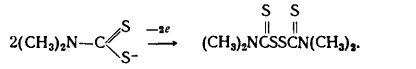


whilst sodium ethyl-, methyl-, and phenyl-mercaptides undergo a similar reaction[42]:

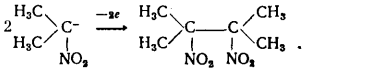
$$2C_2H_5S^- \xrightarrow{-2e} C_2H_5SSC_2H_5,$$

giving the disulphide.

Electrolysis of dimethyldithiocarbamate produces some tetramethylthiuram disulphide[96]:



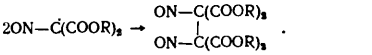
Zelinskii and Shilov[51] obtained some interesting results by electrolysing a concentrated aqueous solution of the potassium salt of nitroisopropane, $K[(CH_3)_2CNO_2]$, and showed that a dimeric product is formed at the anode:



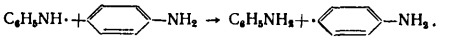
The radicals formed in solution during electrolysis of sodiomalonic ester dimerise to give tetracarboxylic acid derivatives:

$$2H\dot{C}(COOR)_2 \rightarrow (ROOC)_2CH-CH(COOR)_2.$$

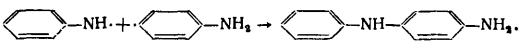
Oximido-derivatives of malonic acid undergo a similar reaction[52]:



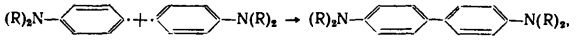
Dimerisation processes are observed during electrolytic oxidation of several amines, *e.g.* aniline[55–57]. Thus, electrolysis of an aqueous solution of aniline hydrochloride or sulphate with a platinum anode affords *p*-aminodiphenylamine. It seems probable that $C_6H_5NH\cdot$ radicals are formed initially at the anode, and that these subsequently react with the benzene ring, abstracting a hydrogen atom from the *para*-position:



The free radicals formed by this process can now react with the primary radicals:

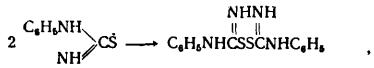


The reactions of dimethyl- and diethyl-aniline are particularly interesting[97,98]. They produce *N,N,N′,N′*-tetraalkylbenzidines, suggesting direct combination of two radicals:



where R = CH_3 or C_2H_5.

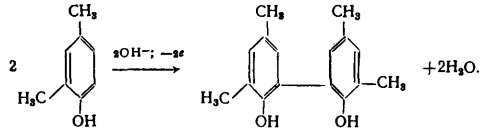
Some curious phenomena have been observed[58] in the electrochemical oxidation of hydrochloric acid solutions of phenylthiourea. It would seem that the primary process is the formation of the free radical $C_6H_5NH-\underset{\underset{S}{\|}}{C}-NH\cdot$, and that the anodic reaction follows the scheme suggested by Khomutov[56]. This is followed by a redistribution of electrons within the molecule, the unpaired electron being transferred to the sulphur atom with formation of the free radical $\begin{matrix}C_6H_5NH\\NH\end{matrix}\geqslant C-S^{\cdot}$. This radical can now dimerise



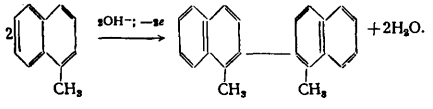
forming phenylformamidine disulphide. Electrolysis of thiourea, symmetrical diethylthiourea, and allylthiourea gives analogous results[58].

Lastly, we can distinguish a class of dimerisation processes in which the organic radicals are apparently formed by reaction with inorganic radicals, produced at the anode as the primary product. Reactions of this type usually involve the hydroxyl radical, as shown in the following list of examples.

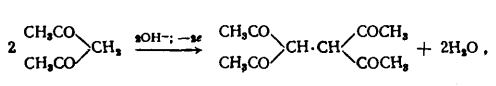
Oxidation of 2,4-dimethylphenol gave a derivative of biphenyl[99]:



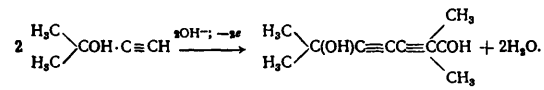
1-Methylnaphthalene undergoes a similar reaction at the anode[100]:



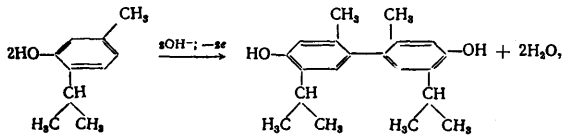
Also interesting are the dimerisation of acetylacetone[48]:



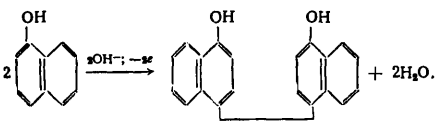
and of dimethylethynylcarbinol [101]:



Other reactions of this type include the synthesis of dithymol by oxidation of thymol at a lead dioxide anode [102]:



and the synthesis of 1, 1′-dinaphthol by the oxidation of 1-naphthol under similar conditions [103]:



Dimers of the same type are formed, by anodic dehydrogenation, in the electrolysis of several other organic compounds, *e.g.* *m*-cresyl methyl ether [104], *p*-cresyl methyl ether [104], veratrole [105], guaiacol [48], and a monoether of resorcinol [105].

An interesting anodic dimerisation is observed [67] during electrolysis of a solution of potassium perchlorate in acetonitrile, the perchlorate radical (formed as a primary product) reacting with the organic solvent. The resulting organic radicals dimerise to form succinonitrile:

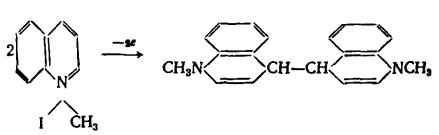
$$2\dot{C}H_2CN \rightarrow CNCH_2CH_2CN.$$

Cathodic dimerisation. Some instances of the formation of dimers from cathodically generated radicals will now be discussed.

The tropyl radical, which appears at the cathode when tropylium ions are discharged, dimerises to bitropyl [18]:

$$2C_7H_7^{\cdot} \longrightarrow C_7H_7C_7H_7.$$

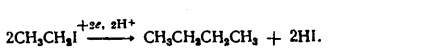
Dimerisation processes sometimes occur in the electrolysis of quaternary ammonium ions. Thus, electrolysis of methylquinolinium iodide gives a low yield of the dimer [106]:



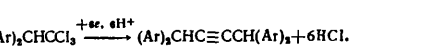
and a similar reaction takes place in the electrolysis of ethylquinolinium iodide.

Like these typical dimerisations of organic cations, dimerisation processes involving cathodic dehalogenation *via* a free radical intermediate have not been studied systematically. The following are a few examples of this type of reaction.

1. Electrolytic dehalogenation of ethyl iodide produces butane [69]:



2. Dehalogenation of 1, 1, 1-trichloro-2, 2-diphenylethane and of some of its derivatives containing substituents in the benzene ring affords a good yield of acetylene derivatives [70–75]:



3. Symmetrisation of organometallic compounds can also be regarded as a dimerisation process. The reaction has been studied with organic compounds of mercury [76,77], tin [78], lead [79,80], and arsenic [81].

The cathodic reduction of multiple bonds has been the object of more detailed studies. Following the suggestion of Knunyants [107], reduction of an organic compound accompanied by simultaneous dimerisation is usually called hydrodimerisation.

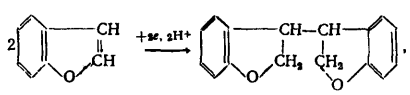
Hydrodimerisation processes can be carried out by purely chemical means (using various reducing agents) or by cathodic reduction. The following classes of compounds undergo hydrodimerisation: unsaturated and aromatic hydrocarbons, ketones, aldehydes, and compounds containing conjugated double bonds, such as 1, 2-unsaturated aldehydes, ketones, carboxylic acids, and nitriles. These unsaturated compounds frequently yield unsymmetrical derivatives as well as symmetrical hydrodimers.

We shall now discuss the hydrodimerisation of different classes of organic compounds.

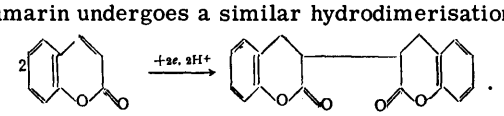
1. Hydrodimerisation at a C–H bond. Unsaturated aliphatic hydrocarbons can be converted into their hydrodimers by chemical hydrogenation [107], but little is known about their hydrodimerisation by electrolytic reduction.

The preparation of the hydrodimers of acyclic aliphatic hydrocarbons by electrolysis has not yet been accomplished, probably because isolated double bonds are relatively inactive and not easily reduced at a cathode. When conjugation is present, however, double bonds become much more reactive, and hydrodimerisation by electrolytic reduction is possible with heterocyclic and aromatic compounds, and with 1, 2-unsaturated aldehydes, acids, ketones, and nitriles.

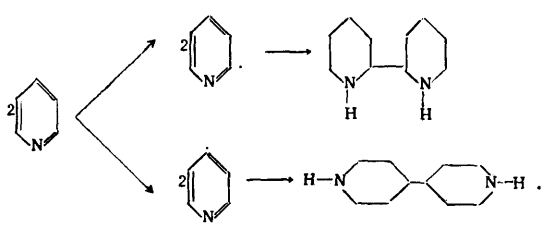
For example, coumarone forms a hydrodimer when reduced electrolytically at a mercury cathode [108]:



and coumarin undergoes a similar hydrodimerisation [109]:†



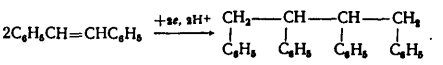
From pyridine, 2, 2′- and 4, 4′-bipiperidyl can be isolated [110,111]:



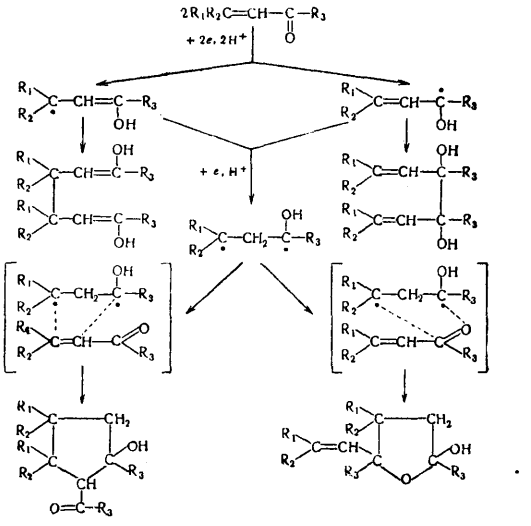
The formation of dimeric and trimeric reduction products has been observed in the electrolytic reduction of quinoline [112,113], quinaldine [114–116], and lepidine [117–120].

† But see R. Patzak and L. Neugebauer, Monatsh., 82, 662 (1951) (Ed. of Translation).

Dimeric products have been reported also from the reduction of 1, 2-diphenylethylene (stilbene) at a mercury cathode [7]:

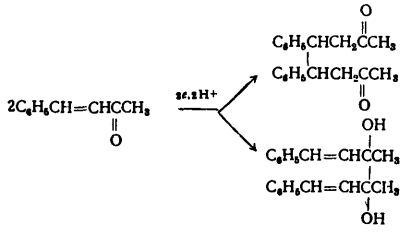


The formation of dimers by electrolytic reduction of crotonaldehyde, acrolein, and mesityl oxide has been explained [121-127] by the following scheme:

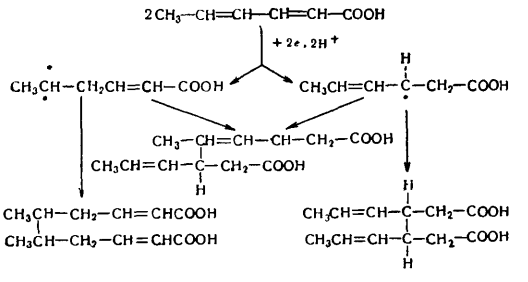


In this reaction cyclic derivatives of cyclopentane and furan are formed as well as linear dimers.

Methyl styryl ketone can give two hydrodimers by electrolytic reduction [128]:

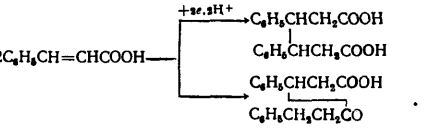


Three different dimers have been isolated from the cathodic hydrodimerisation of sorbic acid [129]:



The reduction of vinylacrylic acid follows exactly the same path [130,131].

Electrolytic reduction of cinnamic acid gave the isomeric β,γ-diphenyladipic acids and other similar products, among which a keto-acid was isolated and identified [132-134]:



Adiponitrile can be prepared by the hydrodimerisation of acrylonitrile:



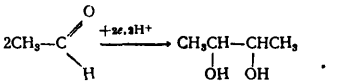
Some α,β-unsaturated nitriles, such as

$C_6H_5CH=CHCN$,
$CH_3CH=CHCN$,
$(CH_3)_2C=CHCN$, etc.,

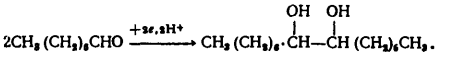
undergo an analogous dimerisation, induced by the development of a free valency at the β-carbon atom [135].

2. Hydrodimerisation at a >C=O bond. The hydrodimerisation of aldehydes has been demonstrated in a number of interesting systems.

Electrolytic reduction of acetaldehyde in an alkaline medium produces 2, 3-butylene glycol [136]:



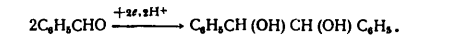
Octanal gives rise to hexadecan-7, 8-diol at a mercury cathode [137]:



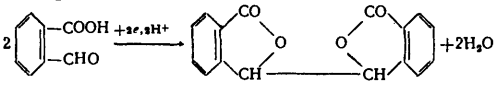
Tartaric acid has been prepared in good yield from glyoxylic acid [138,139]:



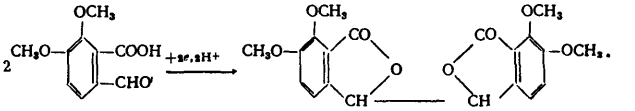
Benzaldehyde and many of its ring-substituted derivatives are reduced to hydrobenzoins [140,141]:



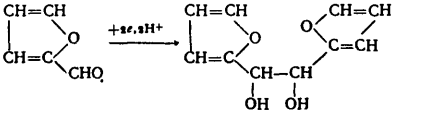
Derivatives of benzaldehyde with a carboxylic group in the *ortho*-position undergo a distinctive type of electrolytic reduction. Thus, two isomeric biphthalidyls [142] are formed from salicylic acid [*sic*. *o*-formylbenzoic acid (Ed. of Translation)]:



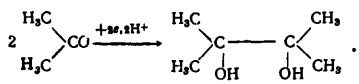
whilst electrolytic reduction of opianic acid follows a similar path, with formation of isomeric bimeconinyls [114]:



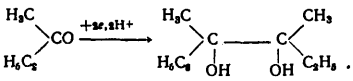
Furfural gives a high yield of hydrofuroin [143]:



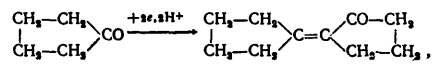
Ketones, like aldehydes, can undergo cathodic hydrodimerisation. Pinacone (tetramethylglycol) is obtained in good yield from acetone [144-165]:



1,2-Diethyl-1,2-dimethylglycol can be prepared by electrolytic reduction of ethyl methyl ketone [145]:

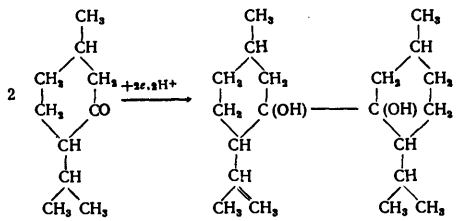


The reduction of cyclopentanone follows a rather unusual path, giving the dimer cyclopentylidenecyclopentanone [2]:

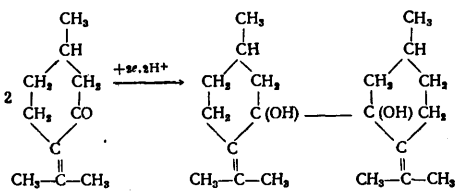


and also some more complex products with up to four molecules of cyclopentanone [166].

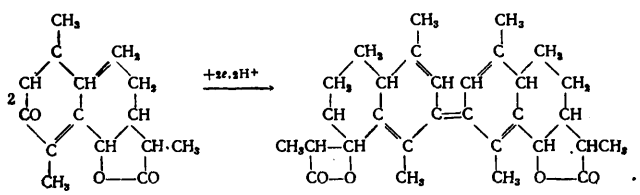
L-Menthone is converted into the corresponding pinacone [167,168]:



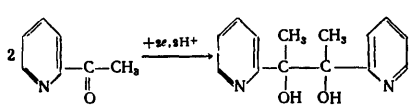
and pulegone undergoes a similar reduction [165]:



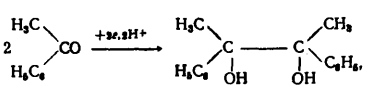
A hydrodimer of santonin has been prepared by electrolytic reduction [169,170]:



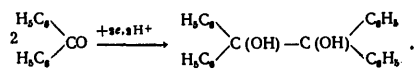
Hydrodimerisation can also be carried out with heterocyclic ketones. This has been demonstrated [171] in the case of acetylpyridine:



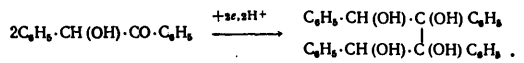
Aromatic ketones, however, have a much higher tendency to form dimeric products. Acetophenone, for example, can be reduced to diphenyldimethylglycol almost quantitatively [140,172]:



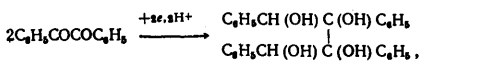
and benzophenone readily gives benzopinacone [145,169,172,178]:



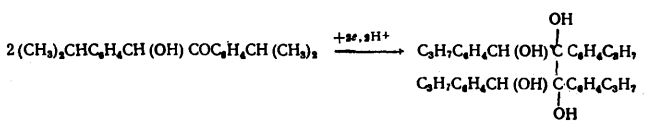
Some derivatives of benzophenone (hydroxybenzophenone, phenyl tolyl ketone, and 2,4-dimethylbenzophenone) show the same behaviour under conditions of cathodic reductions [145,178]. Benzoin forms 1,2,3,4-tetraphenylerythritol [140]:



The same product was obtained by electrolytic reduction of benzil [140]:



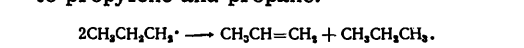
and an analogous hydrodimer was isolated from the acyloin of cumene [141]:



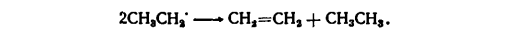
b. Disproportionation Reactions

Disproportionation reactions are one of the less frequently observed types of free radical reaction in the electrolysis of organic compounds.

Salts of saturated aliphatic acids give unsaturated hydrocarbons by disproportionation. Thus, the propyl radicals formed during electrolysis of butyric acid can disproportionate [179] to propylene and propane:



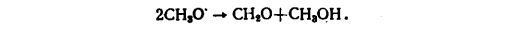
Ethyl radicals from propionic acid form ethylene and ethane [180]:



A similar explanation probably applies to the formation of unsaturated hydrocarbons by the electrolysis of isobutyric [181], valeric [182], and various other acids [183].

The hydrocarbon radicals formed during electrolysis of aliphatic organomagnesium compounds also show a tendency to disproportionate [184]. Propane and propylene are produced by disproportionation during the electrolysis of n-propylmagnesium, and t-butylmagnesium bromide yields isobutane and isobutylene [95].

The methoxy-radicals resulting from the discharge of methoxyl ions in the electrolysis of methanolic solutions of sodium methoxide disproportionate to formaldehyde and methanol [49]:



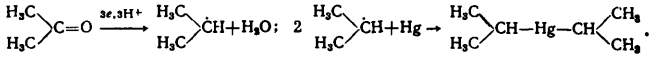
c. Reactions with the Electrode Metal

When organic substances are electrolysed, the electrode is sometimes attacked with formation of organometallic compounds. Reactions of this type appear to be confined almost exclusively to systems in which an aldehyde or ketone is electrolytically reduced at a lead or mercury

cathode. For example, diisopropylmercury has been prepared by electrolysis of acetone with a mercury cathode[185], and diisobutylmercury and dimenthylmercury have been obtained by a similar reaction from ethyl methyl ketone[186] and menthol[187] respectively. At a lead cathode, acetone forms a mixture of diisopropyl- and tetraisopropyl-lead; ethyl methyl ketone forms tetrabutyllead, and diethyl ketone forms tetrapentyllead[188,189].

Organomercury compounds have been isolated and identified when the following ketones are reduced in a sulphuric acid medium: phenylacetone, cyclohexanone, cyclopentanone, 2-, 3-, and 4-methylcyclohexanones[190]. Organolead compounds have been isolated from the electrolysis of various aldehydes[167,191], but not characterised. Electrolysis of aqueous alkaline solutions of acrylonitrile, with a tin cathode, has yielded tetra-(2-cyano-ethyl)-stannane[192].

Processes of this type may be explained by assuming that the primary electrode process forms active free radicals which spontaneously react with the cathode material to form organometallic compounds. For example, the formation of di-isopropylmercury by reduction of acetone at a mercury cathode can be represented by the reaction series:



Similar equations can be written for the other reactions listed above.

We should stress, perhaps, that the formation of organometallic compounds has been observed only with substances capable of giving hydrodimers on electrolytic reduction. This is further proof that the two processes are similar in that as they stem from the reactivity of the resulting free radicals.

Organometallic compounds have also been reported[193] among the products of the electrolytic reduction of alkyl halides at a lead cathode. The first stage of this reaction is obviously the formation of a free radical, by reduction of the alkyl halide, which then reacts with the cathode material.

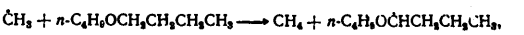
Organometallic compounds have also been detected in some anodic processes. When solutions of organometallic compounds are electrolysed, the anode material is sometimes attacked by the free radicals formed at the anode, resulting in metal exchange as the overall reaction. For example, if diethylzinc (containing ethylsodium) is electrolysed with a lead anode some tetraethyllead is formed[194]. A recently patented[195-198] method of preparation of tetraethyllead involves electrolysis of a triethylaluminium complex salt solution with a lead anode; metallic aluminium is deposited on the cathode.

Similarly, many alkyls of the alkali and alkaline earth metals, of gallium, indium, thallium, silicon, germanium, tin, and lead have been prepared[199] by the electrolysis of a mixture of diethylzinc and triethylaluminium containing lithium and sodium chloride (or fluoride). The preparation of organolead compounds by electrolysis of a solution of a Grignard reagent, using a lead anode, has been described[200,201].

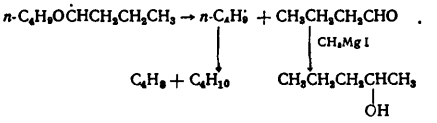
The formation of alkoxides during electrolysis of alcoholic solutions can also be mentioned here. When a solution of sodium methoxide in methanol is electrolysed with a magnesium or copper anode, magnesium or copper methoxide is formed[202]. Clearly, the anode material is attacked by the methoxy-radicals produced at the anode.

d. Interactions with the Solvent

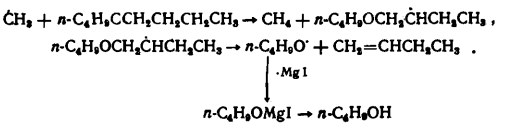
Free radicals can sometimes react with the solvent. The most detailed studies of reactions of this type have been concerned with the electrolysis of organomagnesium compounds. Thus, the methyl radicals formed anodically by the discharge of complex ions during electrolysis of methylmagnesium iodide in di-n-butyl ether undergo the following series of reactions[203-205]:



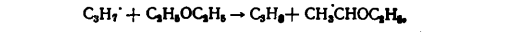
in which a hydrogen atom is abstracted from an α-carbon atom of the ether by a methyl radical, the resulting radical undergoing further transformations:



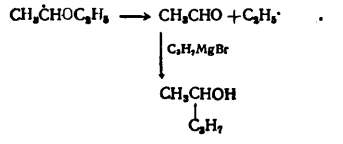
If the methyl radical abstracts a hydrogen atom from the β-position, the reaction follows a different path:



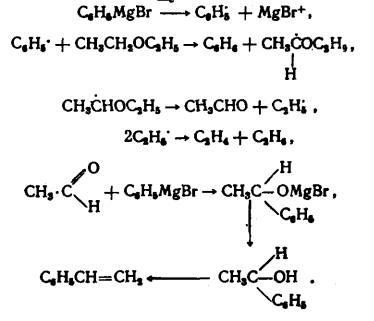
The propyl radical formed during electrolysis of propylmagnesium bromide in diethyl ether reacts as follows:



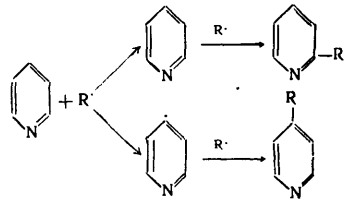
forming propane and a new free radical by solvent interaction. The new radical undergoes further decomposition, of which the final products are pentan-2-ol and an ethyl radical:



Further examples are provided by the reactions of phenyl and benzoyl radicals. Electrolysis of phenylmagnesium bromide in dry diethyl ether produces mainly benzene, styrene, ethane, ethylene, and other products[206], and only traces of biphenyl. The reaction scheme is probably as follows:

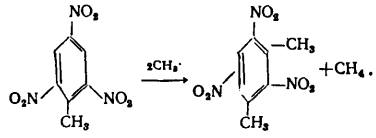


The free alkyl radicals formed in the electrolysis of pyridine solutions of salts of carboxylic acids also attack the solvent:



Reactions of this type have been observed during electrolysis of propionates and butyrates [2] and of benzoates [93].

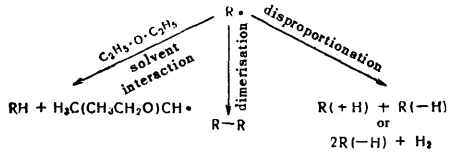
The methyl radicals formed by electrolysis of sodium acetate can react with trinitrotoluene [207]:



The phenyl radical is so reactive that it can remove hydrogen from water and from organic solvents. As a consequence, aromatic acids do not undergo the Kolbe synthesis [208].

This review of the reactivity of the free radicals formed during electrolysis of organic compounds indicates that a great variety of low-molecular-weight products can be expected, and that the path taken by the reaction is controlled by various factors, such as the nature of the radical and of the solvent, the electrode material, and the current density. Unfortunately, the data so far available do not allow us to establish firm relationships between all these factors. Of the few published papers which have dealt with the subject, those discussing the electrolysis of organomagnesium compounds have arrived at the most interesting general conclusions.

The free radicals formed in the electrolysis of organomagnesium compounds behave like typical alkyl radicals: they can react with the solvent, dimerise, or disproportionate. The three possibilities are summarised in the following reaction scheme, which applies to the free radicals formed at the anode when a diethyl ether solution of an organometallic compound is electrolysed:



In practice which reaction predominates is determined largely by the nature of the radical itself.

Some general conclusions concerning the behaviour of alkyl radicals can be made from a study of the relative amounts of the three types of product obtained when different organomagnesium compounds are electrolysed. These are summarised below.

Methyl radicals are the most reactive, and tend to react preferentially with the solvent. The ethyl radicals obtained from the electrolysis of organomagnesium compounds are somewhat less reactive, and undergo a characteristic, nearly quantitative disproportionation. Propyl radicals, on the other hand, tend to dimerise, and undergo solvent interactions and disproportionation only to a minor extent [184].

n-Butyl, isobutyl, and n-hexyl radicals dimerise almost quantitatively [209]. Thus, the stability (and tendency to dimerise) of alkyl radicals is seen to increase with chain length, while disproportionation and reaction with the solvent become progressively less favoured.

We have seen that the phenyl radical is very reactive, and tends to attack the solvent rapidly. The benzyl radical $C_6H_5\dot{C}H_2$, on the other hand, is relatively stable and readily gives dimerisation products. The inertness of the benzyl radical stems (quoting Semenov) from the fact that "when a new bond is formed in a reaction of the type:

$$C_6H_5\dot{C}H_2+RH\rightarrow C_6H_5CH_3+R\cdot,$$

the electron from the benzyl radical has to be extracted, loosely speaking, from the conjugated system of the benzene ring which in this case behaves very much like a 'negative' substituent. This effect decreases the bond energy and correspondingly increases the activation energy" [210].

The remaining type of free radical process observed in the electrolysis of organic compounds (initiation of polymerisation processes) will be considered in the following section.

e. Initiation of Polymerisation Processes

We have already stated that electrolytically generated free radicals can interact with unsaturated compounds present in solution to give various addition products. Under certain conditions this can lead to chain polymerisation, with formation of macromolecular products.

Processes of this type have only recently been discovered, and their study has been confined to relatively few systems. Nevertheless, it is already well established that macromolecular products can be formed by electrolysis of the appropriate monomers at current densities of the order of $10^{-4}-10^{-3}$ A cm^{-2}. At higher current densities the process stops at the dimer or trimer stage. The use of non-aqueous solvents and a high monomer concentration favours polymerisation.

We shall now discuss some electrode reactions which have led to the formation of macromolecular products.

The radicals formed at the anode in the electrolysis of potassium propionate or acetate (dissolved, respectively, in anhydrous propionic or acetic acid) can initiate the polymerisation of styrene [1]. A similar effect is shown by the radicals formed in the electrolysis of a solution of potassium iodide in anhydrous pyridine [211].

Polymerisation of acrylonitrile can be initiated by cathodically generated radicals when an aqueous solution of a ferric salt and hydrogen peroxide is electrolysed [212], and also in aqueous hydrochloric acid electrolysed with a cathode of high hydrogen overpotential [213].

Acrylonitrile in aqueous solution is not polymerised by sodium amalgam, but in dry dimethylformamide polymeric products of molecular weight between 4100 and 5430 are formed [214].

Methyl methacrylate polymerises fairly readily at a cathode [214,215], giving a polymer of molecular weight proportional to the hydrogen overpotential of the cathode.

Although the number of publications dealing with the electrochemical initiation of polymerisation is quite considerable [216], most of these fail to comment on the mechan-

ism of the relevant electrode processes. The first serious study of cathodic processes in the electrochemically initiated polymerisation of methyl methacrylate was published by Fedorova *et al.*[217], who used polarography as well as isolation of the products formed at a large-area cathode. They initiated the polymerisation of methyl methacrylate by reducing oxygen at a dropping mercury electrode, and showed that the effect of oxygen on the reaction under study is twofold, both inhibition and initiation of the polymerisation process being attributable to the oxygen present in solution. The initiation reaction seems to involve the $HO_2^{\cdot}$ radicals formed at the cathode by the reduction of oxygen:

$$O_2 + e + H^+ \rightarrow HO_2^{\cdot}.$$

No initiation was observed in carefully deoxygenated solutions.

The polymerisation products were also allowed to accumulate for extended periods, so that their molecular weight could be ascertained. These experiments were carried out at constant cathode potential and constant concentration of methyl methacrylate. The molecular weight, deduced from viscosity measurements on benzene solutions of the polymer, was found to be $2.5-3 \times 10^6$. The authors believe that the polymerisation of methyl methacrylate under their experimental conditions proves that free radical intermediates are present in the electrolytic reduction of oxygen.

The F· radical, which appears at the anode when anhydrous hydrogen fluoride is electrolysed, can initiate the polymerisation of chlorotrifluoroethylene[214]. Similarly, tetrafluoroethylene polymerises under the influence of the radicals generated by the electrolysis of trifluoroacetic acid[219].

5. BEHAVIOUR OF FREE RADICALS FORMED DURING ELECTROLYSIS

Free radicals formed by electrolysis can differ in their behaviour and properties from the same free radicals prepared by other methods.

This phenomenon must be due to some specific feature of electrochemical reactions, such as the fact that the reaction occurs exclusively at the electrode surface. It follows that high concentrations of free radicals can be expected to arise at the surface of the electrode and in a thin layer of solution immediately adjacent to it: this favours reaction of the resulting free radicals with each other and with the electrode material rather than with the organic molecules in the bulk of the solution. The high concentration of electrolytically formed free radicals in a limited volume of the solution and their short lifetime (due to dimerisation) account for the electrochemical initiation of polymerisation only being possible under a narrow range of conditions.

The peculiarities of electrolytic free radicals can be studied by subjecting differently prepared free radicals to various reactions and comparing their behaviour. Some examples are given below.

A detailed free radical mechanism has been proposed for the processes occurring when potassium propionate solutions in anhydrous propionic acid are electrolysed[220], and for the decomposition of propionyl peroxide.

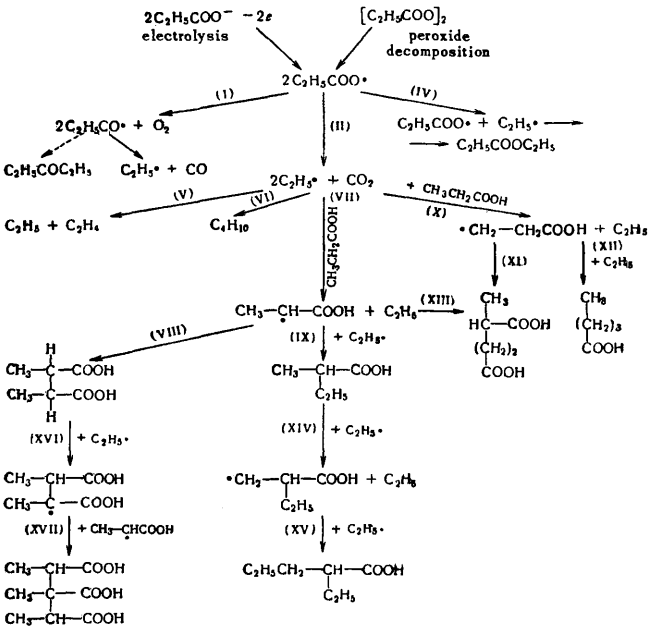
When propionic acid is electrolysed with a platinum anode, propionate ions are discharged and free radicals are formed:

$$2C_2H_5COO^- \xrightarrow{-2e} 2C_2H_5COO^{\cdot}.$$

The decomposition of propionyl peroxide produces the same free radicals:

$$[C_2H_5COO]_2 \rightarrow 2C_2H_5COO^{\cdot}.$$

The $C_2H_5COO\cdot$ radicals, whether chemically or electrochemically prepared, react further to give the same products but in different proportions (see below).

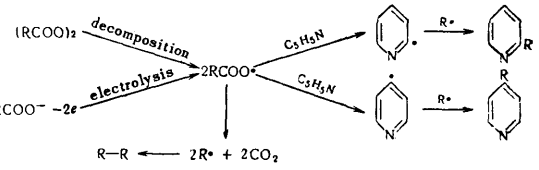


Reactions (I) and (IV), giving diethyl ketone and ethyl propionate respectively, need no comment.

The disproportionation reaction (V) produces ethane and ethylene, whilst the dimerisation reaction (VI) yields butane. All the other products stem from reactions between ethyl radicals and propionic acid in which a hydrogen atom is removed from the α- or from the β-carbon atom of the acid, reactions (VII) and (X) respectively. New free radicals are thus produced, and these react together (XIII), forming methylglutaric acid, or with more ethyl radicals, forming ethylmethylacetic (IX) and butyric acid (XII). The dimerisation reaction (VIII) produces dimethylsuccinic acid which, like ethylmethylacetic acid, undergoes further reaction with ethyl radicals (XIV) and (XVI). The final products are tribasic acids, resulting from the reaction (XVII) between dimethylsuccinic acid and the free radical of reaction (VII). All the other products are also formed by free radical reactions. Thus the mechanism put forward by these authors[220] satisfactorily explains the formation of all the products.

The yield of butane, by reaction (VI), is 15.8% by electrolysis and only 6.9% when the peroxide is decomposed. This is further confirmation that electrolysis favours dimerisation as a result of the high concentration of $C_2H_5^{\cdot}$ radicals at the electrode surface. For the same reason, the yield of ethylene is higher (5.6%) in the electrolytic than in the decomposition reaction (3.0%): disproportionation is more effective under electrolysis conditions.

An even more striking illustration of the abnormal behaviour of electrolytically generated free radicals is provided by comparative studies of the electrolysis of pyridine solutions of acetic, propionic, and butyric acid and of the decomposition, in pyridine, of the corresponding peroxides [221]. The reactions can be summarised as follows:



Electrolysis gives mainly hydrocarbons (by the dimerisation of alkyl radicals), with traces of alkylpyridines. Decomposition of the peroxides, on the other hand, produces alkylpyridines in yields of 84–87%.

To quote one final example of the unusual behaviour of electrolytic free radicals, Lindsey and Peterson [3] have made a study of the electrolysis of alcoholic solutions of potassium acetate and 1,3-butadiene, acidifed with acetic acid. Among the electrolysis products some dimers were detected which must have arisen from the following reactions:

$$2CH_3COO^- \xrightarrow{-2e} 2CH_3COO^{\cdot},$$

$$2CH_3COO^{\cdot} \rightarrow 2\dot{C}H_3 + 2CO_2.$$

Even in the absence of butadiene the methyl radicals produced by electrolysis can recombine to give ethane:

$$2\dot{C}H_3 \longrightarrow C_2H_6.$$

Some of the methyl radicals, however, reacted with the butadiene, giving products of two types:

$$2\dot{C}H_3 + 2CH_2{=}CHCH{=}CH_2 \rightarrow 2CH_3CH_2\dot{C}H{=}CHCH_2^{\cdot} \rightarrow$$

$$\rightarrow CH_3CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2CH_3 \text{ (deca-3,7-diene)},$$

$$2\dot{C}H_3 + CH_2{=}CHCH{=}CH_2 \rightarrow CH_3CH_2CH{=}CHCH_2CH_3 \text{ (hex-3-ene)}.$$

Analysis of the products showed that in this reaction only some 30 to 50% of the methyl radicals react with butadiene, the remainder recombining to give ethane.

Goffman and Jenner, on the other hand, had shown [222] that the dimerisation of butadiene in the presence of hydroxyl free radicals generated by Fenton's reagent produces exclusively C_{10}-dienes: neither ethane nor hex-3-ene were detected among the products. Lindsey and Peterson [3] explain this difference by pointing to the large excess of free radicals (as compared with butadiene) which may exist at the electrode surface, thus greatly increasing the probability of radical–radical reactions.

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METAL COMPLEXES OF HYDROXY-ACIDS

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1. INTRODUCTION

Metal complexes of hydroxy-acids are of considerable interest in various branches of chemistry and chemical technology. Various hydroxy-acids are able to form such complexes with more than sixty elements of the Periodic System. Investigation of the properties of this group of compounds is still far from complete. Nevertheless, sufficient experimental results are already available for several generalisations to be made concerning the process of complex formation. The present paper deals only with complex compounds of aliphatic hydroxy-acids. The most typical and widespread representative is tartaric acid, and therefore our attention will be concentrated mainly on the tartrato-complexes of metals. In several cases, in order to elucidate the influence of the structure of hydroxy-acids on the chemical properties of the complex compounds, data on the complexes of citric, trihydroxyglutaric, and several other hydroxy-acids will also be considered.

It had been noted during the previous century that, in the presence of tartaric acid, the cations of many heavy metals lost their ability to be precipitated by alkali in the form of insoluble hydroxides, and other characteristic analytical properties had changed. Qualitative investigation showed that these phenomena were associated with the hydroxyl groups of the tartaric acid. Other organic compounds containing hydroxyl groups were also found to develop a similar masking action, but replacement of the hydroxyl groups by basic or acidic groups, such as HS, CN, NH_2, Cl, etc., resulted in a considerable loss of complexing power [1,2]. In this way the special role of hydroxyl groups in complex formation was revealed.

Subsequently, complexes of hydroxy-acids were investigated by a great variety of methods. At first, preparative work played the main part. Later, physicochemical methods of studying complexes in solution acquired increasing significance. Below a brief account is given of the characteristic features of the investigation of hydroxy-acid complexes by various methods.

2. PREPARATIVE METHOD OF INVESTIGATION

The method consisted essentially in the preparation of the complex compounds, their isolation from solution, and subsequent analysis of the products. The tartrato-complexes of most metals are usually readily soluble in water, and precipitation with alcohol was used to isolate them in the solid form. An elementary analysis was then made on the resulting compounds: valuable results were obtained. It was established that tartaric acid (also other hydroxy--acids) forms two groups of compounds with metal cations, depending on the participation of carboxyl and hydroxyl groups in complex formation. The first class of compounds are of the simple salt type, formed by replacing the hydrogen atoms of the carboxyl groups by metal cations; they were generally obtained from acid solutions. Examples are the tartrates of manganese, cobalt, and nickel, represented by the empirical formulae $MnC_4H_4O_6$, [3,4] $CoC_4H_4O_6$, [5] and $NiC_4H_4O_6$. [5-7] The complex nature of these compounds was established later from a physicochemical investigation of the properties of the solutions. The second class comprises complexes whose formation was represented as involving the substitution of metal cations for the hydrogen atoms of the hydroxyl groups. This class includes, for example, compounds of the type $BaCuC_4H_2O_6.xH_2O$, [8] $NaCuC_4H_3O_6$, [9] and $NH_4Al(OH)C_4H_3O_7$, [10] which were usually precipitated only from alkaline solutions. However, it was only in rare instances that replacement of the hydroxyl hydrogens by the metal could be reliably established from the elementary analysis. This question long remained a matter of controversy, and many workers suggested that in these cases basic salts of various compositions were formed without involving the hydrogen atoms of the hydroxyl groups. In this connection the synthesis of lead tartrate from a solution of heavy-oxygen water is of interest. The compound formed under these conditions has the normal isotopic composition, and therefore corresponds to the formula $NaPbC_4H_3O_6$, not $NaPb(OH)C_4H_4O_6$. [11]

The preparative method for investigating complexes of hydroxy-acids had great defects. Elementary analysis gave only the empirical formula of the compound, but no information on its structure. It was only in exceptional cases that tartrato-complexes could be isolated in crystalline form. Separation of the compound from solution usually yielded an oily mass or a gluey precipitate, the chemical individuality of which was doubtful. This was observed, for example, in the preparation of the tartrato-complexes of aluminium [10], iron [12], cadmium [13], copper [9], antimony [14], etc. It was an extremely complicated matter to obtain anhydrous compounds, which made it difficult to establish correctly and unambiguously the structure of the complexes: compounds containing water could always be given either the formula of a basic salt or that of a normal salt containing water of crystallisation. The molecular weight of the complexes could be determined only in rare instances. Therefore the simplest formulae were usually assigned to the compounds, although the formation of viscous substances indicated in many cases that polymerisation was

occurring. The preparative method also gave no information on the interconversion of complexes in solution by change in pH and in concentration, or on their stability.

The results of the preparative work are summarised below in Table 1.

3. PHYSICOCHEMICAL METHODS OF INVESTIGATING COMPLEXES IN SOLUTION

Polarimetric Method

Tartaric acid contains two asymmetric carbon atoms, and its solutions rotate the plane of polarisation of light. Complex formation with metal cations was accompanied by a change in the angle of this rotation, associated with the formation of more optically active reaction products. The polarimetric method has been used to study the tartrato--complexes of copper[15-19], beryllium[20], cadmium[21], boron[22-24], aluminium[25-32], titanium[33], thorium[34], germanium[35], tin[36], arsenic[37], antimony[24,37], bismuth[38,39], molybdenum and tungsten[40-49], uranium[26,50,51], iron[26,52], cobalt[26], nickel[26,53], cerium[54], etc.

The following are the main variants of this method of investigation.

A. Study of rotatory power of aqueous solutions of tartrato-complexes of different concentrations. The aim of these experiments was to determine the effect of dilution on the dissociation of the complexes. It was found in this way that, for example, the specific rotation of solutions of complex beryllium tartrates is practically independent of concentration, and hence that these compounds undergo hardly any decomposition into their component parts on dilution. On the other hand, the tartrato-complexes of boric and arsenious acids were found to exist only in concentrated solution, and to be readily hydrolysed on dilution. Tartrato-compounds of molybdenum and tungsten undergo quite extensive hydrolysis, although it is not complete even in very dilute solutions.

B. Study of variation in rotatory power of complexes with acidity of solution. One of the most widely used methods is the measurement of the angle of rotation in a series of solutions having a constant molar ratio of the metal cation to the hydroxy-acid (usually equimolar) and a variable amount of alkali. These experiments showed that acidity had a marked effect on the polarimetric properties of solutions of the complexes (of bismuth, lead, etc.); the specific rotation varied not only in magnitude but also in sign. Such phenomena were usually attributed to a change in composition or structure of the compounds, although in several cases a satisfactory interpretation of the observed facts could not be found. In most of the earlier work, unfortunately, the pH of the solutions was not usually measured, so that the results are qualitative in character.

C. Determination of angle of rotation as a function of the molar ratio of the reactants in order to establish the composition of the tartrato-complexes in solution. In the earlier work the concentration of tartaric acid was usually kept constant in a series of experiments, only that of the metal salt being varied; later the method of isomolar series began to be used. This variant was of particular value with the tartrato-complexes of molybdenum and tungsten, for which other methods were of little use. The composition of the tartrates of iron, aluminium, etc., has been established by the isomolar series method.

In spite of the large numbers of papers, the field of application of the polarimetric method was limited. It could be used only to study the complexes of hydroxy-acids containing asymmetric carbon atoms. It gave no definite conclusions on the structure of the complexes. Furthermore, the dependence of specific rotation on the molar ratio of the reactants was often found to be too complicated, which resulted in a certain arbitrariness in the interpretation of the experimental results. Thus in a polarimetric study of the tartratoferrate(III) complexes Pariselle[52] found the maximum specific rotation to correspond to equimolar solutions of iron nitrate and tartaric acid: *i.e.* one iron atom was associated with one tartrato-residue in the complex. However, various structural formulae could be suggested with this molar ratio, since the iron could react either with the carboxyl groups or with both carboxyl and hydroxyl groups of the tartaric acid. In an isomolar series of solutions of iron nitrate and sodium tartrate† a minimum rotation at an Na_2T : Fe ratio of 3 : 1, and maxima at ratios of 1 : 1 and 9 : 1 were observed; it was difficult to attribute the latter maximum to the formation of a compound containing the components in these proportions. Similarly complicated relations were observed also with the tartrato-complexes of other metals. Finally, the stability of the complexes in solution could be assessed very roughly.

Absorptiometric and Spectrophotometric Methods

These methods have not been very extensively used mainly because the formation of coloured compounds is not very characteristic of aliphatic hydroxy-acids. Absorptiometric measurements have been employed in studying the tartrato- and citrato-complexes of copper[55-57], vanadium[58,59], chromium[60,61], uranium[62-64], iron[12,65,66], cobalt[67], nickel[55,70,71], and rare-earth elements[68]. In some cases this work enabled not only the composition but also the instability constants of the complexes in solution to be determined.

The composition of a compound was usually determined by measuring the optical density of a series of solutions having a constant concentration of the central ion and a variable concentration of the hydroxy-acid. The isomolar series method was also employed. Both these methods were suitable mainly for determining the composition of complexes in solutions sufficiently acid to prevent hydrolysis of the metal salt. Hydrolysis at higher pH-values was sometimes avoided by adding an additional complexing agent, for example a solution of sodium salicylate in studying the tartrato- and citrato-complexes of iron[65,66] by the isomolar series method. In most cases, however, a suitable auxiliary complexing agent could not be found, which made it impossible to employ the isomolar series method at high pH-values, especially in strongly alkaline solutions.

† *cf.* Job's method of continuous variations [Ed. of Translation].

Electrical Conductivity Measurements

Sometimes the composition of complexes could be established from the break on the conductimetric titration curves of metal salts with hydroxy-acids[55]. Conductivity measurements on isomolar series of solutions have been employed to determine the composition of tartrato-complexes of aluminium[69], gallium[72], thorium[73], and vanadium[58]. In most cases, however, this method has served merely as a qualitative criterion of complex formation. Interaction has been detected in this way in the boric, arsenious, and tartaric acid systems[23,74,75]. In studying complex formation between hydroxy-acids and molybdic and tungstic acids, mixtures of molybdic acid with various hydroxy-acids have been found[76-78] to possess a considerably higher electrical conductivity than the separate components. This effect was not observed, however, with non-hydroxylated carboxylic acids. Hence it was concluded that only organic compounds containing alcoholic groups form complexes with molybdic and tungstic acids, the products being complex acids of considerably greater strength than the original components.

Electrochemical Methods

Polarographic and especially potentiometric methods have proved to be most suitable for investigating the complexes of hydroxy-acids. They have often enabled not only the composition of the complexes to be established but also their stability in aqueous solution to be determined, which is of great importance for the chemical characterisation of these compounds and for their practical application. The polarographic method has been less widely used, since it requires a sufficient rate of dissociation of the complex ion on the surface of the mercury electrode, whereas quite often the dissociation of hydroxy-acids is fairly slow.

The polarographic method has been used to study the tartrato- and citrato-complexes of zinc[79,80], cadmium[80,81] indium[82], lead[83], vanadium[84], bismuth[85], iron[65,86], and several rare-earth elements[87].

The potentiometric method of investigation proved to be the most promising, based on measurement of the activity of the metal ions in a solution of the complex compound. It makes possible a direct estimation of the stability of the complexes. The most convenient technique involved metal-ion activity measurement with a variable concentration of the ligand (taken in great excess) and a constant pH. The composition of the compound was then found from the slope of the straight line obtained on plotting the logarithm of the metal-ion activity against the concentration of the hydroxy-acid. Subsequent study of the variation of the metal-ion activity with pH at a constant ligand concentration showed which groups, carboxyl or alcoholic, were involved in formation of the complexes.

In several cases application of the potentiometric method was restricted by the poor reversibility of the metal electrodes (antimony, etc.).

The potentiometric method has been used to study the tartrato-complexes of copper[74,88-92], zinc[79,80], cadmium[80,93,94], tin[95], lead[79,83,91,96], antimony[91], bismuth[85,97], and iron[65].

Potentiometric pH-titration, used mainly to determine the composition of the complexes, was of less value. It has yielded information on complexes of copper[55,98], beryllium[99], aluminium[100], titanium[36], zirconium[99], thorium[73,101], germanium[36], vanadium[102], antimony[37,103], bismuth[104], uranium[64], iron[65], nickel[55], and cobalt[55]. A noteworthy modification of the isomolar series method is based on measuring the pH of mixed solutions of hydroxy-acids and metal salts, and plotting the deviation from additivity.

The procedure in these determinations was as follows: (*a*) the hydrogen-ion concentrations of solutions of the metal salt of various concentrations were measured; (*b*) the hydrogen-ion concentrations of solutions of tartaric acid of different concentrations were measured; (*c*) the results were used to calculate the total hydrogen-ion concentrations for mixed solutions of the metal salt and tartaric acid; (*d*) the hydrogen-ion concentrations of these mixtures were determined experimentally; (*e*) the increase in hydrogen-ion concentration due to interaction in the system (the deviation from additivity) was calculated from the difference between (*d*) and (*c*). The position of the maximum on the curve (*e*) indicated the composition of the complex. This method has been used to study complexes of beryllium[105], aluminium[69], indium, and gallium[72,106], and to estimate their relative stability in aqueous solution.

Study of Heterogeneous Equilibria

Several variants of the solubility method have been used to investigate hydroxy-acid complexes. One modification consisted in studying the equilibrium between sparingly soluble hydroxides, sulphides, or tartrates of metals and aqueous solutions of the complexes formed by these metals with tartaric and other hydroxy-acids. This has enabled both the composition and the stability of the complexes to be determined. This method has been applied to tartrato- and citrato-complexes of copper[57,107,108], zinc[79,80], lead[109,110], bismuth[97,111], and iron[91]. In some cases sufficiently reliable results were not obtained owing to an unfortunate choice of compound as the solid phase; thus iron sulphide and hydroxide[91] gave colloidal solutions, and their properties changed owing to aging phenomena, etc.

In several cases the composition of the complexes was found in the following manner. In a series of experiments, increasing quantities of the hydroxy-acid solution were added to a solution of the metal salt, and then a solution of ammonium hydroxide or an alkali was added. The molar ratio of the components at which no great formation of insoluble metal hydroxide occurred was regarded as corresponding to the composition of the complex[97,112]. This method is of limited value[113] and sometimes leads to incorrect conclusions. It was shown that correct results could be obtained only when a definite relation existed between the instability constant of the complex and the solubility product of the hydroxide.

Bobtelsky[114] used heterometric titration to determine the composition of the complexes. The principle of this method consists in measuring the optical density of suspensions formed by gradual addition of the hydroxy-acid or a salt thereof to a solution of the metal salt (or conversely). The critical points of incipient turbidity, maximum optical density of the suspension, and complete dissolution of the precipitate were noted on the heterometric curves. The molar ratios of the components corresponding to the critical points indicated the composition

TABLE 1 (cont'd.)

Formula	Negative logarithm of instability constant, $-\log K_i$	Method of investigation	Conditions of formation (acidity)	References
1	2	3	4	5
		Gallium and indium		
$GaHTX_2$	—	cond, pH	acid medium	72
$GaTX$	—	ditto	ditto	72
$MGaT_2$	—	»	alkaline medium	72
$Ga_2T''X_2$	—	»	pH = 7	72
$InHTX_2$	—	»	acid medium	106
$In(HT)T$	6.8	pol	pH < 2.6	82
$In(OH)T$	—	prep	alkaline medium	106
$M_2In(OH)T_2$	18.51	pol	pH > 2.6	82
		Titanium		
$(TiO)_2OT\cdot 7H_2O$	—	prep	acid soln.	150
$MTiO(HT)T$	10.54	extr	pH 4.6	122
$MTiOT'$	18.2	»	pH 5.5—6.2	122
M_4TiOT_2''	25.39	»	pH 9—9.5	122
		Zirconium		
$ZrOT$	—	prep	acid soln.	151
M_2ZrOT_2	—	»	$M_2T + Zr(NO_3)_4$	152
$M_2ZrT_4\cdot 8H_2O$	—	»	weakly acid	2
$Zr_3(OH)_8T''\cdot 6H_2O$	—	»	ditto	152
		Thorium		
$M_2ThOT_2\cdot 8H_2O$	—	prep	$MHT + Th(OH)_4$	155
$M_2ThOT''\cdot 4H_2O$	—	prep	alkaline medium	155
$Th_3(OH)_4\cdot T_4\cdot 5H_2O$	—	prep	$M_2T + Th(NO_3)_4$	153, 154, 155
		Germanium		
$GeOT$	6.15	prep, pot pH, rot	acid medium	36, 35, 156, 157
		Tin		
M_2SnOT_2	—	prep	$Na_2T + Sn(OH)_4$	158
$M_2SnOT''\cdot 5H_2O$	—	prep	alkaline medium	159
Sn : T = 1 : 1 and 1 : 2	—	rot	acid soln.	36
		Lead		
$MPb(HT)_3$	4.7	pot	pH 2.5—5	79
PbT	2.9	prep, hm, pot	acid soln.	160, 161, 116, 96
$M_2Pb(OH)_2T$	14.1	pot	alkaline medium	79
$MPbT'$	—	prep, rot	pH > 7	161, 162
M_2PbT''	14.38; 14.68 13.5	prep, pot rot	alkaline medium	91, 163, 83
$Pb_2(HT)_2X$	—	pol	pH < 7	164
$M_2Pb_2OT_2$	—	pot	weakly alkaline	74
$M_4Pb_2OT_2''$	—	rot	alkaline soln.	161
$M_2Pb_2T_2''$	—	hm	pH > 7	116
$M_3Pb_2T'T''$	—	hm	pH > 7	116
Pb_2T''	—	hm	pH 8—9.5	116
$M_4Pb_4T_3''$	—	hm	pH > 7	116
		Vanadium		
$VO(HT)X$	—	cond, sph	pH < 3	58
M_2VOT_2	—	cond, sph	pH > 6	58
M_2VOT''	—	prep, pot pH	alkaline soln.	165, 166, 102
		Niobium		
$H_4Nb(OH)T_2''$	—	prep	acid soln.	167, 168
		Arsenic		
$MAsOT$	—	cr, rot, cond		74, 75, 37
$MAsO_2T$	—	prep		169
		Antimony		
$Sb(HT)_3$	—	prep	acid soln.	14
$Sb(OH)(HT)_2$	—	prep	ditto	14
$MSbOT$	11	prep, pot	alkaline soln.	170, 91, 171, 172
SbT'				
M_2SbOMT''	—	prep	alkaline medium	173
Sb_2T_3	—	prep	—	14
$M_2Sb_2O_2T_2$	—	cr, cond	—	74
		Bismuth		
$MBi(HT)_4$	8.3	pot, soly	pH < 4	97
$Bi(HT)T$	—	prep	acid medium	75, 39, 1
$BiTX$	—	prep	ditto	75, 39
$M_2Bi(OH)_3T$	31	pot, soly	alkaline medium	97
BiT'	19.66	pot, soly	pH 3.5—5.5	92, 111
$MBiT''$	—	pot, soly	alkaline medium	175
$M(BiO)_2T'$	—	prep	—	176
$M(BiO)_3T''$	—	prep, rot	alkaline soln.	75, 39, 3
		Molybdenum and tungsten		
M_2MoO_3T	—	prep, rot	$K_2T + H_2MoO_4$	41, 49
$M_2MoO_2T_2$	—	ditto		44
M_2WO_3T	—	»	$K_2T + H_2WO_4$	41, 49
$M_2WO_2T_2$	—	»		44
		Uranium		
U : T = 1:1, 1:2, 1:3		sph		62

TABLE 1 (cont'd.)

Formula	Negative logarithm of instability constant, $-\log K_i$	Method of investigation	Conditions of formation (acidity)	References
	2	3	4	5
		Manganese		
MnT	—	prep	—	3.4
M_2MnT_2	2.52	prep, soly	pH 5—7	177, 178, 179
		Iron		
$FeTX$	7.34	sph	pH 1—3	180
M_2FeT_2	—	prep, rot, pol	$Fe(NO_3)_3 + Na_2T$	181, 52
M_3FeT_3	—	prep, rot	—	12, 52
$M_4FeT'T''$	—	extr	pH 12	121
$MFeT''$	28.48	prep, sph, pot, pol	pH 4—6	182, 183, 12, 52, 86, 65.
$M_4Fe_4O_3T_3''$	—	prep	weakly alkaline soln.	184
$M_4Fe_4(OH)_4T_3''$	—	prep	ditto	185
		Cobalt		
CoT	—	prep	—	5
M_2CoT_2	—	prep	$Na_2T + CoSO_4$	186, 187
$MCoT'$	—	prep	weakly alkaline medium	186, 187
M_2CoT''	—	prep	alkaline medium	186, 187
		Nickel		
NiT	—	prep	acid medium	6, 5, 7
M_2NiT_2	—	prep		6, 5, 7
M_2NiT''	—	prep		5, 188
		Cerium		
Ce_2T_3	—	prep, rot	pH 3.5—5.5	54, 189, 190
CeT'	—	prep	pH 6.8	190
$MCeT''$	—	prep	pH 6.8—10.7	190

TABLE 2. Stability of citrato-complexes of metals.

Formula	$-\log K_i$	Method of investigation	Conditions of formation (acidity)	References
$MCuH_2CitHCit$	4	sph, soly	pH 3—5	107, 57
$MCuCt$	2.95	sph, pot, pol	pH < 7	55
$M_2Cu(OH)Ct$	16.35	sph, soly	pH 7—11	107, 57
$M_4Cu(OH)_2Ct_2$	18.77	sph, soly	pH > 12	107, 57
M_2CuCi	13.22	pot pH	alkaline soln.	191
BeH_2CtX	1.4	io	pH 3—4	192
$BeHCt$	2.22	»	pH 3—4	192
$MBeCt$	4.52	»	pH 3—4	192
ZnH_2CtX	3.0	pot pH	pH 3—4.3	193
$ZnHCt$	4.9	ditto	pH 4—7.3	193
$MZnCt$	4.25	»	acid soln.	191
$M_2Zn(OH)Ct$	9.4; 10.92	pot, pol, soly	pH 5.5—11	79, 194
M_2ZnCi	7.5; 7.44	pot pH	pH 7.3—8.5	193
$CdHCt$	3.25	pot	pH < 7	94, 195
$MCdCt$	3.38	pot pH	acid soln.	191
M_2CdCi	6.23	ditto	weakly alkaline	191
$M_3TiO(HCt)Ct$	11.92	extr	pH 5—6	123
$M_2Sn(OH)Ct$	20.0	pot	pH > 7	95
$MPbCt$	6.5	—	pH 6.95—7.45	196
$M_2Pb(OH)Ct$	13.72	pot	pH 9—13	197
M_2BiCt_2	14.4	pot, pol	pH 3—6	85
M_2MnCi	8.72	soly	neutral and weakly alkaline soln.	198
$FeHCtX$	6.3	pot pH	acid soln.	199
$FeCt$	11.85; 14.55	pot, sph	ditto	199, 66
$MFe(OH)Ct$	9.4; 9.1	pot pH, pol	pH 4—6.5	199
$M_2Fe(OH)_2Ct$	1.9; 2.6	ditto	pH 6.5—7.5	199
$MFeCi$	21.6	sph	pH 4—6	66
$MCoCt$	4.41	pot pH	acid soln.	191
M_2CoCi	7.08	ditto	weakly alkaline	191
$MNiCt$	4.99	»	acid soln.	191
$M_2Ni(OH)Ct$	13.32	—	alkaline medium	200
M_2NiCi	5.27	pot pH	weakly alkaline	191
M_3YbCt_3	8.0	»	pH 3—6	201
$MYb(OH)Ct$	16.0	»	pH 5—6	201
$M_3Yb(OH)_3Ct$	36.0	»	ditto	201
$MYbCi$	8.0	»	»	201

Most of the compounds which were prepared contained an indeterminate quantity of water, and therefore the water content is not usually indicated. The column headed "conditions of formation" gives the pH limits within which the given compound is formed. In much of the earlier work the pH was not measured, in which cases this column contains either a dash or an indication of other experimental conditions.

Table 2 gives data on the stability of the citrato-complexes of several metals for comparison. Here Ct denotes the $C_6H_5O_7^{3-}$ ion, and Ci the $C_6H_4O_7^{4-}$ ion.

5. DEPENDENCE OF PROPERTIES OF TARTRATO--COMPLEXES ON FORMATION CONDITIONS

Analysis of the accompanying published data enables the fundamental laws governing the formation of hydroxy--acid complexes to be established with tartaric acid as example.

Composition and Structure of Complexes

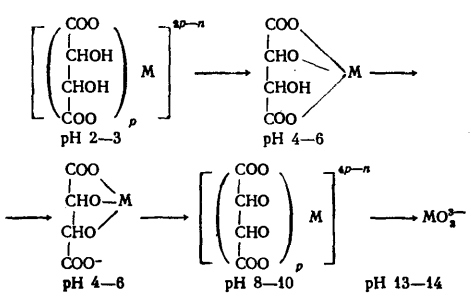
Let us first consider the variation in composition of the complexes with the concentration conditions. Table 1 shows a great variety of composition among the compounds, but nevertheless some general principles can be deduced.

At low ligand concentrations, compounds are usually formed in which one tartaric acid radical is associated with one metal ion, *e.g.*, $CuC_4H_4O_6$, $ZnC_4H_4O_6$, $CdC_4H_4O_6$, etc. These might appear to be simple salts, but they are complex in nature, since they are distinguished by low degrees of dissociation in solution. Increasing the concentration of tartaric acid or sodium tartrate in the system results in coordination by the central metal ion of a further ligand, and sometimes of more than one. Thus at tartrate concentrations up to 0.2 M, the solution contains the mainly undissociated $CdC_4H_4O_6$,[80] while over the range of ligand concentrations 0.2 – 1.0 M a second tartaric acid radical is added to form the complex $M_2Cd(C_4H_4O_6)_2$.[81] Analogous phenomena are observed in several other cases. When the relative concentrations of the central metal ion and of the ligand are unfavourable, if the latter is not present in sufficient excess, more complicated compounds are not infrequently formed at some intermediate pH, in which one metal ion is associated with less than one tartaric acid residue. This applies in particular to salts in which the molar ratio of metal to tartrate is 4 : 3, *e.g.* $M_3Cu_4C_{12}\cdot H_7O_{18}$,[127-129,131,132] $M_6Al_4O_3C_{12}H_6O_{18}$,[149] $M_6Fe_4O_3C_{12}H_6O_{18}$,[184] etc. The chemical individuality of these salts has not been proved in all cases, and perhaps a mixture of more than one substance is isolated. However, there is no doubt about the existence of compounds of this type, at least with copper. Many salts have been prepared[128-130] containing the complex anion $Cu_4C_{12}H_7O_{18}^{3-}$, in which the place of the alkali metal is occupied by complex ammines of cobalt and of several other metals. The bismuth tartrate $K(BiO)_3C_4H_2O_6\cdot 4H_2O$, in which the ratio of bismuth to tartrate is 3 : 1, and which was prepared by Rosenheim[75,39], is worth mentioning.

The principal factor affecting the composition and the structure of the complex tartrates is the pH of the solution. In acid medium, dissociation of the hydroxy-groups of tartaric acid is very difficult, and under these conditions complexes involving only the carboxyl groups are formed predominantly. Examples of such compounds are $Cu(HC_4H_4O_6)_2$,[57,107] $M_2Zn(C_4H_4O_6)_2$,[140] $MAl(HC_4H_4O_6)_4$,[69] $ZrOC_4H_4O_6$,[151] $MPb(HC_4H_4O_6)_3$,[79] and many others. It is evident from the table that they are all formed in acid medium. Raising the pH weakens the bond between hydrogen and oxygen atoms in the hydroxyl groups and favours the partial or complete replacement of these hydrogen atoms by metal cations. This yields complexes in which the metal is directly linked with the oxygen of both hydroxyl and carboxyl groups. An illustration is provided by the formula of the so-called ferritartaric acid $HFeC_4H_2O_6$, which was prepared by Paira[182]. Here the ferric ions have replaced the hydrogen atoms of both hydroxyl groups and of one carboxyl group. Alkali-metal salts of this acid are readily soluble, and their behaviour in solution has been studied by many workers[65,86]; these physicochemical researches have confirmed the correctness of the above formula.

In some cases replacement of the hydroxy-hydrogen atoms by metal still occurs in weakly acid medium. This is characteristic, for example, of the cations of iron[65,52], bismuth[92,111], antimony, and other readily hydrolysable metal cations. As a general rule, however, such substitution takes place most readily in alkaline solutions, where the cations of most metals form complexes of this type. In the pH range 10 – 14 compounds are usually obtained in which the metal is now linked only with the oxygen atoms of the hydroxyl groups. Examples of such compounds are provided by salts having the composition $M_2CuC_4H_2O_6\cdot xH_2O$,[8,15,16,55,125,126] $M_2Al(OH)C_4H_2O_6$,[28,29] $MTiOC_4H_3O_6$,[122] $M_2SnOC_4H_2O_6\cdot 5H_2O$,[159] $M_2PbC_4H_2O_6$,[83,91,163] and $M_2VOC_4H_2O_6$.[102,165,166]

Thus the general picture of the variation in composition and structure of the complexes of tartaric acid with increase in solution pH can be represented, for example for a tervalent metal cation, by the scheme:



The last stage of the process, the formation of soluble hydroxo-salts at high pH-values, occurs quite often with cations of metals having amphoteric properties, as will be shown below.

Some writers[107] have doubted whether the hydroxy-hydrogens of tartaric acid can be replaced by metal cations. They have regarded compounds formed in alkaline solutions as hydroxide (basic) salts, for example $M_2Cu(OH)_2C_4H_4O_6$. It has hardly ever proved possible to obtain such salts anhydrous, and therefore the formula $M_2CuC_4H_2O_6\cdot 2H_2O$ could always be written in the above form. Elementary analysis does not usually enable a distinction to be made between these two formulae, as a result of which two opposite views on complex formation by hydroxy-acids existed for a long time. According to one, complexes are formed by the metal displacing the hydrogen atoms of the hydroxyl groups; according to the other, hydroxide salts are formed under these conditions. However, quite convincing direct and indirect proofs are now available of the correctness of the

view that the metal displaces hydrogen atoms from the hydroxyl groups, including the following. (*a*) Such substitution has been established quite definitely in the case of aromatic hydroxy-acids and alcohols[202]. There is no fundamental difference in this respect between aromatic and aliphatic hydroxy-compounds, although the acidic character of the hydroxy-groups is less marked in the latter case owing to the absence of the aromatic radical; in several cases there is no doubt that the corresponding values of p*K* are greater than 14. It will therefore be somewhat more difficult to replace hydroxyl hydrogen by a metal in aliphatic, than in the corresponding aromatic, hydroxy-acids. (*b*) Derivatives of aliphatic hydroxy-acids in which hydroxyl groups have been replaced by amino- and other groups[2,10] have lost the ability to form complexes. (*c*) Replacement of hydroxy-hydrogen atoms by a metal is indicated by elementary analysis of some complexes; thus ferritartaric acid was shown[182] to contain 27.56% of iron and 23.68% of carbon, which corresponds to the formula $HFeC_4H_2O_6$. (*d*) When lead tartrate and some other tartrate complexes are prepared in solutions of heavy-oxygen water, the precipitated complexes contain[11,203] no heavy oxygen, so that the metal has not combined with the hydroxyl groups of water. (*e*) Dimethoxysuccinic acid HOOC.CH(OCH_3).CH(OCH_3).COOH differs from tartaric acid in forming no complexes with the cations of lead, titanium, copper, or aluminium in alkaline solution; it also behaves differently towards iron cations, forming with them complexes having altogether different properties[180]. These experiments indicate directly the role of the hydroxy-hydrogen in the formation of complexes.

Stability of Complexes

It is clear from Table 1 that instability constants have been determined only for a few tartrato-complexes of metals. Nevertheless, the instability constant is the most important thermodynamic characteristic of a complex compound, and a knowledge of it is necessary for most fields of application of such compounds. An attempt is made below to give a qualitative account of the variation in stability of tartrato-complexes of metals with the acidity of the solution, the properties of the complex-forming cation, and the position of the latter in the Periodic System. This account is based primarily on the data on instability constants in Table 1. Published data on the relative stability of the tartrato-complexes of several metals[204-209] are also taken into account.

The influence of the acidity of the solution on the stability of tartrato-complexes depends on the properties of the central ion. In this respect all elements can be usefully divided into two classes. The first includes tungsten, molybdenum, boron, arsenic, etc., whose oxides have a more or less clearly defined acidic character. Quantitative data on the stabilities of the tartrato-complexes of these elements are lacking. The literature contains qualitative observations indicating that the complexes become less stable with increasing pH. The tartrates of molybdenum, boron, tungsten, and arsenic are formed mainly in acid medium, and decompose into their component parts in alkaline or in neutral solutions[37,49,210]. Such peculiar behaviour of these complexes is linked with the ability of the elements to yield cationic forms only in comparatively acid medium. Increase in solution pH considerably facilitates replacement of the hydroxy-hydrogens of tartaric acid by metal cations; however, the tendency of the cationic forms of these elements to pass into anionic forms, which can no longer interact with tartaric acid, grows to a still greater extent. It has been established, for example, that free tartaric acid shows the greatest tendency to form complexes with molybdenum and tungsten[41-43]; acid tartrates occupy an intermediate position, while a tartrate containing two alkali-metal atoms no longer reacts with molybdates or tungstates. An analogous phenomenon is observed also in the formation of the tartrato-complexes of arsenic. Polarimetric measurements have shown that the complex breaks down into its components on neutralisation with alkali[37,210].

The second class includes elements having basic properties, such as copper, cobalt, nickel, iron, bismuth, etc. Here an increase in pH causes enhanced stability, which is associated with a change in structure of the complexes. On passing from acid to alkaline medium, replacement of the hydroxy-hydrogen atoms by metal cations usually begins, dissociation of the hydroxyl groups being greatly facilitated in alkaline solution. This is the principal reason for the more complete binding of metal cations in complexes with rise in solution pH.

Elements having amphoteric properties — zinc, aluminium, lead, etc. — occupy an intermediate position. Here the stability of the tartrato-complexes at first increases with rise in pH. However, at some intermediate pH the tartrato-complex begins to change into a hydroxide salt, depending on the individual properties of the complex-forming cation. Thus in a solution containing tartrate, zinc exists in the zincate form already at pH ~ 12; [80] the tartrato-complex of lead, however, exists even in solutions of pH > 13. [83]

Difficulties arise in comparing numerical data representing the stabilities of the tartrato-complexes of different elements, because the values of the instability constants quite often relate to compounds of differing composition and structure, and therefore cannot be compared directly. Moreover with many compounds, as mentioned above, the instability constants have not been determined at all. The parameter adopted in Table 3 for comparing stabilities is the logarithm of the degree of binding of the metal cation in the tartrato-complex[204], *i.e.* the logarithm of the ratio of the concentration of metal ions combined in the complex to their concentration remaining uncombined under some standard conditions of acidity; the concentration of the ligand, tartaric acid, was taken as unity in all cases. These numerical values have been determined experimentally[204-207,211], or else calculated from the instability constants.

The accompanying numerical data, together with some qualitative observations in the literature, enable the variation in stability within groups and periods in the Periodic System to be traced. Most of the data relate to alkaline solutions, in which the specific complexing action of tartaric acid, due to combination of the metal cation with the oxygen of a hydroxyl group, is most clearly developed. The stability of the tartrato-complexes at high pH-values is also of interest from a practical point of view, since many cases of masking are in fact based on the formation of complexes in alkaline solutions. The ringed numbers denote logarithms of the degree of binding at pH ~13, and those in rectangles at pH ~ 10; with zinc and cadmium, values of the logarithm are given for the complexes in acid medium (pH 5).

The absence of experimental data makes it impossible to

give a quantitative idea of the variation in stability within Group I of the Periodic System. Copper is combined to quite a large extent; silver probably gives a less stable complex, since alkali precipitates silver hydroxide from tartrate solutions. Comparison of the constants in Group II shows the zinc complex to be rather more stable than the cadmium complex. In Group III the gallium complex is the most stable, those of indium, thallium, and aluminium having a lower and almost identical stability. In the first subgroup of Group IV the stability falls on passing from titanium to zirconium and then to hafnium [209]; and in the second subgroup from tin(II) to lead. A similar phenomenon is observed in Group V, the bismuth complexes being less stable than those of antimony. Even these still very incomplete data enable the general conclusion to be drawn that, within individual groups of the Periodic System, the stability of the tartrato-complexes decreases on passing down the group. This can be related to the ionic radii: it is probably a general rule that the complexes become less stable with increasing radius of the complex-forming cation.

The numbers in Table 3 also enable the variation in stability within the Fourth Period to be traced. Comparison of the stability at pH ~ 13 (ringed numbers) shows a sharp increase in degree of binding on passing from manganese to tervalent iron, followed by a decrease on passing to cobalt and nickel. With copper the stability again increases. Comparison of the stability of the tartrates of aluminium, titanium, iron, and quadrivalent vanadium at pH ~10 shows primarily the considerably greater stability of the tartrato--complex of iron than that of titanium. This is probably due to the difference in charge on the two ions, titanyl and iron.

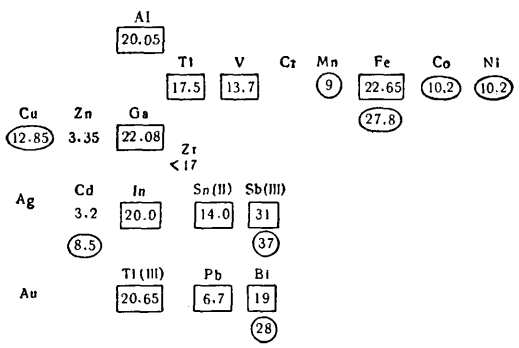
Few data are available for comparison of the stabilities of complexes in the Fifth and Sixth Periods. Only increases in stability in the order cadmium–antimony, tin–antimony, and lead–bismuth can be noted. Thus the variation in stability of the tartrates within the periods is mainly associated with the ionic charge. With identical ionic charges and radii, the stabilities of the complexes can be linked with the values of the covalency index‡ proposed by Yatsimirskii [212]. The correlation between these quantities for manganese, cobalt, nickel, and copper§ can be seen from the following data:

	Mn	Co	Ni	Cu
Covalency index	85	93	97	137
Logarithm of degree of binding	9.0	10.2	10.2	12.85

The stability of metal complexes of tartaric acid is probably determined by those factors which govern the strength of bonding of the metal cation to hydroxyl groups. The order of solubility of the metal hydroxides is in many cases similar to that of the stability of the tartrato-complexes. This point is illustrated by the following data [204], which compare the pH at which hydroxides of the metals start to be precipitated with the logarithm of the degree of binding of these metals of the tartrato-complexes:

	Fe	Cu	Co	Ni	Mn
pH of start of precipitation	1.6	4.2	6.8	6.8	7.4
Logarithm of degree of binding	27.3	12.85	10.2	10.2	9.0

TABLE 3. Variation in stability of tartrato-complexes in the Periodic System.



Analogous trends are observed also with the tartrato--complexes of aluminium, iron, gallium, indium, and thallium [205,207], and the citrato- and trihydroxyglutarato--complexes of manganese, cobalt, nickel, and copper [206]. The readily hydrolysed cations of tervalent antimony form considerably more stable tartrato-complexes than do the cations of bismuth, which show less tendency to hydrolysis. The stability of the tartrato-complexes diminishes also from zirconium to hafnium [209] in conformity with the accompanying decrease in the tendency of the cations of these metals to undergo hydrolysis.

The above correlation between the stability of the tartrato-complexes and the tendency of the corresponding metal cations to undergo hydrolysis can be explained by the analogy between the action of inorganic and organic reagents developed by Kuznetsov [214]. The hydrolysis of metal salts is a manifestation of the tendency to form an M–OH bond by the action of water. Complex formation between metals and organic reagents containing an OH-group, in particular hydroxy-acids, however, reflects, according to Kuznetsov, the tendency to form an M–OR bond under the influence of the reagent H–OR. Such a reagent can be regarded as a derivative of water in which one hydrogen atom has been replaced by an organic radical. The two processes are therefore formally analogous, although the substitution of a complicated organic group for the hydrogen in water can also be reflected in the properties of the reaction product. In particular, this analogy takes no account of chelation involving the metal cation and the organic radical; chelation is not involved in the reaction of a metal cation with water. Nevertheless, this generalisation can be utilised for a rough qualitative assessment of the stability of tartrato--complexes.

6. RELATION BETWEEN STABILITY OF COMPLEXES AND STRUCTURE OF HYDROXY-ACID LIGANDS

Different hydroxy-acids exhibit different powers of complex formation with metal cations. The stability and other

‡ Yatsimirskii defines "covalency index" as the difference between the ionisation potential of an atom and the heat of hydration of the ion derived from it [Ed. of Translation].

§ It is probable that such a relation is not always observed. Thus, while the ionic radii are similar, the covalency index of mercury (226) is considerably greater than the corresponding value for copper, yet qualitative experiments show that the tartrate complex of mercury is not very stable.

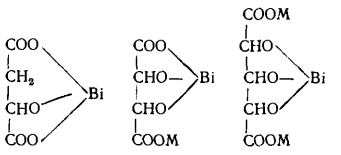
properties of the complexes depend on the numbers of carboxyl and hydroxyl groups in the hydroxy-acid molecule and on their relative positions, on the ability of these groups to dissociate by splitting off hydrogen ions, on the length of the carbon chain, etc. Thus in acid medium, where complex formation is usually due to interaction of the metal cation with the carboxyl groups, the number of hydroxyl groups should have little effect on the properties of the complexes. In alkaline solutions, on the other hand, the number and mutual arrangement of the hydroxyl groups, etc. should be of greatest significance. Too little experimental work has yet been done for a comprehensive consideration of all these factors or a full assessment of their influence on the properties of the resulting complexes. Nevertheless, a few data on this question are available, and are examined in the present section.

The stability of the complexes of tartaric and citric acids can be compared on the basis of the data in Tables 1 and 2. The physical significance of the instability constants of the complexes of the two hydroxy-acids differs, and therefore they cannot be compared directly. It is best, as in the preceding section, to use the degrees of binding as measures of stability.

Let us first examine the relation between the stabilities of the complexes in acid solutions. The citrato- and tartrato-complexes of titanium have been compared[123] using this criterion of stability. That of the citrato-complex of titanium at pH ~ 5 was found to be approximately two orders of magnitude greater than the stability of titanium tartrate, the difference in stability diminishing with rise in pH of the solution. Similar observations have been made for the tartrato- and citrato-complexes of iron[65,66], bismuth[85,92,111], manganese[215], yttrium, and cerium[216]. The masking action of citric acid on the precipitation of the cations of beryllium, vanadium, antimony, cobalt, and nickel by organic precipitants is also considerably more marked in acid solution than is the masking effect of tartaric acid[217]. Thus it follows from these data that citrato--complexes are more stable than the tartrato-complexes. This can be related to the number of carboxyl groups in these hydroxy-acids, which play the main part in complex formation in acid solution. In the case of citric acid the cation (for example of a tervalent metal) is able, by combining with three oxygen atoms in the carboxyl groups, to complete two seven-membered rings, whereas in the case of tartaric acid only one such ring can be formed, which, of course, affects the stability of the complexes.

A different relation is observed in alkaline solutions. Here citric acid usually forms less stable complexes than does tartaric acid. Sodium tartrate has a far stronger masking action than has sodium citrate on the precipitation of the 8-hydroxyquinolinato-complexes of beryllium, titanium, lead, bismuth, and iron; the 1-nitroso-2-naphthol complexes of copper; lead ethyl xanthate; and indium and bismuth diethyldithiocarbamates[217]. The degree of binding of iron in the tartrato-complex has been shown[121] to be about 900 times greater than that in the citrato-complex. Trihydroxyglutaric acid, which contains three hydroxyl groups, gives still more stable complexes under these conditions. An analogous relation is observed on comparing the stabilities of the copper, cobalt, and bismuth complexes in the series trihydroxyglutaric–tartaric–malic acids[218]. The stability of the complexes of all three metals falls in this order.

These phenomena have been explained[121,218] on the basis of the possibility of a larger or a smaller number of closed five-membered rings being formed involving the metal cations and the hydroxyl groups of the acids. Such closed rings probably possess greater stability than analogous rings formed by the metal cations with the carboxyl groups. In alkaline solutions, therefore, where complex formation involves the hydroxyl groups, complexes of hydroxy-acids containing a large number of such groups are the most stable. Thus the complexes formed by bismuth with malic, tartaric, and trihydroxyglutaric acids can be represented by the following structural formulae:



It is seen from these formulae that the greatest stability shown by the trihydroxyglutarato-complex of bismuth may be due to the formation of two chelate rings involving three hydroxyl groups. The tartrato-complex of bismuth is less stable, since the two hydroxyl groups of tartaric acid are able to give only one chelate ring with the bismuth ion. In the case of the malato-complex there is no such chelate ring formed solely by hydroxyl groups, and therefore the complex has the lowest stability. In the citrato-complex of iron the possibility of the formation of a chelate ring involving hydroxyl groups is excluded; the hydroxyl groups of tartaric acid can now form one such ring with iron cations, while in the case of trihydroxyglutaric acid two such rings can be formed. The stability of the complexes also varies in conformity with this.

7. APPLICATION OF COMPLEXES OF TARTARIC AND OTHER HYDROXY-ACIDS IN ANALYSIS

Hydroxy-acids form complexes by replacement of the hydrogen atoms in the carboxyl or hydroxyl groups with metal cations. This affects the acidity of the medium, and quite often simple stoichiometric relations exist between the quantity of hydrogen ions liberated and the quantity of metal ions combined in the complex. This property is utilised in analytical chemistry for the direct determination of several metals by acid–base titration. Some analytical applications exploit the change in absorption spectrum of the metal cations accompanying complex formation, although aromatic hydroxy-acids are most often employed for this purpose. However, the main field of application is based on the ability of tartaric and citric acids to form with the cations of different metals complex compounds of differing stability, and thus to exert a differentiating action on various properties of the elements. This differentiating effect is employed for the separation of rare-earth elements on a chromatographic column, for the chemical separation of elements, for the analytical determination of a mixture of cations of several metals by electrochemical methods, etc.

Utilisation of Acid–Base Properties of Complexes

Methods have been described for the determination of zinc[219,220], cadmium[221], aluminium[112,222], titanium and zirconium[223], cerium[224], tin[225,226], lead[213], chromium[227], iron[228–230], manganese[231], and cobalt[232], based on titration of the acid liberated when these metal cations react with the alkali-metal salts of tartaric and other hydroxy-acids.

Interesting methods for the determination of beryllium and aluminium [233,234] are based on titration of the alkali produced when tartrato-complexes of these elements react with sodium fluoride solution:

$$M_2BeC_4H_2O_6+2H_2O+4MF=M_2BeF_4+M_2C_4H_4O_6+2MOH.$$

In certain special cases these methods possess several advantages, in particular a considerable economy of time. However, they are not very accurate. Quite often the reactions are not completely stoichiometric, and therefore various empirical coefficients must be used in calculating the analytical results. The change in colour of the indicator at the end-point is not usually sufficiently sharp. Moreover, direct determinations are impossible in solutions containing free acid. All these facts considerably limit the widespread use of these methods for the analytical determination of elements.

Formation of Coloured Compounds

Copper, vanadium, chromium, iron, cobalt, and nickel give coloured complexes with tartaric and citric acids. These complexes are characterised by low molar extinction coefficients, and are not very suitable for use in colorimetry. Nevertheless, methods have been described in the literature for the colorimetric determination of the cations of several metals by means of tartaric and citric acids. A method has been suggested [235] for the spectrophotometric determination of iron in the ultra-violet by means of tartaric acid, and a procedure has been worked out for determining iron in rocks by this method. Nickel, cobalt, and copper can be determined when present together [236] by measuring the light absorption in different spectral regions of the complexes formed in alkaline tartrate solutions. The intense dark blue colour of vanadium citrate has been utilised [237] for the colorimetric determination of this metal. Tartaric, citric, and some other hydroxy-acids can be determined quantitatively [238] from the fading which they produce in the colour of ferric thiocyanate solution.

Use of Hydroxy-Acids as Masking Agents

Several examples of the masking action of hydroxy-acids are well known. Thus iron is separated from titanium and aluminium by precipitation with hydrogen sulphide from alkaline solution while the latter elements are masked with tartaric acid. On the other hand, iron is masked with tartaric acid for separation from nickel, which is precipitated with dimethylglyoxime. Aluminium is masked with sodium tartrate while bismuth is precipitated with ammonium sulphide. The use of sodium citrate has been suggested [239,240] for a sharper separation from one another of cations in the chloride subgroup of the fourth analytical group, for keeping titanium in solution during the precipitation of phosphorus with ammonium molybdate [241], and for eliminating the effect of aluminium and zinc on the complexometric determination of iron in their presence [242]. A technique has been worked out [243] for separating beryllium from aluminium, iron, copper, and chromium by precipitating it with ammonium hydroxide from tartrate solution. Masking with tartaric acid has been employed in the separation of niobium and tantalum from titanium [244,245], and of tantalum from niobium [246].

Use of Hydroxy-Acids in Electrochemical Methods of Analysis

Reference must first be made to the great value of hydroxy-acids in electroplating and electroanalysis, where they are used to improve the quality of the coating and to obtain dense deposits of metal on the electrodes. This effect of hydroxy-acids is usually attributed to the formation of complexes with the cations of the metals undergoing deposition. It is observed in the electrodeposition of copper and silver [247]. Citrate solutions have been suggested for the electrodeposition of cobalt–tungsten–molybdenum alloys [248]. Masking with tartaric acid is used in the electrolytic separation of tin and antimony [249], and of nickel and zinc [250].

In the polarographic determination of inorganic ions, tartaric and citric acids are often used as supporting electrolytes, with the aim of forming complexes of these ions in order to obtain separate waves for ions present in a complicated mixture and having identical or similar half-wave potentials. The addition of solutions of hydroxy-acids has been shown, by determination of the half-wave potentials of metal cations with such acids as supporting electrolyte, to produce unequal negative shifts in the potentials of different ions and to create conditions for the simultaneous determination of several ions [251,252]. The tartaric-acid supporting electrolyte proved to be suitable for the simultaneous polarographic determination of copper and bismuth [253], which have almost identical half-wave potentials when dissolved in nitric or sulphuric acid, and for the determination of copper, bismuth, cadmium, lead, and zinc as impurities in metallic tin [254], copper, and iron [255]. Citric acid has been used as supporting electrolyte in the polarographic analysis of aluminium, magnesium, and phosphor bronzes [256]. In tartaric-acid and citric-acid solutions, separate waves have been obtained for nickel and cobalt [257], and for iron and titanium [258], and titanium has been determined in aluminium alloys [259]. Solutions of sodium tartrate and citrate have been employed also as supporting electrolytes in the polarographic determination of indium [260], molybdenum [261,262], tin [263–265], and bismuth [266].

Use of Hydroxy-Acids in Chromatography

The main application of hydroxy-acids in chromatography is their use for the separation of rare-earth elements. This problem has recently acquired great commercial importance in connection with the ever-increasing consumption of these elements in metallurgy [267,268] and other branches of industry.

The chromatographic separation of the rare-earth elements is based to a considerable extent [269] on the differing stabilities of their citrato-complexes. When a solution of citric acid is passed through a chromatographic column elements of higher atomic weight pass most readily into solution, since they are able to form more stable citrato-complexes than are elements of lower atomic weight. Thus in the elution of praseodymium and neodymium, ions of the latter are the first to react with the citric acid, and a pure or considerably enriched solution of neodymium citrate flows out of the column, whereas all or a large part of the praseodymium remains adsorbed on the cation-exchange resin.

A quantitative theory of the extraction of rare-earth cations from a chromatographic column with citrate solutions

has been worked out by Spedding[270]. Several papers on the separation of rare-earth elements have been published[271-273] in the foreign press. It has been shown, for example, that thulium can be separated from erbium and ytterbium[274] by elution with citric acid solution. A similar method is used to separate samarium and niobium[275], zirconium and hafnium[276], etc.

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Research on the complex compounds formed by metals with hydroxy-acids cannot be regarded as complete. Many problems require more thorough study. Thus more complete data are necessary on the stability of the complexes, on the relation between their properties and the position of the central atoms in the Periodic System, and also their dependence on the structure of the hydroxy-acids, etc. In some other directions hardly any work at all has yet been done. Several results indicate, for example, that colloidal solutions are formed in some intermediate pH ranges, especially when the concentration of the central ion is considerable and the excess of hydroxy-acid is insufficient. In this case the salts of the hydroxy-acids act as peptising agents towards the insoluble hydroxides of the metals. These phenomena have been little studied, and the interconversion of colloidal particles and complex molecules is of great interest for an understanding of the chemistry of complex formation. It has also been found[277] that, under certain conditions, complex compounds are obtained in solution containing two different central atoms; as yet, the formation of such ternary tartrato-compounds is known only with copper and aluminium. It is probable that other hydroxy-acids and other central atoms are also able to form compounds of this type, and it would be interesting to study them in greater detail. Finally, it has recently been discovered that tartrato- and citrato-complexes of some metals can be extracted by organic solvents in the presence of substituted organic amines[278]. This field has not been studied at all, and merits close attention.

More thorough investigations on the above lines will undoubtedly lead to the discovery of interesting new facts, which will be of both theoretical and practical value.

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ADVANCES IN THE CHEMISTRY OF AROMATIC DIAZONIUM COMPOUNDS

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INTRODUCTION

The diazotisation reaction, the centenary of whose discovery by Griess was celebrated in 1958,[1-3] is extraordinarily versatile. The complexity of the process, the ease with which diazonium compounds undergo change, and the peculiarities of their conversion into other substances have given rise to numerous controversies concerning the structure, the reaction mechanisms, and the reactions of diazonium compounds. Unfortunately, the theories which have been put forward are far from perfect, and right up to the present time diazotisation and the reactions of diazonium compounds have provided a continuous stimulus to creative chemical research.

Diazonium compounds are very sensitive to the slightest changes in conditions, and this sensitivity is linked with the variety of forms in which they can exist. The scheme of tautomeric changes of diazonium accepted up to the present time, which was worked out by Hantzsch and based on the hypothesis of stereoisomeric changes, has recently been subjected to a fundamental revision. A detailed analysis of the new ideas has been given by Porai-Koshits[4].

The present review discusses the main lines of advance in the chemistry of diazonium compounds during the five years including the first half of 1961. Progress in the practice of diazotisation, the state of ideas on the kinetics and mechanism of diazotisation, and also the changes undergone by diazonium compounds, other than azo-coupling, are covered in the review.

1. CONDITIONS OF DIAZOTISATION AND PROPERTIES OF DIAZONIUM COMPOUNDS

The introduction of new electrometric methods for controlling chemical reactions has enabled continuous methods of diazotisation[5,6] to be applied in practice. German chemists, who have patented a continuous process for the diazotisation of amines[7], suggest the precise regulation of the addition of reagents at a few points in the path of a turbulent flow of the reaction liquor, from which the reaction products are continuously removed. The supply of the diazotising agent is regulated in conformity with the change in redox potential measured with a platinum–calomel electrode system, while the acidity of the medium is controlled by a pH-sensitive system. Diazotisation proceeds smoothly and quantitatively with all the usual amines, for which it is necessary merely to choose the optimum redox potentials.

In the diazotisation of *p*-amino-*p'*-methoxydiphenylamine, for example, the amounts of nitrite added were such that the potential between the electrodes was ~520–580 mV. Later this method was extended to the diazotisation of feebly basic amines [8].

Conditions have been worked out [9] for the conversion of weakly basic amines (for example, 4-amino-2,5-dimethoxy--4'-nitroazobenzene) into a finely dispersed paste of particle size up to 3 μ by dispersion with a condensation product of formaldehyde and a naphthalenesulphonic acid. Subsequent diazotisation in acetic acid (pH 2.9–3.5) with nitrite takes place quantitatively. Good results are obtained by using a mixture of diacetone alcohol (4-hydroxy-4-methylpentan-2-one) with a non-ionogenic dispersing agent [10]. The use of dilute tetrahydrofuran has been suggested [11] for the diazotisation of amines which are insoluble in mineral acids and in glacial acetic acid (for example, 4-amino-3-bromo--4'-nitrobiphenyl). These procedures enable several difficultly diazotisable amines to be diazotised in good yields [12,13].

Various additives have been recommended for accelerating diazotisation; for example, it has been proposed [14] to diazotise amines in sulphuric acid in the presence of soluble metal chlorides. Addition of up to 40%, with respect to the weight of the amine, of sodium xylenesulphonate or naphthalene-1-sulphonate is claimed [15] to increase the yield of diazonium compounds [19], and the diazotisation of 4-amino--3-hydroxynaphthalene-1-sulphonic acid is best carried out in the presence of salts of heavy metals with the addition of non-ionogenic surface-active agents such as esters of fatty acids and polyoxyethylenes, in amounts of 10–20% based on the original amine [16].

Considerable difficulty is encountered in the diazotisation of aminoanthraquinones. Lukin [17] suggests that 1-aminoanthraquinone should be diazotised as the free base in dilute sulphuric or hydrochloric acid, when the yield of products reaches 85–95%. Kozlov and Belov have established the possibility of diazotising aminoanthraquinones in good yields with a nitrite in acetic acid without the use of mineral acids [18].

Examination of the variation in redox potential of the system at the end of diazotisation has enabled it to be used as an end-point indicator in the potentiometric titration of aromatic amines with a nitrite solution. A detailed study of this process and a check of earlier suggested procedures [19] revealed the optimum conditions for titrations [20]: 25 ml of a 0.25 M solution of the aromatic amine is titrated with 2.5 *N* nitrite solution in the presence of 8 g of hydrochloric acid at 19° using a smooth platinum electrode and a saturated calomel electrode. Under these conditions the potential at the end-point is 0.585 V, the error involved in the titration not exceeding 0.2%.

Butt and Stagg [21] established the possibility of applying the usual potentiometric method to the automatic titration of primary aromatic amines with a nitrite solution with satisfactory accuracy.

The behaviour of an already formed diazonium compound towards an electric current is extremely complicated. Attempts to establish a relation between the half-wave potential and the nature of a nuclear substituent in a diazonium compound were unsuccessful, but Budevska [22] established that, in the reduction of 4-diazo-3-hydroxynaphthalene-1-sulphonic acid and its 7-nitro-derivative at pH 4.7 and 9.0 at a dropping mercury electrode, the height of the main wave is proportional to the concentration of the diazonium compound, and she recommended this method for the analytical determination of these acids. Matrka and Sàgner [23], who studied the potentiometric titration of *o*- and *p*-phenylenediamines and of naphthalene-1,4-diamine, consider that 1 mole of nitrite is used up. It is impossible to titrate the *meta*-isomer under such conditions. They recommend that 1,4-diaminoanthraquinone should be titrated in a mixture of 10% sulphuric and 5 *N* hydrochloric acids with sodium *m*-xylenesulphonate.

Recently the production and application of diazotised polymers have been achieved. Natural macromolecular substances have been used, containing primary amino--groups and capable of conversion with nitrous acid into diazonium compounds. It is considered [24] that, when wool is treated with nitrous acid, the tyrosine is diazotised. The presence of the diazonium group is indicated [25] by a comparison of the ultraviolet absorption spectra of such a diazotised fibre with those of diazonium compounds.

The preparation of synthetic polymers and macromolecules capable of diazotisation with nitrous acid is of great interest. The diazotisation of an emulsion of a *p*-aminostyrene–acrylonitrile copolymer has been accomplished [26] in the heterogeneous system; coloured films can be obtained by coupling with well-known azo-components. Use of an ion-exchange resin of high molecular weight and containing sulpho-groups provides an interesting method of stabilising diazonium cations; such diazonium resins are recommended for the quantitative separation of phenols [27]. Mixing with cation-exchange resins is advised [28] for diminishing the water solubility of a diazonium compound. The use of long-chain amines makes it possible to prepare diazonium compounds having several new properties. Diazotised *p*-n-octylaniline couples with naphthionic acid to form a surface-active azo-dye [29]. The 4-mono- and 2,5-di-decyloxybenzenediazonium chlorides, which are moderately soluble in hot benzene and couple with 2-naphthol in the presence of pyridine, have been described [30].

The relative stability and poor water solubility of diazonium phosphates enables them to be isolated from solution in a stable form [31,32]. Several carboxylic acids confer great stability on diazonium salts: excess of oxalic acid enables crystalline diazonium salts, of general formula $Ar-N=N-Ar'-N_2Cl.H_2C_2O_4$ and stable up to 45°, [33] to be isolated from aminoazo derivatives. In the neutralisation of the diazonium solutions for cold dyeing, the use is recommended [34] of the sodium salts of ethylenediaminetetraacetic and nitrilotriacetic acids, which are able, in addition to complex formation and stabilisation of the solution, to shift the pH from weakly acid to neutral and weakly alkaline. The solid diazonium salts formed with perhalogenated carboxylic acids are characterised [35] by good stability. The crystalline products which are isolated show good solubility in polar solvents, are stable in the solid state, and melt at definite temperatures. The diazonium salts obtained from *p*-toluidine and CF_3COOH, C_3F_7COOH, and CCl_3COOH, for example, have melting points of 70°–72°, 50°–53°, and 88° respectively. The comparative stability of double diazonium salts formed with metal chlorides depends to a considerable extent on the nature of the cation. It has been established [36] that the stability of double diazonium salts increases in the sequence of metals

$$Fe^{III} < Sb^{III} < Bi < Hg^{II} < Sn^{IV} \simeq Zn < Cd,$$

and coincides with the order in which their electronegativity decreases.

Le Fèvre[37] and then Wetsel *et al.*[38], who were the first to study the infra-red absorption spectra of double diazonium salts, established that the N≡N group is characterised by a band within the range 2100–2350 cm^{-1}, the displacement of the bands being practically independent of the anionic portion of the molecule. A similar situation was found by Kazitsyna *et al.*[39], who were unable to derive a direct relation between the shifts in the absorption bands in this region and the nature or position of the anion in the molecule of the diazonium salt. Subsequently these workers showed, in the case of the double diazonium salts with bismuth trichloride and antimony pentachloride, that the position of the peak due to the N≡N triple bond in the infra-red spectrum depends on the composition of the double salt and the valency of the metal[40]. Gremillion *et al.*[36] consider, in view of the constancy of the infra-red absorption spectra of a series of double diazonium salts with the chlorides of various metals, that the metal atom interacts with the whole π system of the diazonium salt; an increase in electronegativity of the metal and the presence of vacant *d* orbitals in it strengthen the tendency for electrons to be repelled from the π system towards the metal. In their opinion, the metal ions are situated above the benzene ring, and do not show any preference for either of the nitrogen atoms of the diazonium group. On the other hand Kazitsyna *et al.*[41], in a study of the infra-red and ultra-violet spectra of double diazonium salts with the chlorides of cobalt and of copper, detected in them an absorption corresponding to the band of copper and cobalt complexes containing nitrogen atoms in the complex. This fact led these workers to suggest that a chemical bond was present between the metal atom and the terminal nitrogen of the arenediazonium group.

2. DIRECT INTRODUCTION OF THE DIAZONIUM GROUP INTO AN AROMATIC NUCLEUS

Attention has recently been paid to the direct formation of the diazonium group in the aromatic nucleus. Nemodruk, who extended this process to salicylic acid, noted[42] that it reacts with nitrous acid to form *o*-diazophenol with the simultaneous evolution of CO_2 owing to elimination of the carboxyl group. By using several salts of salicylic acid, which were more reactive in this respect (the Al, Cr, Zn, and Be salicylates), he was able to obtain in acid medium containing five moles of nitrous acid up to 90–93% of 5-diazosalicylic acid[43] with clear evidence of the intermediate formation of 5-nitrososalicylic acid.

The direct introduction of the diazonium group has been the subject of detailed study by the English chemists Tedder and Theaker, who found it to be a general reaction applicable to almost all classes of aromatic compounds: hydrocarbons, phenols, tertiary amines, carboxylic acids, etc.[44] Direct introduction of the diazonium group into the pyrrole and pyrazole rings yielded the very stable diazopyrrole and diazopyrazole, which coupled slowly with 2-naphthol in organic solvents[45,46]. The reaction takes place in the presence of an excess of nitrous acid or of a nitrosyl derivative *via* a nitrosation stage.

Phenols and tertiary amines are smoothly nitrosated with sodium nitrite or ethyl nitrite in alcohol in the presence of HCl, giving with excess of the nitrosating agent 55–80% yields of the diazonium salts; stable intermediate quinone monoximes can be isolated[44].

The success of the reaction is greatly dependent on the first stage, that of nitrosation. Unreactive substances require more acid, active nitrosating agents than nitrous acid, the following being recommended by Tedder: NOCl, $NOHSO_4$, $NOClO_4$, $NOOCOCF_3$,[47] and the complex $N_2O_3BF_3$.[48]

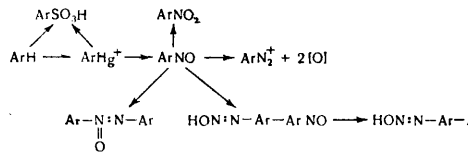
A system which is especially reactive with aromatic hydrocarbons consists of nitrosylsulphuric acid and an inert solvent (nitrobenzene); it is characterised by high acidity and is not readily oxidised by an excess of the nitrosating agent. The method of activation by mercuration has been suggested[44] for the diazotisation of unreactive derivatives of benzene and other hydrocarbons.

The mechanism of the process can be expressed as follows:

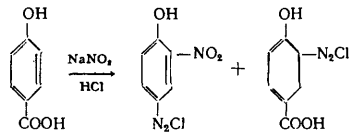
$$ArH + Hg^{2+} \longrightarrow ArHg^{+} + H^{+},$$
$$ArHg^{+} + NO^{+} \longrightarrow ArNO + Hg^{2+},$$
$$ArNO + NO^{+} \longrightarrow ArN_2^{+} + 2[O].$$

The mercury ion is regenerated, and acts as a catalyst for the process.

The introduction of a diazonium group into aromatic derivatives is not a simple process; side-reactions are possible, such as nitration, sulphonation, decarboxylation, alkylation, and also decomposition and coupling of the diazonium derivatives. This is reflected in the following mechanism[44] for the diazotisation of benzene with nitrosylsulphuric acid in the presence of mercuric oxide:



The action of nitrous acid on salicylic, hydroxybenzoic, and hydroxynaphthoic acids in buffer solutions[49] is accompanied by decarboxylation and nitration of the ring. Belikov[50] established that under these conditions direct diazotisation of *p*-hydroxybenzoic acid takes place as follows:

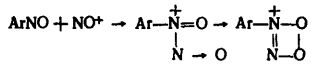


He explained the formation of the 4-hydroxy-3-nitrobenzenediazonium salt by nitration of the starting material *meta* to the carboxyl, replacement of the latter by a nitroso-group, and its subsequent conversion into a diazonium group.

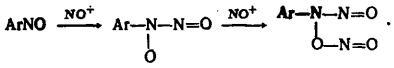
In the reaction of *m*-cresol with ethyl nitrite in alcoholic hydrogen chloride solution it has been found[51] that alkylation of the hydroxy-group occurs in addition to entry of the diazonium group.

Tedder and Theaker established[52] that: (a) the reaction must pass through a stage involving a nitroso-derivative, for, if it is carried out in the presence of Cu^{2+} ions or of sulphamic acid, the formation of diazonium salts is completely suppressed and the process stops at the nitrosation stage with conversion of the nitroso-compound into a copper complex; (b) direct introduction of the diazonium group into the nucleus requires at least three molecules of nitrous

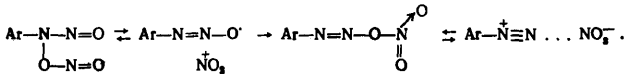
acid per molecule of the aromatic compound. In a strongly acid medium a brownish-red coloration is observed, due to complex ions of the nitroso-compounds with the nitrosyl cation:



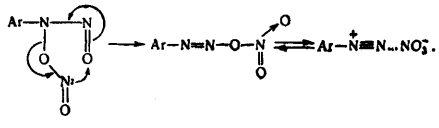
or



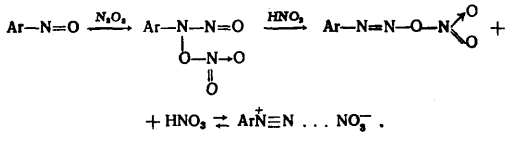
The resulting complexes are converted into diazonium salts on treatment with water, as a result of cleavage and further reactions:



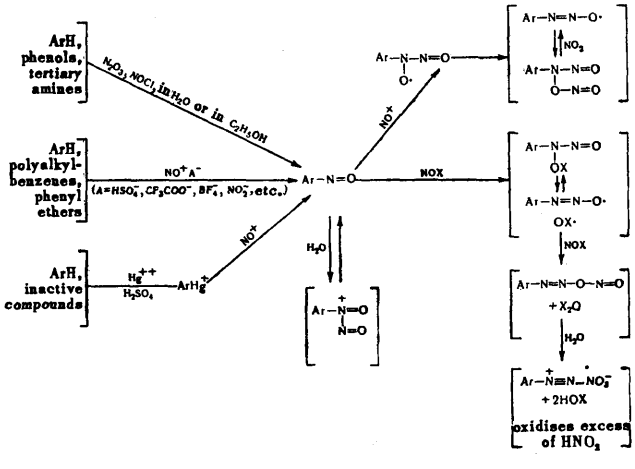
Intramolecular rearrangement is also quite possible:



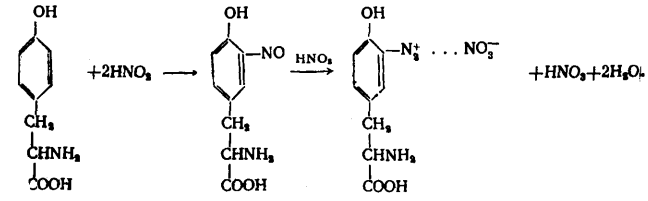
In dilute acids the reaction probably proceeds as follows:



All pathways for the direct entry of the diazonium group into an aromatic nucleus can be represented by the general scheme:



The above considerations on the direct entry of the diazonium group into derivatives of aromatic hydrocarbons have enabled a fresh interpretation to be given of the mechanisms of several reactions, in particular the diazotisation of the proteins of wool and silk. Thus Rodionov and Shleer[53] suggest that the diazotisation of the tyrosine in the keratin of fur involves the intermediate formation of a nitroso--compound:



The absorption spectra of azo-dyes from diazotised pure tyrosine and fur tyrosine are absolutely identical. The suggested interpretation of the process is supported also by the similarity of the ultra-violet absorption spectra of diazotised wool and of 4-diazo-3-hydroxynaphthalene-1-sulphonic acid[25]: *i.e.* the presence of the diazonium group *ortho* to a hydroxy-group is confirmed.

3. KINETICS AND MECHANISM OF DIAZOTISATION

The mechanism of diazotisation is extremely complicated, and has not yet been completely elucidated. The absence of a single interpretation of the mechanism is due primarily to the inaccuracy of and sometimes contradictions in the kinetic measurements, made by a number of investigators from 1899 onwards. In our opinion there are two main reasons for this situation: (a) the lack of sufficiently exact methods for following analytically the process of diazotisation and for the analysis of diazonium compounds; and (b) the neglect by investigators of the effects on the reaction velocity of individual components of the medium in which diazotisation is taking place.

The absence of accurate and convenient direct methods for the analysis of diazonium compounds, with the exception of the azotometric method, which is somewhat clumsy, led to the utilisation of the most diverse indirect methods, a brief account of which has been given in a review by Matrka[54].

The colorimetric analysis of diazonium compounds which yield coloured products on coupling with certain compounds has proved extremely fruitful and valuable. This method is quite widely employed both for exact kinetic determinations and also for technical purposes. Repeated checks of the method[55] have confirmed its accuracy and convenience. Furthermore, the colorimetric method has found wide application in the analysis of organic compounds of various classes and from different sources.

The use of spectrophotometric methods of investigation in the visible and ultra-violet regions of the spectrum[56] opens up still greater prospects for research workers. Dilute solutions of diazonium compounds obey the Beer–Lambert law[57], and can be successfully used for both qualitative and quantitative analyses of diazonium compounds, amines, and nitrite[58,59]. In view of the instability of diazonium compounds in solution to the action of light, the technique of spectrophotometric measurements is somewhat difficult, and may be a source of error. To avoid this, it is advisable for each measurement to be made on a fresh solution of the diazonium compound[60]. Good results are obtained by the use of self-recording instruments and a special oscillographic attachment, on the screen of which the spectrum is outlined after 1–2 min. Differences in nature and concentration of acids, amines, and diazotising

agent have been the cause of discrepancies in the results and in their interpretation. The first investigators of the kinetics of diazotisation worked with dilute (0.002 M) hydrochloric acid, and found the reaction to follow a second-order equation[61]:

$$v = K\,[\mathrm{ArNH_3^+}]\,[\mathrm{HNO_2}]\ . \qquad (1)$$

This finding completely explained the mechanism of diazotisation according to which reaction takes place between the arylammonium ion and undissociated nitrous acid with formation of an unstable adduct, which is stabilised as the diazonium ion. When higher acid concentrations (0.2 M) were used, it was found that in sulphuric and nitric acids the reaction is of third order, its rate being directly proportional to the concentration of free amine and to the square of the concentration of nitrous acid. This has been expressed in a number of mathematical relations[62].

Several workers regarded the third reaction order under these conditions as only apparent, but a careful check of the equations forced chemists to revise their views on the mechanism of diazotisation. It was accepted that the base, not a salt of the amine, undergoes diazotisation. In such a case diazotisation can be represented, in conformity with Bamberger's early work, as an initial nitrosation of the primary amine with subsequent conversion of the aryl-*N*--nitrosamine into a diazonium salt by the action of acid:

$$\mathrm{ArNH_2} \xrightarrow{\mathrm{HNO_2}} \mathrm{ArNH_3^+NO_2^-} \longrightarrow \mathrm{ArNHNO} \longrightarrow \mathrm{ArN:N{\cdot}OH} \rightleftarrows \mathrm{ArN_2^+}\ldots\mathrm{OH^-}.$$

Examination of the infra-red spectra of solutions of aromatic amines in several acids confirmed the presence in them of a definite quantity of free base[63]. Hence there is now no doubt that a free base can be diazotised.

According to Ingold[64] the first step consists of attack by the nitrosating agent, which may be the nitrosyl cation NO^+ or its carrier NOX, on the lone pair of electrons of the amine nitrogen with subsequent protolytic conversion into the aryl-*N*-nitrosamine:

$$\mathrm{ArNH_2} \xrightarrow{\text{slow}} \mathrm{ArNH_2^+NO} \xrightarrow{\text{rapid}} \mathrm{ArNHNO}.$$

The slowest step during these stages is the attack by the nitrosating agent on the unshared electron pair of the amine nitrogen atom, and it is obviously this which determines the rate of diazotisation, since all subsequent steps take place rapidly, and exert no influence on the overall rate of diazotisation.

Several views have been expressed concerning the "apparent" third-order kinetics of diazotisation, among which the most soundly based is that of Hammett[65], subsequently adopted by other workers, who assumed that in strongly acid media the diazotisation is effected by nitrogen trioxide:

$$2\mathrm{HNO_2} \rightleftarrows \mathrm{N_2O_3} + \mathrm{H_2O}.$$

Turney[66] made a spectroscopic and chemical study of this equilibrium in $HClO_4$ solutions of less than 46% concentration, and found the equilibrium constant at 20° to be $K_a = 0.20 \pm 0.05$.

In hydrochloric acid medium N_2O_3 and nitrosyl chloride act as diazotising agents:

$$\mathrm{HNO_2} + \mathrm{H_3O^+} + \mathrm{Cl^-} \rightleftarrows \mathrm{NOCl} + 2\mathrm{H_2O}.$$

Subsequent reaction of N_2O_3 and NOCl with the amine involves intermediate formation of the *N*-nitrosamine and results in the diazonium compound.

Investigations of the kinetics and the mechanism of diazotisation which have recently been made by the Ingold school have led to definite progress on this matter. As a result of the measurements[67], it was recognised that, depending on the conditions, more than one kinetic equation was applicable to diazotisation. According to Ingold, the active nitrosating agents fall in the following sequence of diminishing electrophilic reactivity: NO^+, $H_2NO_2^+$, NOX, $NONO_3$, $NONO_2$, NOOAc, and NOOH. Each of the kinetic equations is linked with the use of definite nitrosating agents, which can be formed under the given conditions.

A. Uncatalysed Diazotisation

Determination of the kinetics of the diazotisation of aniline in concentrated (0.05 M) and dilute (0.002 M) perchloric acid by Ingold *et al.*[68] shows the reactions to be of third and second orders respectively, represented by the following kinetic equations:

$$v = K_3^{\prime\prime\prime}\,[\mathrm{ArNH_2}]\,[\mathrm{HNO_2}]^2, \qquad (2)$$

$$v = K_2^{\prime\prime\prime}\,[\mathrm{HNO_2}]^3. \qquad (3)$$

In Ingold's opinion, N_2O_3 is the nitrosating agent in both cases. In concentrated solutions the formation of nitrogen trioxide does not restrict the reaction, and therefore the rate of the process is linked with the stage of attack by the N_2O_3 on the primary amine, and depends on the concentration of the latter. In very dilute acid the slowest reaction is the formation of the nitrogen trioxide, which determines the kinetics of the process. Each molecule of N_2O_3 formed reacts immediately with the amine:

$$\mathrm{HNO_2} \overset{\text{rapid}}{\rightleftarrows} \mathrm{H^+} + \mathrm{NO_2^-},$$

$$\mathrm{H^+} + \mathrm{HNO_2} \overset{\text{rapid}}{\rightleftarrows} \mathrm{H_2NO_2^+},$$

$$\mathrm{NO_2^-} + \mathrm{NO{\cdot}OH_2^+} \overset{\text{slow}}{\rightleftarrows} \mathrm{O_2N{\cdot}NO} + \mathrm{H_2O}.$$

It is improbable that N_2O_3 is formed as a result of interaction of NO^+ and NO_2^- ions, since the presence of NO^+ in a weakly acid solution is extremely problematic. The distinction between NO^+ and $NO.OH_2^+$ may seem difficult because one is the hydrate of the other, but it can be settled by experiments based on oxygen exchange[69].† In the absence of an amine in the solution nitrogen trioxide can be readily hydrolysed to nitrous acid. The velocity of this reaction has been studied[70] by means of water labelled with oxygen-18. The rate of transfer of oxygen is consistent with the rate of diazotisation and especially with Eqn. (3) This shows that oxygen transfer and diazotisation have identical intermediate complexes, formed from two molecules of nitrous acid, and that the process involves rupture of an N–O bond. The presence of N_2O_3 under these conditions has been shown also from the absorption spectra of solutions of $NaNO_2$ in perchloric acid[71].

B. Catalysed Diazotisation

Diazotisation catalysed by the carboxylate ion. A study of the rate of diazotisation of several amines in the presence of sodium acetate and phthalate in perchloric acid (pH 5.0) showed that these salts to some extent accelerate the reaction[72], although they do not affect its order. The general kinetic equation for this case is

$$v = K^{\mathrm{OAcyl^-}}\,[\mathrm{HNO_2}]^2\,[\mathrm{OAcyl^-}]. \qquad (4)$$

† The above sentence has been modified according to Ref. 69.

It is seen from this equation that the rate-determining stage of diazotisation is in this case [as also with Eqns. (2) and (3)] the formation of nitrogen trioxide. Most likely it is this stage which is catalysed by the carboxylate ion. Two mechanisms are possible for the formation of N_2O_3 with the participation of $OAcyl^-$:

$$NO_2^- + NO.OH_2^+ \xrightleftharpoons{\text{rapid}} NO_2.NO + H_2O, \qquad \text{(A)}$$
$$AcylO^- + NO.NO_2 \xrightleftharpoons{\text{slow}} AcylONO + NO_2^-,$$

and

$$AcylO^- + NO.OH_2^+ \xrightleftharpoons{\text{rapid}} AcylONO + H_2O, \qquad \text{(B)}$$
$$NO_2^- + NO.OAcyl \xrightleftharpoons{\text{slow}} NO.NO_2 + OAcyl^-.$$

Mechanism (A) is improbable[73], and its first stage contradicts that given in the previous subsection and the kinetic equation (4). Mechanism (B) can be regarded as more correct, and it is fully consistent with the kinetic equations (3) and (4). The catalytic effect of different carboxylate ions is shown to different extents: the phthalate ion is more active in accelerating the reaction than is the acetate ion [the respective values of K^{OAcyl^-} in Eqn. (4) are 160 and 38 litre^2 mole^{-2} sec^{-1}].

Diazotisation catalysed by the hydrogen ion. Rate constants determined by Ingold[74] for the diazotisation of feebly basic amines at low HNO_2 concentrations in acid solution proved to be greater than in the cases described earlier. As an example, the velocity of the reaction of 0.002–0.06 mole of *o*-chloroaniline with 0.0001 mole of nitrous acid in the presence of 0.005–0.02 mole of H^+ exceeded the second-order reaction velocity by a factor of 12. The kinetic measurements show that the reaction is of first order with respect to the amine, the nitrous acid, and the hydrogen ion:

$$v = K_3^{H^+}[ArNH_3][H^+][HNO_2]. \qquad (5)$$

Such a marked acceleration of the reaction is due, in the opinion of these workers, to the catalytic action of the proton, which adds on to the HNO_2 molecule and thereby activates the nitrosating agent:

$$H^+ + HNO_2 \xrightleftharpoons{\text{rapid}} H_2NO_2^+.$$

This step in the process occurs rapidly, and does not affect the overall reaction velocity; hence the rate-determining stage will be the attack on the amine by the active nitrosating agent.

These workers assume the possibility under certain conditions of further heterolytic charge transfer and elimination of the nitrosyl cation from the protonated form of nitrous acid:

$$ON-OH_2^+ \xrightleftharpoons{\text{slow}} NO^+ + H_2O.$$

The slowness of this process would undoubtedly influence the whole kinetics of the reaction and yield the following kinetic equation:

$$v = K_2^{H^+}[H^+][HNO_2]. \qquad (6)$$

However, neither the kinetic measurements nor the regularities in the reaction order permit unreserved acceptance of the presence of the nitrosyl cation in the solution. A quantitative examination of the behaviour of nitrous acid in 46% perchloric acid solution showed that the protonated form of nitrous acid is converted into the NO^+ cation only to the extent of 3%.[75,76]

Diazotisation catalysed by ions of strong acids. Recent kinetic measurements[77] on the diazotisation of aniline and *o*-chloroaniline in dilute perchloric acid in the presence of various anions have shown that the reaction velocity is unaffected by ClO_4^-, NO_3^-, or F^-. The appreciable catalytic action of the Cl^- and Br^- ions is characterised by a reaction of first order with respect to the concentration of the hydrogen ion, the amine, nitrous acid, and the halide ion:

$$v = K_4^{Hal}[ArNH_2][H^+][HNO_2][Hal^-]. \qquad (7)$$

A different kinetic equation is possible for the iodide ion:

$$v = K_3^{Hal}[H^+][HNO_2][Hal^-]. \qquad (8)$$

These findings were explained in terms of the already known facts of the formation of nitrosyl halides, which are extremely active diazotising and nitrosating agents. These substances can be formed by interaction of the nitrosyl cation or of protonated nitrous acid with the halide ion:

$$NO^+ + X^- \xrightarrow{\text{rapid}} NOX,$$
$$H_2NO_2^+ + X^- \xrightarrow{\text{rapid}} NOX + H_2O.$$

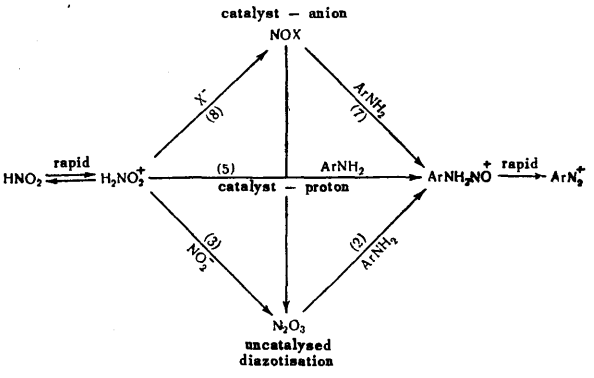
Schmid and Fouad[78] explain the high rate of diazotisation in the presence of hydrobromic acid by the greater polarisation of the NOBr molecule compared with that of the nitrosyl chloride molecule.

Schmid and Essler [79] regard diazotisation in the presence of the chloride ion as analogous to a process of acid–base catalysis, in which the nitrosyl cation NO^+ plays the part of the proton, while the anion is Cl^-.

The iodide ion acting as the catalyst shows greater difficulty in reacting with the protonated form of nitrous acid, so that this stage of the process proves to be rate-determining and is represented by the kinetic equation (8):

$$H^+ + HNO_2 \xrightleftharpoons{\text{rapid}} H_2NO_2^+,$$
$$X^- + H_2NO_2^+ \xrightleftharpoons{\text{slow}} NOX + H_2O.$$

Ingold suggested the following general mechanism for the diazotisation of amines in aqueous solutions of acids[73]:



It is evident that not all possible diazotising agents are utilised in this mechanism. Thus N_2O_4, NO.OAcyl, and HNO_2 are absent. The low efficiency of nitrous acid in diazotisation naturally excludes the undissociated form HNO_2 from such a mechanism. A necessary intermediate product in diazotisation and nitrosation is the protonated form of nitrous acid, which is able in subsequent stages to change into various other forms of diazotising agent.

C. Diazotisation in Very Concentrated Acids

The diazotisation of amines in concentrated acids is distinguished by its great rapidity and by the reactivity of the diazotising agent. The nitrosyl cation[80], formed by the reaction of HNO_2 with concentrated sulphuric acid,

$$O{=}N{-}OH + 2H_2SO_4 \rightleftarrows [O{\equiv}N]^+ + H_3O^+ + 2SO_4H^-,$$

is, owing to its strongly electrophilic character and its coordination unsaturation, a more active diazotising agent than are $H_2NO_2^+$, N_2O_3, and NOX. The presence of reactive nitrosyl cations in concentrated sulphuric acid is supported also by the ultra-violet absorption spectra of these solutions[81,82].

Study of the kinetic laws of the diazotisation of amines in perchloric acid[83,84], and also of the ultra-violet absorption spectra of solutions of a nitrite in concentrated $HClO_4$,[85] shows that the chief diazotising agent in these cases is NO^+ formed by the ionisation of nitrosyl perchlorate.

Nitrosyl salts can be formed even with weak acids, such as glacial acetic acid, and therefore nitrosyl acylates can be formed by interaction of the nucleophilic nitrite ion with the reactive carbonyl centre of acetic acid or acetic anhydride[86]:

$$HNO_2 + AcOH \rightleftarrows AcO{\cdot}NO + H_2O,$$

$$AcO{\cdot}NO \rightleftarrows AcO^- + [N{\equiv}O]^+.$$

Kozlov and Belov exploited the high nitrosating and diazotising activity of the nitrosyl acylates to show the possibility of smoothly diazotising amines in concentrated carboxylic acids[87,88]. The greatest diazotising effect is associated with high electrolytic dissociation constants of these acids. Weak acids (for example propionic acid) greatly complicate diazotisation by forming diazoamino--compounds.

Schmid found the rate of diazotisation of aniline and the isomeric chloroanilines to increase in the sequence

aniline < *p*-chloroaniline < *m*-chloroaniline < *o*-chloroaniline.

The diazotisation rate constant is higher, the lower the basic dissociation constant of the amine[89].

Introduction of electrophilic substituents into the amine molecule diminishes its basic strength and thereby hinders the attack of the diazotising agent on the lone pair of electrons on the amino nitrogen; introduction of a nucleophilic substituent has the opposite effect. The second stage, stabilisation of the intermediate product as a diazonium cation, is favoured by increasing mobility of the hydrogen atoms attached to the nitrogen, and this mobility is in turn linked with the electronegativity of the nucleus and depends on the nature of the substituent.

Since the slowest stage in diazotisation is the first (formation of the amine nitrite), the influence of substituents in the amine will obviously operate in only one way: if they increase the basic strength of the amine, they will increase its reactivity; if they diminish the basic strength, they will decrease the reaction velocity. These generalisations were later confirmed by determining the rates of diazotisation of substituted anilines by an electrometric method[90].

The rate of diazotisation of aniline in hydrochloric acid depends[91] on the ionic concentration of the solutions, being doubled by an increase from 4 M to 8 M Na_2SO_4 at constant concentrations of HNO_2, $ArNH_2$, Cl^-, and H^+. These observations and kinetic measurements have enabled the general formula for the rate of diazotisation of aniline in nitric and perchloric acids to be corrected for the molecular and ionic activities of the reactants[92]:

$$v = \frac{k_1 [\mathrm{ArNH_3^+}] [HNO_2]^3}{k_2 [H^+] + [\mathrm{ArNH_3^+}] + X [\mathrm{ArNH_3^+}] [HNO_2]\, m^3 \frac{a^2}{aH_2O}},$$

where m and a represent the polarity and the activity coefficient of the nitric or perchloric acid, and aH_2O is the activity coefficient of water.

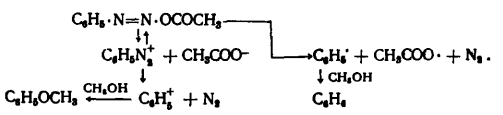
4. CONVERSION OF DIAZONIUM COMPOUNDS INTO OTHER COMPOUNDS

A. Action of Reducing Agents

Diazonium compounds react in two ways with reducing agents: the weaker reductants split off the diazonium group and convert diazonium compounds into hydrocarbons; stronger reducing agents reduce diazonium compounds to the corresponding arylhydrazines.

Alcohols form extremely convenient mild reducing agents. The way in which they react with diazonium compounds depends on several conditions, such as the nature of the substituents in the diazonium compound, the nature of the alcohol, the additives present, and the pH of the medium. Unsubstituted benzenediazonium salts and their homologues are converted mainly into phenyl ethers. The presence of negative substituents in the diazonium compound increase the yield of hydrocarbon.

The pH is especially important. In acidified methanol a diazonium salt breaks down to form mainly (up to 93%) phenyl ether[78], but in the presence of an acetate buffer the chief product (60%) is benzene. In the latter case the reaction is accompanied by the formation of several by-products, such as anisole, azobenzene, and biphenyl. The observed phenomena suggest that reaction takes place by an ionic mechanism in acid medium, and by a radical mechanism in the acetate buffer:



Decomposition by a radical mechanism can be represented in greater detail[93] as follows:

$$C_6H_5N_2^+ + CH_3O^- \rightleftarrows C_6H_5N{=}N{-}OCH_3,$$
$$C_6H_5N_2^+ + AcO^- \rightleftarrows C_6H_5{-}N{=}N{-}OAc,$$
$$C_6H_5N{=}N{-}OCH_3 \rightarrow C_6H_5\cdot + N_2 + CH_3O\cdot,$$
$$C_6H_5N{=}N{-}OAc \rightarrow C_6H_5\cdot + N_2 + AcO\cdot,$$
$$CH_3O\cdot + CH_3OH \rightarrow CH_3OH + CH_2OH\cdot,$$
$$C_6H_5\cdot + CH_3OH \rightarrow C_6H_6 + CH_2OH\cdot,$$
$$CH_2OH + C_6H_5N_2^+ \rightarrow CH_2OH^+ + N_2 + C_6H_5\cdot,$$
$$C_6H_5\cdot + C_6H_5\cdot \rightarrow C_6H_5{-}C_6H_5,$$
$$C_6H_5\cdot + \cdot CH_2OH \rightarrow C_6H_5CH_2OH,$$
$$C_6H_5N_2^+ + CH_3OH \rightarrow C_6H_5OCH_3 + N_2 + H^+.$$

The fact that addition of benzene to the reaction mixture does not increase the yield of biphenyl excluded the possibility of formation of the latter by the reaction

$$C_6H_5\cdot + C_6H_6 \rightarrow C_6H_5{-}C_6H_5 + H\cdot .$$

Further investigation of this reaction showed[94] it to be dependent on the presence of oxygen. In a vacuum two processes take place simultaneously, a radical reaction and a slower ionic process; the reaction velocity is little affected by the total concentration of the CH_3COO^- ion, but is considerably increased by the addition of copper sulphate. In solutions saturated with air[95] the initial reaction velocity is considerably diminished, and the overall rate is represented, not by a first-order equation, but by

$$\frac{d[ArN_2^+]}{dt} = k_1[ArN_2^+] + k_{1/2}[ArN_2^+]^{1/2}.$$

An explanation of this phenomenon in terms of the preferential formation of peroxide radicals by the reaction of $C_6H_5^\cdot$ and $CH_2OH^\cdot$ with O_2 was later formulated on the basis of three modes of decomposition of diazonium salts in methanol[96]: (1) an ionic process resulting in the formation of ethers; (2) a chain radical process resulting in reduction, which is suppressed by oxygen; and (3) a non-chain radical process, consisting in transfer of a hydride ion: $Ar^+ + CH_3OH \rightarrow ArH + CH_2OH^+$.

Mel'nikov found that the reaction of thiophosphates with arenediazonium salts in strongly acid medium does not result in the formation of mixed esters of thiophosphoric acid but leads to replacement of the diazonium group by hydrogen and the separation of a disulphide[97]:

$$2(RO)_2{-}P(=S){-}SH + ArN_2X \longrightarrow (RO)_2{-}P(=S){-}S{-}S{-}P(=S){-}(OR)_2 + ArH + HX + N_2.$$

The diazonium group is replaced smoothly by hydrogen also as a result of the action of sodium borohydride[98], dioxane, tetrahydrofuran, 1,3-dioxolane, and tertiary aliphatic amines in the presence of sodium acetate in aqueous medium[99].

Fokin showed that, when substances such as alcohols, dioxane, glucose, formic acid, and formaldehyde are used as reducing agents, reaction takes place by a chain mechanism, as is confirmed by the considerable acceleration of the process in the presence of $FeSO_4$ and $K_2Cr_2O_7$.[100] He distinguishes two stages, chain initiation and chain growth. The first depends to a decisive extent on the addition of an initiator (an oxidising agent or a reducing agent), and consists in the transfer of electrons to the arenediazonium ion with conversion of the latter into a free radical:

$$ArN_2^+ \xrightarrow{e} ArN_2^\cdot + Fe^{3+},$$

$$ArN_2^\cdot \longrightarrow Ar\cdot + N_2,$$

$$Ar\cdot + R{-}CH_2OH \longrightarrow ArH + R{-}CHOH.$$

The resulting free radicals ensure growth of the chains:

$$ArN_2^+ + RCHOH \longrightarrow Ar\cdot + R{-}\overset{+}{C}HOH + N_2$$

$$R{-}\overset{+}{C}HOH \longrightarrow R{-}C(=O){-}H + H^+ .$$

Diazonium compounds react quite differently with powerful reducing agents, the diazonium group being converted either into an arylhydrazine or into an aryl azide.

The reduction of diazonium salts to arylhydrazines with sulphites obeys a second-order kinetic equation, the reaction velocity being considerably increased by increasing the ionic strength of the system, for example by adding common salt[101]. On this basis, the following mechanism has been suggested for the ionic reaction mechanism:

$$C_6H_5N{=}N{-}SO_3^- + SO_3^{2-} \longrightarrow C_6H_5N(SO_3^-)N^-\cdot SO_3^-, \quad 1)$$

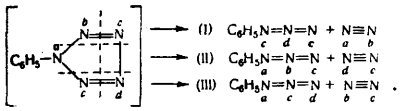
$$C_6H_5N(SO_3^-)N^-SO_3^- + H_2O \longrightarrow C_6H_5N(SO_3^-)NHSO_3^- + OH^-, \quad 2)$$

$$C_6H_5N(SO_3^-)NHSO_3^- + H_2O \longrightarrow C_6H_5NH\cdot NHSO_3^- + HSO_4^-, \quad 3)$$

$$C_6H_5NHNHSO_3^- + H_2O + 2HCl \longrightarrow C_6H_5NH\cdot NH_2\cdot HCl + H_2SO_4 + Cl^-. \quad 4)$$

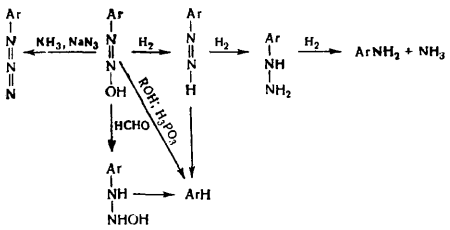
Lewis and Suhr established that the *syn*-diazosulphonate is formed here, but this can pass into the *anti*-form; both isomers are further reduced to the hydrazine derivative, but at different rates[102].

Diazonium compounds can be reduced to arylhydrazines also by an electrochemical method[103]. In the reaction of diazonium compounds with azides the intermediate product in the formation of aryl azides is an unstable pentazole, which can break down in three ways:



In fact, the aryl azide (I) is not formed at all, the isomers (II) and (III) being obtained in the ratio 85 : 15; nucleophilic substituents in the diazonium compound diminish, and electrophilic substituents raise, the yield of the isomer (III).[104] Aryl azides are highly sensitive to light, and are therefore recommended as the main components of light-sensitive layers for offset printing[105].

The overall mechanism of reductive changes undergone by diazonium compounds can be represented as follows:



B. Replacement of the Diazonium Group by Other Substituents

Replacement of the diazonium group by the hydroxyl, resulting in the formation of various phenols, which is important for preparative purposes, is best carried out by boiling solutions of diazonium salts in dilute sulphuric acid.

Phillips suggested that synthetic guaiacol could be obtained by diazotising *o*-anisidine at elevated temperatures

with simultaneous decomposition of the diazonium salt and distillation of the product in superheated steam [106].

The main products of the decomposition of dilute solutions of diazonium salts in 0.005–0.05 M H_2SO_4 were found to be phenols, the rate of the process obeying a first-order equation and being independent of the acid concentration, the nature of the anion forming the salt, and the presence of $CuSO_4$. [107] With diazotised isomeric naphthylamines, formation of naphthols was accompanied by azo-coupling, the quantity of azo-compounds formed increasing with diminution in the acid concentration and fall in temperature.

Consideration of all the changes possible in the reaction, and the fact that the rate obeys a first-order equation, suggested a heterolytic mechanism involving the diazonium cation [108].

A different situation is observed in the decomposition of concentrated (15–17%) solutions of diazonium sulphates. In this case a series of side-products — *p*-hydroxybiphenyl, phenyl ether, *p*-hydroxyazobenzene, and diphenyl sulphate — are formed together with the phenol. The process is often complicated by resin formation, which supports the view that the diazonium compound undergoes homolytic breakdown into free radicals, which react in various combinations to yield the side-products:

$$Ar{-}N{=}N{-}OH \longrightarrow Ar\cdot + N_2 + \cdot OH.$$

Thermal decomposition of naphthalene-1,2(and 2,1)-diazonium oxides yields a substance $C_{20}H_{12}O_2$, the structure of which corresponds to 2′-indenylidene-1,2-naphtho-1′,3′-dioxole [109].

The thermal decomposition of *p*-diazonium oxides (for example 3,5-dibromobenzene-1,4-diazonium oxide) at 70° and above results in the evolution of nitrogen and bromine and the formation of substituted poly(phenyl oxides) having molecular weights of 1600–3600. [110]

Measurement of the magnetic susceptibility of 10% dimethylaminobenzenediazonium chloride solution showed the formation of free radicals under the influence of ultra-violet radiation [111].

Boiling diazonium compounds in acetic acid, or better in acetic anhydride, results in the formation of acetic esters of the corresponding phenols.

Bogatskaya showed that a series of acetylated products (for example aspirin) could be obtained by diazotising amines in acetic acid with subsequent decomposition of the diazonium compounds [112]. Kozlov and Belov established the possibility of smoothly replacing the diazonium group in the acetate salts of isomeric diazotised aminoanthraquinones by the acetoxy-group [113].

Views on the mechanism of the replacement of the diazonium group by chlorine have been fundamentally revised. A comparatively recent investigation [114] of the Sandmeyer reaction indicates that it has a free-radical mechanism. The metal ion (copper) acts as a chain-terminator in the decomposition:

$$Ar\cdot + MCl_n^q \longrightarrow ArCl + MCl_{n-1}^q.$$

This process obviously involves interaction of the radicals with complex ions of metals accompanied either by the formation of a covalent bond or by electron transfer [115].

Kochi [114] denies the cyclic nature of the Sandmeyer decomposition of diazonium compounds, and considers the reaction to take place in two stages:

$$ArN_2^+ CuCl_2^- \longrightarrow Ar\cdot + CuCl_2 + N_2,$$

$$Ar\cdot + CuCl_2 \longrightarrow ArCl + Cu^{I}Cl.$$

The production of free radicals under these conditions is confirmed by the formation of *p*-iodonitrobenzene from *p*-$NO_2C_6H_4N_2Cl$ in the presence of iodine, and of *p*-nitrophenol (up to 46%) on treatment of *p*-$NO_2C_6H_4N_2HSO_4$ with cuprous chloride in the presence of oxygen and a limited quantity of Cl^- ions in aqueous acetone. In aqueous media the aryl radical can react in three ways: (a) dimerisation to a biaryl; (b) interaction with the diazonium ion and the cuprous salt to form azo-compounds; and (c) interaction with $CuCl_2$ to form the main product, the halogeno-derivative.

Clusius and Endtinger [116] prepared toluene-*p*-diazonium chloride labelled with ^{15}N $[Ar{-}N{\equiv}{}^{15}N]^+$, and converted it by the Sandmeyer reaction into the main product (ArX) and a secondary product (Ar–N=N–Ar). The resulting azo-compound contained the same quantity of the nitrogen isotope as did the original diazonium compound. This fact, in the opinion of these workers, again confirms a radical mechanism for the Sandmeyer reaction:

$$\left[Ar{-}N{\equiv}{}^{15}N\right]^+ + Cu^+ \longrightarrow Ar\cdot + N{\equiv}{}^{15}N + Cu^{2+},$$

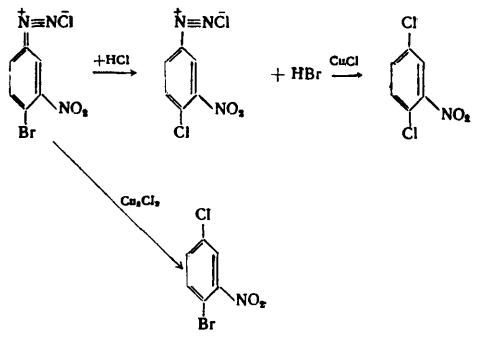
$$Ar\cdot + Cl^- + Cu^{2+} \longrightarrow ArCl + Cu^+,$$

$$Ar\cdot + \left[Ar{-}N{\equiv}{}^{15}N{\rightarrow}CuCl\right]^+ \longrightarrow Ar{-}N{=}{}^{15}N{-}Ar + (CuCl)^+.$$

The side reactions are considerably affected by the solvent: water diminishes the yield of the main product and directs the reaction towards the formation of the unsaturated hydrocarbon. An aqueous acetone solution lowers the yield of halogeno-derivative to a less extent, by forming the more stable acetonyl radical:

$$Ar\cdot + CH_3COCH_3 \longrightarrow ArH + CH_3\dot{C}OCH_3.$$

This radical readily dimerises or reacts with $CuCl_2$, forming chloroacetone and reducing Cu^{II} to Cu^{I}. [117] Apart from the main free-radical decomposition of diazonium salts in the Sandmeyer reaction, secondary reactions occasionally take place. Lamm [118] describes the interchange of halogen in the decomposition of diazonium compounds in the presence of an excess of hydrochloric acid and cuprous chloride:



Study of the decomposition of diazonium salts in acid solutions of bromides and iodides has shown the simultaneous occurrence in these solutions of two reactions, of first and second order.

Carey isolated toluene-*o*-diazonium triiodide dihydrate (yield 15–20%, decomposes at 54°) by the action of KI solution on *o*-$CH_3C_6H_4N_2^+$ in sulphuric acid solution at 5°; this compound breaks down at 40° into iodotoluene, N_2, and I_2.[119] The ease of formation of ArI was explained by a definite proportion of the diazonium ions oxidising I^- to I_2 with the formation of the strongly polarised complex anion I_3^-, which is able to displace nitrogen in ArN_2^+. These reactions can be represented by a unimolecular and bimolecular mechanism:

$$ArN_2^+ \longrightarrow Ar^+ + N_2,$$
$$Ar^+ + I_3^- \longrightarrow ArI + I_2,$$
$$ArN_2^+ + I_3^- \longrightarrow ArI + I_2 + N_2,$$
$$I_2 + I^- \longrightarrow I_3^-.$$

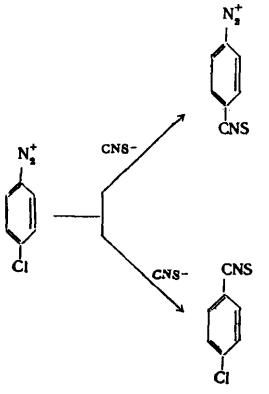
The diazonium group can be replaced by fluorine by decomposing diazonium fluoroborates in solution or in the solid state at elevated temperatures[120].

Brunton and Suschitzky[121] showed that the reaction is simpler, and the yield of fluorinated derivatives not diminished, when a mixture of diazonium fluoroborates (instead of the individual substances) is decomposed. Replacement of the diazonium group by fluorine is sometimes accompanied by secondary reactions. In the thermal decomposition of dry diazonium fluoroborates isolated from hydrochloric acid solutions chlorinated products are formed together with the fluorinated arenes[122].

Treatment of diazonium chlorides and acetates with alkali-metal selenides and polyselenides results in the smooth formation of diaryl selenides and of diaryl diselenides[123].

When $CH_3SC_6H_4X$ and $CH_3SeC_6H_4X$ (X = H, OCH_3, CH_3, Hal) react with 2,4-dinitrobenzenediazonium chloride, N_2 is evolved, the CH_3S and CH_3Se groups are demethylated, and sulphides or selenides of general formula $XC_6H_4-Y-C_6H_3(NO_2)_2$, where Y = S or Se, are formed[124]. The process probably involves the intermediate formation of an unstable diarylmethylsulphonium or diarylmethylselenonium ion.

Lewis and Suhr[125] studied the rate of reaction of a ^{14}C-labelled thiocyanate with *o*- and *p*-halogenated benzenediazonium ions, and found that in this case two reactions, replacement of halogen by thiocyanate and decomposition of the diazonium ion, take place in parallel:



The overall constants were calculated, their values depending on the dielectric constant of the medium and the reactivity of the halogen: F < Cl < Br < I.

Aromatic selenocyanates can be prepared by the action of potassium selenocyanate on diazonium salts[126]. The 4-, 5-, and 8-nitronaphth-1-yl and 1-nitronaphth-2-yl selenocyanates obtained in this way[127] were oxidised to the corresponding nitronaphthaleneseleninic acids, which are characterised by a certain sensitivity to light[128]. Nesmeyanov *et al.* obtained 35–40% yields of diaryl selenides by the decomposition of arenediazonium fluoroborates in the presence of zinc dust and $SeCl_4$.[129]

Diazonium compounds react in a peculiar fashion with sulphur dioxide, various products being obtainable depending on the conditions. Meerwein *et al.* prepared arenesulphonyl chlorides in good yields by the decomposition with cupric chloride dihydrate of concentrated solutions of diazonium chlorides in a saturated (30%) solution of sulphur dioxide in glacial acetic acid. During the reaction the copper salt is partly reduced to cuprous chloride by the sulphurous acid[130]. In the case of diazonium compounds containing electronegative groups, sulphonyl chlorides can be formed even in the absence of a catalyst, the reaction then taking place by an ionic mechanism:

$$Ar-\dot{N}\equiv\bar{N} \rightleftarrows Ar-\bar{N}=\dot{N} + :S(=O)_2 \longrightarrow Ar-S^+(=O)_2 + N_2,$$
$$Ar-S^+(=O)_2 + \bar{Cl} \longrightarrow ArSO_2Cl.$$

The catalytic action of copper is explained on the basis of Waters' well-known views on the function of cuprous ions as electron-donors and the breakdown of the diazonium compound with the formation of free radicals.

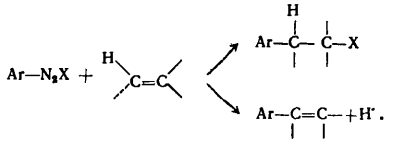
Substitution of a cyano-group for a diazonium group in an aromatic nucleus is effected in the presence of cuprous cyanide by a process analogous to the Sandmeyer reaction. The medium is usually sodium cyanide solution, and therefore the reactants undergo several initial changes: the diazonium compounds form the corresponding *syn*-diazocyanides with the CN^- ions, and with an excess of hydrocyanic acid these are able to form complexes of the type Ar–N=N–Cn·HCN.[131]

Treatment of diazonium salts with an excess of a nitrite in the presence of cuprous and cupric salts results in a smooth exchange of the diazonium for the nitro-group even in the cold. The acid diazotised solution can conveniently be added to a mixture containing an excess of nitrite, sodium carbonate, and an anti-foaming agent[132]. This method has been used to prepare *o*- and *p*-dinitrobenzenes (yield 90%), 1,4-dinitronaphthalene (92–96%), and 5,6,8-trinitrotetralin (49%). Little work has been done on the mechanism and kinetics of this substitution, although there are indications in the literature that this reaction follows a second-order equation and is of the nucleophilic substitution type[133].

C. Replacement of the Diazonium Group by Groups Containing Carbon

This type of substitution includes numerous reactions involving elimination of nitrogen and formation of a new

C–C bond. The most important reaction of this type is that discovered by Meerwein between diazonium compounds and $\alpha\beta$-unsaturated carbonyl compounds. Nitrogen is evolved in the reaction, and either replacement of hydrogen by the aryl radical or else addition of halogen and the aromatic radical at the multiple bond takes place, depending on the nature of the unsaturated compound:



This reaction takes place in a peculiar way with cinnamic and some other unsaturated acids: in this case elimination of nitrogen and hydrogen halide is accompanied by that of CO_2 owing to decarboxylation, and the corresponding stilbene derivatives are formed:

$$ArN_2X+Ar_1-CH=CH-COOH \rightarrow Ar-CH=CH-Ar_1+N_2+HX+CO_2.$$

The Meerwein reaction can be successfully accomplished in the presence of sodium acetate and cupric chloride as catalyst in aqueous acetone solution. The yields of the final products fluctuate within wide limits depending on the nature of the unsaturated compound, the nuclear substituent in the diazonium compound, and the anion of the diazonium salt. The presence of electronegative groups in the *para*-position in diazonium chlorides and bromides ensures that a good yield of a pure product will be obtained. The range of unsaturated substances which can undergo the Meerwein reaction has been considerably extended recently.

Dombrovskii and Bondarchuk[134] obtained a good yield of triphenylethylene by the reaction of 1,1-diphenylethylene with ArN_2Cl under the conditions of the Meerwein reaction. With butadiene and its homologues, it was found that in all cases the chloroarylation of the unsaturated system takes place in the 1,4-position[135].

$\alpha\beta$-Unsaturated aldehydes (acrolein and its aryl derivatives)[136] and ketones (methyl vinyl ketone)[137] condense with diazonium chlorides in the presence of HCl and $CuCl_2$ in aqueous acetone solution to form derivatives of 2-chloro-3-phenylpropionaldehyde and 3-chloro-4-phenylbutan-2-one respectively.

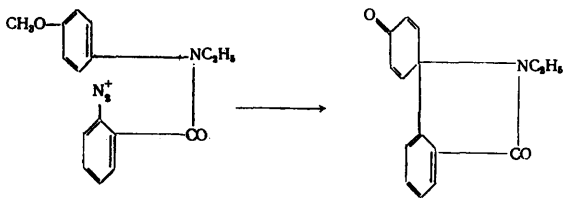
Unsaturated acids are, perhaps, most reactive in the Meerwein reaction, undergoing arylation with or without simultaneous decarboxylation, and also halogenoarylation, depending on the conditions. Arylation together with decarboxylation is most often observed: sorbic acid[138] reacts with diazonium chlorides to form 1-arylpenta-1,3-dienes. *p'*-Nitrostilbene-*p*-sulphonic acid has been obtained from *p*-$NO_2C_6H_4N_2Cl$ and *p*-sulphocinnamic acid in aqueous medium. An elevated temperature, a catalyst ($CuCl_2$), and the presence of chlorine *ortho* and *para* to the diazonium group increase the yield of the main reaction product[139].

Arylation by means of diazonium compounds has been extended to several other compounds. Diazonium salts act on *p*-benzoquinone[140] and on toluquinone[141] in the presence of sodium acetate in aqueous solution to yield monoarylquinones. Further reaction of the monoarylquinones with the diazonium compounds gives diarylquinones as mixtures of isomers[142].

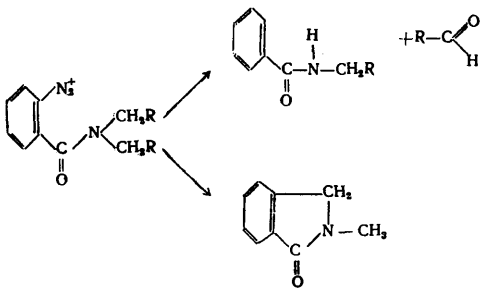
Anthracene, 9-phenylanthracene, and anthrone-9-carboxylic acid are arylated by diazonium chlorides to 9-mono- and 9,10-di-arylanthracenes respectively[143].

Puchkov was the first to succeed in substituting a phenyl radical for the diazonium group in anthraquinone-1-diazonium acetate[144] and in its derivatives substituted with chlorine and the benzamido-group in the other benzene ring[145]. Good yields (55–70%) are obtained in an emulsified mixture of benzene and sodium carbonate solution. Reaction can occur in this way only in alkaline medium (pH 8–9): according to Kozlov and Belov's experiments[113], decomposition of solid anthraquinone-1-diazonium acetate in benzene results in the formation of anthraquinon-1-yl acetate. The arylation of pyridine *N*-oxides by means of diazonium compounds has been described[146].

Several diazonium salts have been found not to undergo Pschorr internal cyclisation on thermal decomposition; for example, the diazonium sulphate from *o*-amino-*N*-ethyl-*p'*-methoxybenzanilide does not yield 10-ethyl-3-methoxyphenanthridone[147], but forms instead a spiro-dienone[148]:



In the decomposition of diazonium sulphates, cyclisation is probably a subsidiary process, while formation of the corresponding *N*-substituted benzamides is the main reaction, for example:



side-product[149]

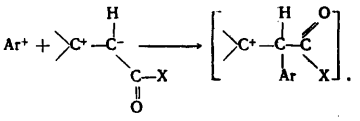
Heterocyclic compounds, for example pyridine[150] and isoquinoline[151] derivatives, can be obtained by intramolecular cyclisation *via* diazonium salts.

The arylation of both $\alpha\beta$-unsaturated and other compounds is usually accompanied by the formation of several secondary products, such as aryl halides, aromatic hydrocarbons, biaryls and polyarenes, and resins. Conditions can be selected under which the subsidiary reaction proves to be the main reaction. The possibility of obtaining symmetrical biaryls and polyarenes from diazonium salts is extremely important, and is utilised for the synthesis of polyphenyl hydrocarbons[152]. Symmetrical polyarenes are formed from diazonium compounds, with the creation of a C–C bond at the site of the diazonium group, when diazonium salts are decomposed in a solvent (alcohol, acetic acid) in the presence of copper powder.

The mechanism of the Meerwein reaction and of the arylation of aromatic compounds with diazonium compounds has formed the subject of serious discussion, which has

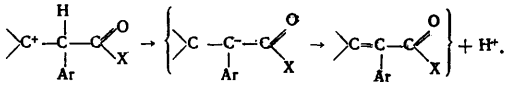
revolved mainly around two points: (a) the type of cleavage of the C–N bond (homolytic or heterolytic), and (b) the role of bivalent copper and the specificity of the solvent (acetone). Meerwein suggested an ionic reaction mechanism, in which the arenediazonium salt, in the ionic form, breaks down into nitrogen and an aryl cation.

The aryl cation adds on to the polar double bond, which carries a partial negative charge due to the conjugated multiple bond with the carbonyl group:

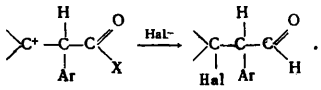


This cation can be stabilised in various ways [153].

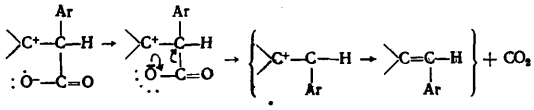
(1) With elimination of a proton and subsequent reformation of the double bond:



(2) By the addition of Hal^-:



(3) By intramolecular saturation (in the case of $\alpha\beta$-unsaturated acids) involving formation of unstable β-lactones from the carboxylate ion. These substances break down with the elimination of CO_2 and formation of an unsaturated hydrocarbon:



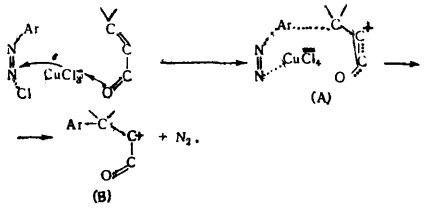
Meerwein supports an ionic mechanism by observations indicating that the reactions are favoured by the presence in the diazonium compounds of nuclear substituents having a large electronegative effect and by a readily polarisable anion. The favourable influence of the polarising action of carbonyl compounds, of polar solvents (water, pyridine, acetone), and of the addition of salts (CH_3COONa) also supports an ionic mechanism.

On the other hand, several features of the reaction — addition of the aryl radical to the β-carbon atom of $\alpha\beta$-unsaturated acids, the catalytic action of the Cu^{2+} ion, the formation of side-products — are not explained by such mechanism.

Kochi [154], who studied the role of copper in the Meerwein reaction, established that the actual catalyst here is the Cu^+ ion formed by the reduction of Cu^{2+} by the acetone:

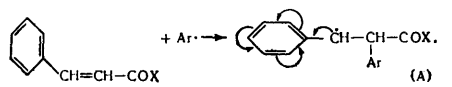
$$2CuCl_2+CH_3COCH_3 \longrightarrow 2CuCl+CH_3COCH_2Cl+HCl.$$

In his opinion [155] this fact shows that the Sandmeyer and Meerwein reactions have similar mechanisms. In the presence of an olefine the aromatic radicals formed by the decomposition of ArN_2X under the influence of CuCl add on to the double bond, and this is followed by addition of a chlorine atom to the newly formed radical, or by oxidation of the latter to a carbonium ion, which is supported by the formation of a mixture of 1-chloro-p'-nitro-1,2-diphenylethane and p-nitrostilbene by the reaction of p-$NO_2C_6H_4^{\cdot}$ with styrene. From the fact that decomposition of p-$NO_2C_6H_4N_2.HSO_4$ in aqueous acetone solution containing styrene and CuCl (*i.e.* with a limited content of Cl^-) yields 21% of p-nitrostilbene, whereas with an excess of Cl^- only 9% is formed, Kochi concludes that the direct transfer of halogen involves a more highly chlorinated complex ion of the metal than does the reaction with electron transfer [156]. A roughly similar view is held by other investigators [157], who postulate also that peroxide radicals may be formed (when the reaction is carried out in the air). Still other views are held concerning the role of bivalent copper. It is assumed that $CuCl_2$ helps to effect the transfer of electrons from activating groups in the unsaturated compounds, which are comparatively rich in electrons, to the diazonium nitrogen with the formation of a radical-cation (A). The diazonium radical, which after elimination of nitrogen is converted into an aryl radical, combines with (A), after which the resulting cation (B) loses a proton or adds on Cl^-: [158]

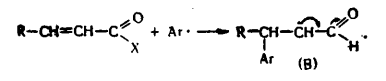


This mechanism of the arylation of unsaturated compounds does not explain the peculiarities of the process in aqueous or in pyridine medium, where it is difficult to postulate the reduction of Cu^{2+} and Cu^+. Perhaps the most plausible hypothesis in this connection is that of Dombrovskii and Terent'ev, according to which a copper complex is formed in this case, the presence of which is supported by their polarographic and spectrophotometric studies of the interaction of arenediazonium salts with $CuCl_2$. [159,160]

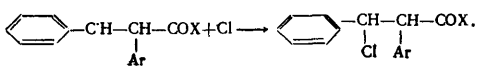
Dombrovskii gives an expanded treatment of the process [161], which reduces in essence to the following: (1) the diazonium salt is converted from an ionic form into a covalent molecular form, the change being favoured by the reaction conditions (pH, organic solvent, etc.); (2) $CuCl_2$ strongly catalyses the breakdown of the molecular form of the diazonium compound into free radicals, perhaps through the formation of copper complexes; (3) the reactive aryl radical immediately interacts with the multiple bond of the unsaturated molecule, the point where addition occurs being determined by the nature of the substance. In the case of aliphatic–aromatic unsaturated compounds the aryl radical adds on to the α-carbon atom, forming a stable radical (A) with a minimum energy content:



Aliphatic $\alpha\beta$-unsaturated carbonyl compounds direct the aryl radical to the β-carbon atom, with formation of the radical (B):



The radicals (A) and (B) then add on a halogen atom, for example:



On the basis of a radical mechanism, it is not difficult to imagine the formation of side-products by the combination of free radicals entering the reaction system:

$$Cl\cdot + CH_3COCH_3 \longrightarrow CH_3COCH_2Cl + H\cdot,$$
$$Ar\cdot + Cl\cdot \longrightarrow ArCl,$$
$$Ar\cdot + CH_3COCH_3 \rightarrow ArH + CH_3COCH_2\cdot \rightarrow \text{resin formation.}$$

It has recently been found that arenediazonium fluoroborates behave peculiarly during arylation. When they undergo decomposition in esters of $\alpha\beta$-unsaturated acids, for example, the aryl adds on to the α-carbon atom [162,163]. This fact allows a heterolytic mechanism to be postulated for the decomposition of the arenediazonium fluoroborates.

A radical mechanism has also been attributed to the arylation of aromatic hydrocarbons by means of diazonium salts in non-polar solvents. Important evidence for the formation of free radicals is the fact that the aryl enters predominantly *para* or *ortho* to an existing substituent independently of the nature of the latter, whereas it enters the α- or β-position of naphthalene depending on the electrophilic character of the substituents [164]. Moreover, the inert solvent plays an extremely important part, for it can act as a source of free radicals: Ushenko [165], for example, obtained 2-methylthio-6-phenylbenzothiazole from 6-amino-2-methylthiobenzothiazole by decomposition of the diazonium compound in benzene. In general, benzene is a good medium for the formation of free radicals; for example, stable diazonium salts which are soluble in benzene (*p*-n-decyloxybenzenediazonium chloride) exhibit a very great tendency to break down with the formation of free radicals [166]. If carbon tetrachloride or chloroform is used as solvent, chlorobenzene and other chlorinated products are formed, which also supports a radical mechanism for the reaction [167,168]. Decomposition of a diazonium acetate in benzene yields biphenyl, nitrogen, and acetic acid with the evolution of carbon dioxide, a typical cleavage product of the acetoxy radical:

$$C_6H_5N{=}NOCOCH_3 \longrightarrow C_6H_5\cdot + N_2 + \cdot OCOCH_3 \longrightarrow CO_2 + CH_3\cdot.$$

There is no doubt that the reaction has a radical mechanism, but in some cases it does not entirely correspond in detail to the mechanisms described above. Addition of metals definitely catalyses the process, the role of the metal being, just as in the Sandmeyer reaction, the transfer of electrons:

$$ArN_2X + Hg \longrightarrow Ar\cdot + N_2 + Hg^+ + X^-.$$

Furthermore, metals accumulate on their surfaces the less energy-rich acetate anion instead of the acetoxy-radical, which also favours this type of reaction.

The Nesmeyanov school has shown that, in contrast to other diazonium salts, benzenediazonium fluoroborates and fluorosilicates break down heterolytically with formation of the phenyl cation $C_6H_5^+$. When $C_6H_5N_2.BF_4$ breaks down in acetophenone [169], in benzoic esters [170], and in nitrobenzene [171], the phenyl is oriented exclusively *meta* to an existing substituent. Similar results have been observed in the decomposition of benzenediazonium fluorosilicate [172].

Heterolytic breakdown of $C_6H_5N_2.BF_4$ in chlorobenzene and in bromobenzene yields diphenylchloronium fluoroborate $(C_6H_5)_2Cl^+.BF_4^-$ [173] and diphenylbromonium fluoroborate $(C_6H_5)_2Br^+.BF_4^-$ [174] respectively, from which salts of the onium compounds with various anions are obtained by double decomposition.

The arylation of ferrocene by diazonium compounds probably goes by a free-radical mechanism, as is supported by the isolation of *pp'*-azoanisole in the preparation of *p*-methoxyphenylferrocene [175]. Introduction of acetyl and *p*-nitrophenyl groups into the ferrocene nucleus sharply diminishes the ability of the hydrogen atoms in the latter to undergo aromatic substitution. For example, reaction between diacetylferrocene and diazonium compounds results, not in the expected arylation [176], but in destruction of the ferrocene nucleus with formation of an arylazoacetylcyclopentadiene [177,178]. In Weinmayr's opinion [179], ferrocene reacts with diazonium compounds in strongly acid medium as the oxidised form, the ferricinium cation, forming mono- and poly-arylferrocenes, probably as a mixture of isomers.

The above examples of the peculiar course of the reaction under discussion show how necessary it is to proceed with caution in formulating its mechanism and how far the structure of the compound and the reaction conditions influence the mechanism of the process.

D. Formation of Organometalloid Compounds by the Decomposition of Diazonium Salts

Methods involving the use of diazonium compounds occupy an important position among the numerous procedures for obtaining organometalloid compounds.

Mel'nikov *et al.* obtained by the diazonium method moderate yields of several mixed esters of dithiophosphoric [180], thiophosphoric [181], and mono- and di-thiophosphonic acids [182] possessing a definite insecticidal action. The reaction takes place in the presence of copper, and according to these workers is homolytic in character, since it proved possible during the process of separation to isolate an intermediate dialkyl arenediazonium dithiophosphate [183]:

$$ArN_2Cl + (RO)_2PSSH \longrightarrow HCl + ArN_2SPS(OR)_2 \longrightarrow N_2 + ArSPS(OR)_2.$$

The amount of copper salt present plays an important part in this decomposition. Depending on the proportions of reactants and copper salts, three interlinked reactions [184] can take place at once between nitrobenzenediazonium fluoroborates and phosphorus trichloride: (1) formation of a phosphonic group, (2) reduction of the nitro-group, and (3) chlorination.

The role of copper in this process is in essence to transfer an electron to the diazonium ion:

$$Cu^+ - e \rightarrow Cu^{+2},$$
$$Ar{-}N_2^+ + e \longrightarrow Ar\cdot + N_2,$$
$$Ar\cdot + S^-{-}P(=S)(R)(R_1) \longrightarrow Ar{-}S{-}P(=S)(R)(R_1) + e,$$
$$Cu^{+2} + e \longrightarrow Cu^+.$$

The diazonium method has considerable advantages for the preparation of arsinic and arsonic acids by the reaction of solid diazonium salts with $AsCl_3$, a difficultly separable

mixture of arylarsonic and diarylarsinic acids being formed. Reutov and Bundel'[185] established that Nesmeyanov decomposition of double diazonium salts goes successfully in acetone in the cold, in the presence of iron powder and $AsCl_3$ or phenyldichloroarsine, and yields a mixture of mono-, di-, and tri-substituted products. They showed that, by varying the proportions of the reactants, the reaction can be controlled so that a particular substance is formed predominantly.

The mechanism of such a decomposition can be represented as follows:

$$(ArN_2Cl)_2 \cdot ZnCl_2 + 2AsCl_3 \rightleftarrows 2ArN_2Cl \cdot AsCl_3 + ZnCl_2, \quad (a)$$

$$ArN_2Cl \cdot AsCl_3 + Fe \longrightarrow ArAsCl_2 + N_2 + FeCl_2. \quad (b)$$

Excess of $ZnCl_2$ sharply lowers the reaction velocity. This indicates the considerable ease of decomposition of the double salt $ArN_2Cl.AsCl_3$ compared with double salts containing iron and zinc chlorides.

Nesmeyanov's reaction has proved extremely valuable for the synthesis of organic compounds of tin, the importance of which has greatly increased during recent years[186]. Great advances have been made in the synthesis of organoantimony compounds, which can be obtained by the arylation with diazonium compounds of derivatives of the types $ArSbX_2$ and Ar_2SbX, yielding products of the types $ArAr'SbX_3$ and $Ar_2Ar'SbX_2$.[187] The Nesmeyanov reaction has been employed in the synthesis of organometallic compounds of lead, bismuth, and thallium, although in low yields. The best results are obtained by using arenediazonium fluoroborates.

Interaction of arenediazonium fluoroborates with zinc dust in acetone in the presence of $GeCl_4$ between -8° and +5° for 2 days, followed by treatment of the mass with 20% NaOH, yields aromatic compounds of germanium of the type $(p\text{-}RC_6H_4GeO)_2O$.[188] Decomposition of $ArN_2.BF_4$ with metallic Mg in tetrahydrofuran, dioxane, ether, etc. results in organomagnesium compounds, which form ArCOOH on carboxylation[189]. The double diazonium salts formed with $ZnCl_2$ and $FeCl_3$ proved extremely convenient for the synthesis of mixed organoarsenic compounds of the types $ArAr'AsX$ and $ArAr'_2As$.[190]

The efforts of chemists of the Nesmeyanov school have led to the development of a series of methods for the preparation of organometallic compounds of elements of Group V of the Periodic System[191].

Decomposition of the double diazonium salts formed with metal chlorides is usually accompanied by the formation of side-products, hydrocarbons and chlorination products of the solvents. This phenomenon has served as a basis for regarding the mechanism of the Nesmeyanov reaction as a homolytic process involving the formation of free radicals. It is supposed that reduction of the double diazonium salt during the reaction yields the free metal, which reacts with the arenediazonium halide by a radical mechanism, for example:

$$ArN_2Cl \cdot HgCl_2 + 2Cu \rightarrow ArN_2Cl + Hg + CuCl_2,$$

$$Ar\text{—}N_2\text{—}Cl + \cdot Hg \cdot \rightarrow ArHgCl + N_2.$$

However, several discrepancies occur here. Firstly, homolytic breakdown is a side-reaction, since double diazonium salts are able, under the conditions of the Nesmeyanov reaction, to dissociate with formation of the free arenediazonium chloride[192]:

$$ArN_2Cl \cdot MCl_n \rightleftarrows ArN_2Cl + MCl_n$$

Decomposition of an arenediazonium chloride with a metal powder yields free radicals which react with the solvent.

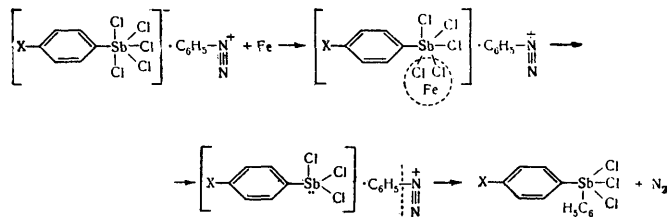
Reutov *et al.*[193] investigated the dependence of the reaction velocity of

$$p\text{-}XC_6H_4SbCl_4 \cdot C_6H_5N_2Cl + Fe \rightarrow XC_6H_4(C_6H_5)SbCl_2 + N_2 + FeCl_2$$

on the nature of X, and found that substituents increase the rate of reaction in the order in which their electron-donor properties increase, *i.e.* in the sequence

$$O_2N < Cl < H < CH_3 < C_2H_5O.$$

The observed relation gives grounds for supposing that the decomposition of the double salts with iron powder is heterolytic[194]:



It is quite clear that the addition of $C_6H_5^+$ at the free electron pair of the antimony atom should be facilitated by substituents which direct *ortho–para* and hindered by those which direct *meta*.

A heterolytic mechanism for the Nesmeyanov reaction is supported also by the facts of the varying stability of salts of the type $ArSbCl_2.Ar'N_2Cl$ depending on the nature of Ar and Ar'.[195] Substituents which direct *ortho–para* lower the stability of the double salts when they are present in the radical of the organoantimony component, and improve it when present in that of the diazonium component. Substituents which direct *meta* have the opposite effect.

The heterolytic mechanism of the Nesmeyanov reaction is confirmed also by the possibility of obtaining good yields of organomercury compounds in aqueous medium. It is interesting that antimony derivatives are not formed under these conditions, owing to the ease of hydrolysis of their double salts with diazonium compounds. All this convincingly demonstrates the heterolytic nature of the Nesmeyanov reaction, in contrast to the homolytic mechanism of the Waters reaction, involving the intermediate formation of double diazonium salts with metal chlorides[196].

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PHENOL–DIENONE REARRANGEMENT IN THE REACTIONS OF PHENOLS

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and G. N. Bogdanov

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1. INTRODUCTION

Study of the chemistry of phenols is of great practical value, apart from its relevance to theoretical aspects of organic chemistry. The use of phenols and their derivatives in the production of various plastics, dyes, effective bactericides, insecticides, herbicides, etc. is well known. Phenols are successfully employed as oxidation inhibitors in motor fuels, oils, and edible fats. Finally, as Emanuel' *et al.* have shown[1-3], phenolic inhibitors can be utilised in experimental oncology and in other types of biological research. However, the literature contains too few general accounts of the chemical properties of phenols. It is only recently that a number of review papers have been published, dealing with individual properties of phenols[4-9].

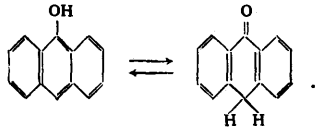
The present paper discusses reactions of phenols involving disruption of the aromatic bond system of the phenol and leading to the formation of cyclohexadienones. The formation of such substances is very often postulated also as an intermediate stage in many reactions of phenols. Cyclohexadienone compounds are in some cases stable, and can be isolated in the free form, whereas in other cases their existence can be assessed only by spectroscopic methods. The conversion of a phenolic structure into a cyclohexadienone structure has been termed a phenol–dienone rearrangement. It must be remembered that such a change does not correspond to the usual concept of a rearrangement in organic chemistry, since it occurs during the reaction of the phenol with some reagent and results in the formation of a compound containing a new substituent in the carbon ring. This rearrangement is essentially a rearrangement of the aromatic bond system of the phenol. The reverse process, the conversion of *gem*-substituted cyclohexadienones into phenols, which is a typical rearrangement and is usually accompanied by a migration of substituents within the ring, is called a dienone–phenol rearrangement. In view of its fundamental difference and intrinsic significance, the latter rearrangement will not be considered here.

Phenols usually undergo the phenol-dienone rearrangement when acted on by reagents of electrophilic or radical type. In this respect the halogenation of phenols has been most fully studied, and to a less extent their nitration, some alkylation reactions, and several radical reactions of phenols. Below we shall examine only those aspects of these well-known reactions that have a direct bearing on the phenol–dienone rearrangement of monohydric monocyclic phenols and that lead to the formation of compounds having a "quinolide" structure. We apply the term "quinolide", in contrast to "quinonoid", to the structure of cyclohexadienones in which a carbon atom *ortho* or *para* to the carbonyl is linked by single bonds (not by a double bond) to two atoms or groups of atoms.

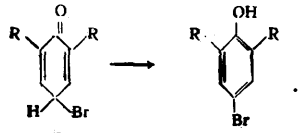
2. EFFECT OF STRUCTURE OF PHENOL ON EASE OF FORMATION OF DIENONE COMPOUNDS

The formation of cyclohexadienone structures might be most simply explained by a tautomeric change in the phenols. However, tautomerism has not been detected in monohydric monocyclic phenols containing no other functional group[10]. In several simple phenols cyclohexadienone structures are formed only at the instant of reaction with electrophilic and radical reagents. If, on the other hand, the existence of tautomerism is postulated in the phenol–dienone system,

and it is remembered that keto–enol tautomerism usually involves migration of a proton, the transition to a dienone system of bonds could be regarded, in the case of phenols, as the simplest example of electrophilic substitution. In this case the question of tautomerism would be reduced to that of the stability of the resulting dienones. If it is assumed that an intermediate compound having a quinolide structure is nevertheless formed as a result of interaction of the phenol with a proton, this compound would be so unstable that its existence could not be detected†. In the naphthol series, and especially with anthrol, however, such compounds are quite stable, and can even be isolated in the free state. In the case of anthrol, a tautomeric form having the carbonyl structure exists, and is called anthrone:



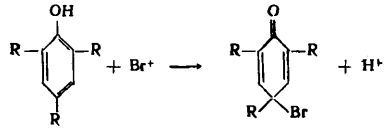
Among monohydric monocyclic phenols, stable quinolide compounds are obtained only when at least one *gem*-substituent in such a compound is not a hydrogen atom. Thus in the bromination of some 2,6-dialkylphenols[12,13], for example, quite stable quinobromide compounds (I) have been isolated, which gradually undergo spontaneous rearrangement to the *p*-bromophenols (II):



(I) (II)

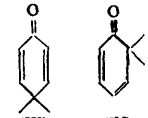
The migration of the hydrogen atom involved in this change is not reversible.

It is generally accepted at the present time[14,15] that, in the action of electrophilic reagents on a phenol, an intermediate compound with a *p*- or an *o*-quinolide structure is formed initially as a transition state. This intermediate subsequently rearranges to the energetically more favourable aromatic system of a phenol. The tenability of this concept is supported by the fact that intermediate compounds of quinolide structure are formed in some cases by the action of electrophilic agents on phenols, depending on the structure of the original phenol and on the reaction conditions. These compounds may be fairly stable, and in several cases have either been detected in dilute solution by spectroscopic methods[13,16] or have been isolated in the free state[12,13]. If the reaction is stopped at the initial stage, stabilisation of the aromatic system does not occur, and a cyclohexadienone is formed solely as a result of the phenol–dienone rearrangement of the initial phenol:



† Some writers postulate that, in the case of the simplest phenols, *p*- and *o*-quinolide structures exist as mesomeric forms[11].

Cyclohexadienones can exist in two isomeric forms (III) and (IV), corresponding to a *p*-quinolide (III) and an *o*-quinolide (IV) structure:



(III) (IV)

The existence of one form or the other will, of course, depend on the nature of the compound. If cyclohexadienones are formed by the action of electrophilic reagents on alkylphenols, for example, the cyclohexa-2,5-dienone system is obtained preferentially, for electrophilic substitutions of phenols have a lower activation energy in the *para*- than in the *ortho*-position, and the *para*-isomers, to which also corresponds the transition state having a *p*-quinolide structure, usually predominate among the reaction products. The fact that electrophilic reagents attack mainly the *para*-position in the phenol molecule has been discussed quite fully in the literature (see, for example, Ref. 17), and is beyond the scope of the present paper. Unfortunately, however, hardly any work has appeared on a quantitative assessment of the factors governing the course of reactions accompanied solely by a phenol–dienone rearrangement.

An analysis of published data which are available at the present time leads to the following general conclusions concerning the phenol–dienone rearrangement.

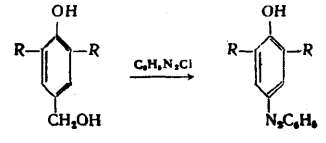
1. Cyclohexadienones are formed most readily by the action of electrophilic reagents on 2,4,6-trisubstituted phenols. They are formed considerably more rarely in the absence of substituents in the *ortho*- or *para*-positions.

2. Reactions accompanied by phenol–dienone rearrangement take place by the action mainly of strong electrophilic reagents on the appropriate phenols (during halogenation, nitration, etc.).

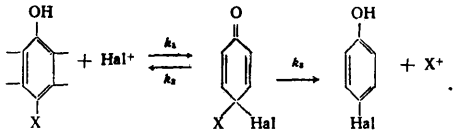
3. The ease of the phenol–dienone rearrangement increases with increasing steric hindrance of the phenolic hydroxyl, *i.e.* with increasing bulk of the substituents in the 2,6-positions of the phenol.

The rules governing phenol–dienone rearrangement are somewhat different for reactions involving radical substitution of phenols (which will be discussed below).

It does not follow from the above generalisations that a phenol in which the *para*- and even both *ortho*-positions are occupied by some kind of substituents must necessarily form a stable dienone compound when acted on by a sufficiently strong electrophilic reagent. Very often the resulting dienone, for which a transition to an aromatic structure with elimination of a proton is impossible, undergoes a similar conversion involving either migration of a substituent in the ring (dienone–phenol rearrangement) or elimination of one of the previous substituents. In the latter case it is customary to speak of the substituting action of the electrophilic reagent, and the most diverse substituents and groups can thus be eliminated, depending on the conditions. Cases are known of halogenation, nitration, and azo-coupling involving replacement of a CH_2OH group[18], for example:

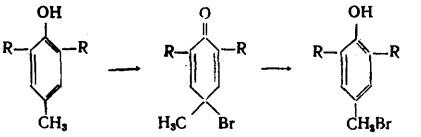


3,5-Dibromobenzoquinoneimine chloride (Gibbs reagent) reacts with phenols containing the substituents OR, CH_2NRR', Cl, COOH in the *para*-position, with the formation of deeply coloured indophenols, which are also obtained from the corresponding phenols containing no substituents in the *para*-position[19]. If the phenol contains a *p*-OR group, the latter is eliminated with formation of the corresponding alcohol, while a CH_2NRR' group results in the formation of formaldehyde and an amine. Among the above reactions of phenols involving substitution, halogenation has been studied in the greatest detail. On the whole this process depends on the stability of the quinolide structure obtained, and comprises two stages, each of which takes place independently. According to Cannell's data[16], the rate of substitutive bromination of several phenols depends ultimately on the rate of decomposition of the quinolide structure (the latter reaction is of first order). Halogenation accompanied by substitution can in general be represented as follows:



Accumulation of the intermediate quinolide compound may occur in this process depending on the relative reaction velocities. Thus, for example, tribromophenol is obtained by the bromination of sodium 3,5-dibromo-4-hydroxybenzenesulphonate in aqueous solution at 25°. Chlorination of this compound takes place similarly. There is no reaction with iodine. Ultra-violet and visible spectra show that the reaction involves the intermediate formation of a 2,6-dibromocyclohexadienone structure, which is sufficiently stable for its spectrum to be obtained in dilute solutions[16]. However, the bromination of sodium 4-hydroxy-3,5-dinitrobenzenesulphonate is considerably more rapid. In this case the presence of a cyclohexadienone structure could not be detected even at 0°, and with excess of bromine one of the nitro-groups was also replaced, with the formation of 2,4-dibromo-6-nitrophenol[20]. From this example, it is clear that the stability of the quinolide structure, which ultimately determines the main mode of the reaction, is substantially influenced by the nuclear substituents. Substitution of nitro-groups for halogen atoms in the 2,6-positions of phenol appreciably increases the rate of the corresponding reaction. On the other hand, an increase in the activation energy of decomposition of the quinolide structure, which determines its stability, would also depend on the nature of the bond between the displaced group and the aromatic ring: *i.e.* in order to make the quinolide structure more stable, the substituent X should be chosen such that the activation energy required to rupture its bond with the carbon atom would be increased. This hypothesis is supported by the fact that the stability of the quinolide structure increases in the sequence $X = H \ll COO^- < SO_3^- < Br < CH_3$.[20] For example, substitutive bromination of 3,5-dibromo-4-hydroxybenzoic acid ($X = COO^-$) in aqueous solution at 0° is complete in 7 sec, but the half-reaction time at 25° of a substance having a cyclohexadienone structure when $X = SO_3^-$ is 126 min. The rate of bromination of phenol, in which X = H, is 200 times as rapid as the rate of substitutive bromination of hydroxybenzoic acid ($X = COO^-$), the initial stage of the reaction showing little or no tendency to reversibility in the first case, whereas in the second case ($X = COO^-$) the reaction is reversible[21].

An alkyl group is firmly bound to the aromatic ring, and is seldom eliminated during halogenation or nitration. The bromination of *p*-cresol, for example, yields the corresponding quinobromide[22]. Compounds of this type are quite stable. They can rearrange[23] to form the aromatic phenol system in a new way, with conversion into the corresponding benzyl bromides (see below):



In some cases the reverse reaction — debromination of the quinobromide — may take place, with a return to the aromatic structure of the original phenol[24,25].

The strength of the bond between the alkyl group and the aromatic ring is appreciably diminished in t-alkylphenols. Phenols containing a *p*-t-butyl group, for example, can be halogenated with substitution, the reaction being accompanied by the evolution of isobutene[26]. This reaction occurs especially readily during bromination; chlorination in these cases, however, often stops at the formation of a substance having a dienone structure.

If the phenol contains a *para*-substituent in which the α-carbon atom is linked to oxygen or nitrogen[19], it is also displaced by the action of some electrophilic agents. For example, the action of chlorine water on phenols containing the groups CH_2OH, CHO, and COOH in the *para*-position yields in all cases 2,4,6-trichlorophenol[27]. Bromination[28] and nitration[29] of these phenols take place in a similar manner.

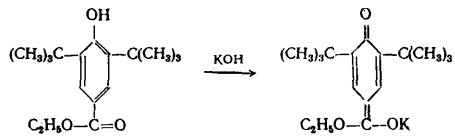
With substitutive nitration of the *p*-substituted phenols as an example, it has been shown[30] that the strength of the bond between the substituent and the ring increases in the sequence $CH_2OH < COOH < CHO \ll CH_3$.

Examples are known in which substitutive bromination, especially with excess of the brominating agent, does not stop at the substitution stage, but continues further to form the correspoinding *gem*-dibromocyclohexadienone[22].

Electrophilic reagents can result in displacement also of *ortho*-substituents in the phenol[30,31]. This usually requires more severe conditions[32,33].

An increase in the bulk of the *ortho*-substituents exerts a substantial influence on the ease of formation of cyclohexadienones from phenols. It is noteworthy that most reactions of phenols involving the phenol–dienone rearrangement have been studied with sterically hindered phenols as examples, which on the whole possess properties rather different from those of ordinary phenols. This is because steric hindrance of the phenolic hydroxyl disturbs the coplanarity between the aromatic ring and the hydroxyl, and also prevents hydrogen-bond formation between the phenol molecules. Spectroscopic methods have shown the complete absence of hydrogen bonds in 2,6-di-t-butylphenol[34]. The molecules of *o*-t-butylphenol have been found to be dimeric, whereas with *o*-s-butylphenol molecules polymeric association is possible[35]. With sterically hindered phenols, the tendency to form dienones is so great that it even results in the ready dissolution in alkalis of 3,5-di-t-butyl-4-hydroxybenzaldehyde, 3,5-di-t-butyl-4-hydroxybenzonitrile, and ethyl 3,5-di-t-butyl-4-hydroxybenzoate[36,37], which involves rearrangement of the phenolic

to a quinolide structure, the appropriate functional group taking part in salt formation.

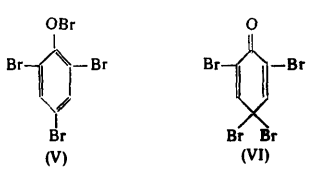


Owing to steric hindrance of the phenolic hydroxyl, 2,6-di-t-butylphenols do not form phenoxides under normal conditions, and do not dissolve in alkalis[38].

3. HALOGENATION OF PHENOL. TRIBROMOPHENOL BROMIDE

Nowadays, synthetic methods enable us to obtain the most diverse halogenated phenols. However, direct halogenation of a phenol in many cases yields immediately trisubstituted phenols, in which a further hydrogen atom can be replaced by halogen under the influence of an excess of the halogenating agent. Such reactions have been most fully studied in the case of the bromination of phenol, which results in a compound containing four bromine atoms. In the literature this compound has been called "tribromophenol bromide". It was first obtained by Benedikt[39] by the action of bromine water on phenol.

The question of the structure of tribromophenol bromide and analogous compounds has been the subject of research and controversy since it was prepared, and has not yet been finally settled. Different writers assign to tribromophenol bromide either the structure of a phenyl ester of hypobromous acid (V) or a *p*-quinolide structure corresponding to 2,4,4,6-tetrabromocyclohexadienone (VI):



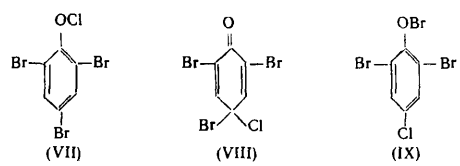
Benedikt regarded tribromophenol bromide, in view of its properties, as a hypobromous ester. It is unstable, readily losing a bromine atom on being heated or on treatment with reducing agents, and reacts with aniline to form tribromophenol and tribromoaniline[40]. Heating tribromophenol bromide with sulphuric acid yields tetrabromophenol‡, which is similar to the compound obtained by Körner[41], together with pentabromophenol, by heating tribromophenol with bromine in a sealed tube at 160°. Pentabromophenol can also be obtained by the action of bromine on tribromophenol in the presence of metallic iron[42]. Further halogenation of polyhalogenated phenols results in the formation of substances resembling tribromophenol bromide in properties and structure. The action of bromine water on tetrabromophenol or pentabromophenol yielded tetrabromophenol bromide and pentabromophenol bromide respectively, which have the general properties of tribromophenol bromide[43]. Chlorination of 2,4,6-trichlorophenol in acetic acid yielded trichlorophenol chloride and pentachlorophenol chloride, both of which contained active chlorine[44,45].

‡ If a quinolide structure is accepted for tribromophenol bromide, these reactions are readily explained as a dienone–phenol rearrangement, which occurs best in acid medium.

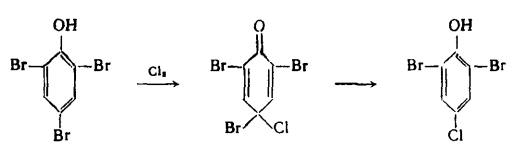
In 1887 Hantzsch[46], and later Zincke[44,47], suggested that tribromophenol bromide has a quinolide structure (VI). In 1900 Thiele[48] showed that, on being heated with lead diacetate in acetic acid, it yields 2,6-dibromobenzoquinone, which in his view provided convincing proof of the quinolide structure of tribromophenol bromide. In 1902 Kastle[49] made an attempt, based on a phenolic structure for the compound, to obtain tribromophenyl benzenesulphonate by the action of sodium benzenesulphonate or tribromophenol bromide. He obtained no such ester, and on this basis attributed a quinolide structure to tribromophenol bromide. Another attempt at a synthetic proof of the structure of the compound, undertaken by Kastle and Loevenhart[50], consisted in treatment with diethylzinc. If the structure were phenolic, an ethyl ether of the phenol would be expected to result, but in fact, a vigorous reaction yielded zinc tribromophenoxide and ethyl bromide.

However, Lauer[51] in 1926, and then Suknevich[52], from a comparison of the products of the chlorination of tribromophenol and of the bromination of 2,6-dibromo-4-chlorophenol, cast doubt on the quinolide structure for tribromophenol bromide, and again suggested a phenolic structure for this and analogous compounds, regarding them as hypobromous (or hypochlorous) esters. Shilov[53] drew attention to the unconvincing character of the rejection of the quinolide structure by Lauer and by Suknevich.

In 1948 Elston *et al.*[54] made an attempt to explain the structure of some polyhalogenophenols on the basis of their chemical properties and their spectra. These workers considered that the spectroscopic data enabled the possibility of a quinolide structure for these compounds only to be supposed, not demonstrated. It was at first assumed that the chlorination of 2,4,6-tribromophenol can yield a compound having structure (VII), tautomeric with (VIII), which is in turn tautomeric with (IX):



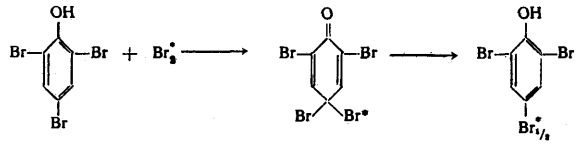
However, they concluded, by analogy with the chlorination of 2,6-dibromo-3,5-dimethylphenol, that a compound probably having the *p*-quinolide structure (VIII) is, nevertheless, formed in the chlorination of tribromophenol. This compound loses a bromine atom on being boiled in alcohol. Hence the overall process can be regarded as chlorination with the replacement of bromine by chlorine:



The reverse reaction, substitution of bromine for chlorine, does not take place. Chlorination with replacement of iodine by chlorine also occurs readily in the case of 2,4,6-triiodophenol[55].

In 1951 a fresh attempt was made to elucidate the structure of tribromophenol bromide and the conditions under which it is formed, using now a tracer method[56]. The compound was obtained by the action of labelled bromine

on tribromophenol. This method of preparation took account of the role of proton-acceptors. Thus in carbon tetrachloride or glacial acetic acid solution, for example, bromine does not react at all with tribromophenol, and does not exchange bromine atoms with it. However, addition of small amounts of pyridine in the first case, or of water in the second, causes the immediate appearance of a precipitate of tribromophenol bromide. Since debromination of labelled tribromophenol bromide roughly halved the original activity, the compound was assigned a quinolide structure (the bromine atoms in position 4 would be equivalent).



If the tribromophenol bromide has a hypobromite structure (V), the product of its decomposition should be inactive. In aqueous suspension tribromophenol bromide exchanges bromine atoms neither with bromine water nor with sodium bromide. A fairly slow exchange occurs when hydrogen bromide acts on the compound, as a result of the reaction

$$C_6H_2Br_3Br^*O+HBr \rightleftarrows C_6H_2Br_3OH+BrBr^*.$$

Tribromophenol bromide and tribromophenol prepared separately exchange bromine with difficulty by themselves in aqueous suspensions, but exchange take place if pyridine, for example, is added to the mixture. The hypothesis that exchange involves the formation of an *o*-quinobromide is not, in the opinion of these workers, inconsistent with the probable *p*-quinolide structure of ordinary tribromophenol bromide, since the equilibrium between the isomers will result in the accumulation in the final product of the most stable *p*-quinolide form.

After publication of the work using labelled bromine, the results of which provided convincing evidence of the quinolide structure of tribromophenol bromide, the existence of this compound as a phenyl hypobromite seemed improbable. In 1958, however, Schulek[57], on the basis of an investigation of a series of its reactions, again ascribed an aromatic structure to it, but now on the assumption that the bromine linked to oxygen bears a partial positive charge.

In 1959 Shilov concluded on the basis of a tracer method that tribromophenol bromide and analogous compounds nevertheless have a quinolide structure[58]. However, Schulek[59] showed, by isotopic exchange of tribromophenol and tribromophenol bromide with $^{82}Br^-$ ions and molecular $^{82}Br_2$, that all the bromine atoms in the latter compound are equivalent, which may be due either to an equilibrium among different structures or to the exchange of all four bromine atoms in the tribromophenol bromide with $^{82}Br^-$ or $^{82}Br_2$. Thus the application of labelled bromine provides no final answer to the structure of tribromophenol bromide; however, most of the published data support a quinolide structure for it.

This is confirmed also by a spectroscopic examination of tribromophenol bromide[60], whose absorption maximum in the infra-red region (5.99 μ) is due to the presence of a conjugated carbonyl group; it has a band in the ultra-violet at 280 mμ, which indicates a *p*-quinolide system of bonds.

The chlorination of phenols follows, in relation to the phenol–dienone rearrangement, somewhat different rules from those for their bromination. This must be borne in mind in attacking the problem of the structure of tribromophenol bromide by the chlorination method. Polyhalogenated, and especially polychlorinated, phenols probably tend initially to form cyclohexa-2,4-dienones, corresponding to an *o*-quinolide structure, on being treated with a chlorinating agent. This has been studied quite thoroughly with t-butyl hypochlorite as example, this chlorinating agent yielding with phenol itself mono- and di-chlorophenols[61]. When, however, this reagent acts on certain 2,6-dihalogenated phenols, substances are obtained which were at first regarded as aryl hypochlorites[62]. Shortly after, however, an *o*-quinolide structure was adopted on the basis of infra-red, ultra-violet, and Raman spectroscopic data and values of the magnetic susceptibility for these substances[63–65]. Such aryl pseudo-hypochlorites prepared by the chlorination of brominated phenols are less stable than those obtained from chlorophenols, and decompose with the evolution of bromine. The process of decomposition obviously involves preliminary isomerisation to a compound having a *p*-quinolide structure, since spectroscopic examination has shown that this is accompanied by disappearance of the band at 350–380 mμ, characteristic of cyclohexa-2,4-dienones, and the appearance of a band at 250–280 mμ, characteristic of cyclohexa-2,5-dienones[64].

Polychlorocyclohexa-2,4-dienones are usually more reactive than, and readily pass into, polychlorocyclohexa--2,5-dienones. For example pentachlorophenyl pseudo--hypochlorite, which has an *o*-quinolide structure, is converted irreversibly into the isomeric compound with the *p*-quinolide structure (slowly on prolonged storage, more rapidly on being heated with 1.5% of $FeCl_3$ or $AlCl_3$ or on intense ultra-violet irradiation[65]). It has also been shown[66] that an *o*-quinolide polychlorophenol chloride reacts considerably more readily with alcohol than does the corresponding compound having a *p*-quinolide structure.

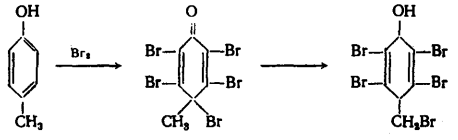
2,3,4,5,6,6-Hexachlorocyclohexa-2,4-dienone (*o*-quinolide structure) contains two reactive chlorine atoms, oxidises an alcohol to an aldehyde, chlorinates phenols and hydrocarbons, condenses with sodium benzenesulphonate with formation of pentachlorophenyl benzenesulphonate, gives an adduct with maleic anhydride, is stable towards hydrogen chloride and sulphur dioxide at 95°, and does not react with metallic sodium at 100°.[63,65]

In 1950 Shorygin also isolated two isomers of pentachlorophenol chloride (m.p. 51° and 106°). The first isomer was readily converted into the second. On the basis of the Raman spectra, however, the isomer melting at 51° was assigned a hypochlorite structure, while that melting at 106° was regarded as 2,3,4,4,5,6-hexachlorocyclohexa-2,5-dienone[67].

4. HALOGENATION OF ALKYLPHENOLS

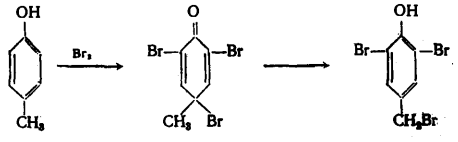
Compared with unsubstituted phenol, alkylphenols show a greater tendency to form cyclohexadienone structures when undergoing halogenation. This tendency becomes more marked with increasing number of alkyl groups in the phenol. The general rules of halogenation accompanied by phenol–dienone rearrangement are maintained with the alkylphenols. In contrast to the halogenation of phenol itself, however, the formation of quinolide structures in these cases has not been, and is not at present, open to serious doubt by investigators working in this field. The halogenation of alkylphenols is more complicated than that

of phenol itself, and is accompanied by side-reactions, since the halogenocyclohexadienones thus formed, which have been termed "quinohalides" are extremely reactive compounds, which readily undergo various changes. Only *m*-cresol is halogenated in a similar manner to phenol[68], treatment with bromine water yielding tribromo-*m*-cresol bromide, which possesses the same properties as tribromophenol bromide. However, exhaustive halogenation of the unsubstituted positions in the phenol occurs even with *o*- and *p*-cresols, followed by halogenation accompanied by phenol–dienone rearrangement. The resulting halogenated cyclohexadienones can readily rearrange to the corresponding benzyl halides. Thus the bromination of *p*-cresol[69] yields the tetrabromoquinobromide (X), which can rearrange to the *p*-hydroxybenzyl bromide (XI).



(X) (XI)

Under milder conditions the exhaustive bromination of *p*-cresol may not occur. The action of bromine water on *p*-cresol, for example[22], produces dibromo-*p*-cresol bromide (XII) together with 3,5-dibromo-4-hydroxylbenzyl bromide (XIII) and 3,5-dibromo-4-hydroxybenzyl alcohol; the last compound is probably formed by hydrolysis of both bromides:

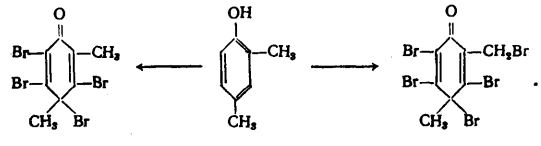


(XII) (XIII)

Dibromo-*p*-cresol bromide (XII) also rearranges to the *p*-hydroxybenzyl bromide (XIII) on being heated to its melting point or on standing in sunlight[70]. On the other hand, bromination of cresols and other alkylphenols with free bromine under more severe conditions (100° and above) at once yields substances in which the bromine is in the benzyl condition[71-77].

The chlorination of *p*-cresol results, just as with phenol, in the formation of polychlorinated compounds having an *o*-quinolide structure. The isomer having a *p*-quinolide system of bonds is also obtained at the same time[69].

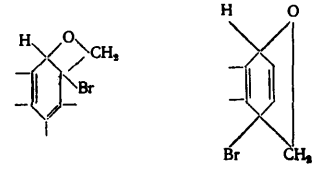
The above generalisations concerning the halogenation of cresols with the formation of cyclohexadienones apply also to the halogenation of polyalkylphenols. For example, the bromination of *m*-xylenol occurs as follows[69,78,79], depending on the conditions:



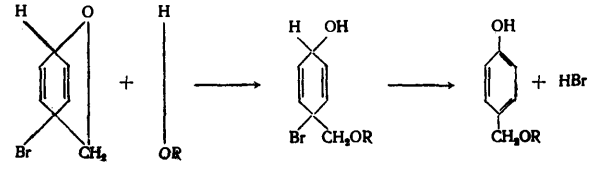
The chlorination of 2,4,6-tribromo-3,5-dimethylphenol, just like that of tribromophenol, involves the replacement of bromine by chlorine, probably *via* a cyclohexadienone structure[54].

The quinohalide compounds obtained from alkylphenols possess all the usual properties characteristic of such compounds: they do not dissolve in alkalis, and they react with alcohols, amines, aqueous acetone, etc. The chemical properties and conditions of formation of these compounds were explored quite thoroughly at the end of the past century[69,79-89]. During 1895–1897 Zincke[69,81] concluded, from an analysis of earlier work and the properties of the compounds obtained by the bromination and chlorination of cresols, xylenols, and 2,4,5-trimethylphenol, that "pseudo-phenols" existed as a separate class of organic compounds, and he suggested that they had a quinolide structure.

Later Auwers came to regard the "pseudo-phenols" as derivatives of β- or γ-oxides[85-89]:

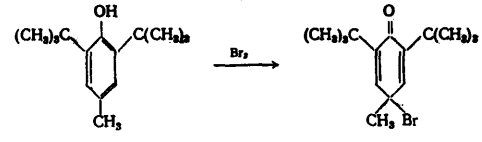


In his view, the first stage in the interaction of a quinobromide with, for example, an alcohol consisted in rupture of the oxide ring with subsequent elimination of a molecule of hydrogen bromide:



However, the oxide form of "pseudo-phenols" was subsequently abandoned, especially in view of the isolation of substances which, according to their properties, would have been methylenequinones[75].

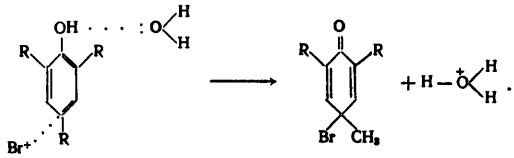
On the basis of the above work, carried out mainly by Auwers and by Zincke, the view arose in the literature that quinobromide compounds can be formed from alkylphenols only after preliminary nuclear bromination of the initial phenol. For a long time quinobromide compounds could not be obtained from 2,4,6-trialkylphenols by the action of one equivalent of bromine. It is only during recent years that it has been possible to obtain such compounds, and only from sterically hindered phenols[33,90-92], 2,4,6-tri-t-butylphenol, and Ionol (4-methyl-2,6-di-t-butylphenol):



The formation in these cases of quinobromide compounds in which only one bromine atom has entered the nucleus was explained by the presence of bulky substituents in the *ortho*-positions of the phenols on the one hand facilitating the formation of a cyclohexadienone structure, and on the other causing steric hindrance to the entry of additional bromine atoms in the *meta*-positions of the phenol.

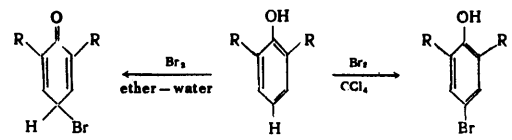
In 1962 Ershov and Volod'kin found[93-95] that, if bromination of the most diverse 2,4,6-trialkylphenols is carried out in the presence of substances possessing proton-acceptor properties (ether, dioxane, pyridine, water, etc.), *p*-quinobromides containing one bromine atom in the molecule are always formed. The effect of proton-acceptors on the formation of quinobromides is linked primarily with their

ability to form a hydrogen bond with the phenolic hydroxyl even in the case of sterically hindered phenols. This has been convincingly demonstrated by means of spectroscopic data in the case of 4-methyl-2,6-di-t-butylphenol[96]. The presence of proton-acceptors facilitates the splitting off of a hydrogen ion from the phenolic hydroxyl by its addition to the lone electron pair of the acceptor, and, furthermore, this is accompanied by an additional increase in electron density in the aromatic nucleus as a whole and in the *para*-position in particular. Electrophilic attack by the bromine is thus directed mainly at the *para*-position, with formation of a quinolide compound:



In the absence of a proton-acceptor, conditions for preferential attack at the *para*-position are not created, and therefore ordinary bromination of the phenol in the unsubstituted *meta*-position takes place. If bulky alkyl groups are present in the *ortho*-positions of the 2,4,6-trialkylphenol, preventing the entry of bromine in the *meta*-position, substitutive bromination in the *ortho*-position, with elimination of the corresponding olefine, can occur in the absence of proton-acceptors.

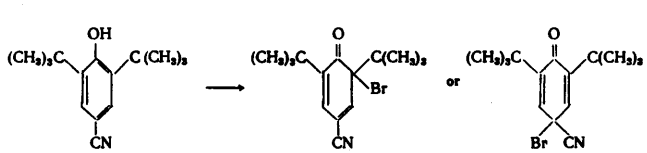
The influence of proton-acceptors is shown very clearly in the reaction of bromine with 2,6-dialkylphenols[12,13]. In this case good yields of quinolide compounds are also obtained in their presence, whereas bromination in non-polar solvents (for example in carbon tetrachloride) at once yields 2,6-dialkyl-4-bromophenols directly:



Since quinohalides are extremely reactive, their preparation from alkylphenols (usually in very good yields) is carried out at low temperatures (between -10° and 0°).

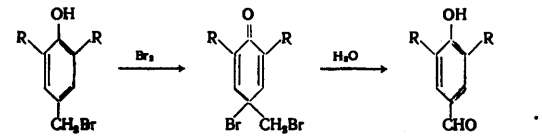
The formation of quinolide compounds has been reported also in the chlorination of some sterically hindered phenols[33,97].

If a 2,4,6-trisubstituted phenol does not contain an alkyl group in the 4-position, quinolide compounds can also be formed in the halogenation of such phenols. However, less work has been done on this question. Quinobromides are probably formed by the action of bromine on 3,5-di-t-butylbiphenyl-4-ol[98] and on 4-hydroxy-3,5-di-t-butylbenzonitrile (XIV)[32], although in the latter case the structure of the product is not proved but is taken to be the *o*-quinolide (XV) on the isomeric *p*-quinolide form (XVI):



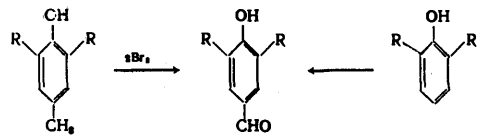
(XIV) (XV) (XVI)

Bromination of various 2,6-dialkylphenols containing a 4-bromomethyl group also yields quinobromide compounds (XVII), which readily form 3,5-dialkyl-4-hydroxybenzaldehydes (XVIII)[99] on hydrolysis:



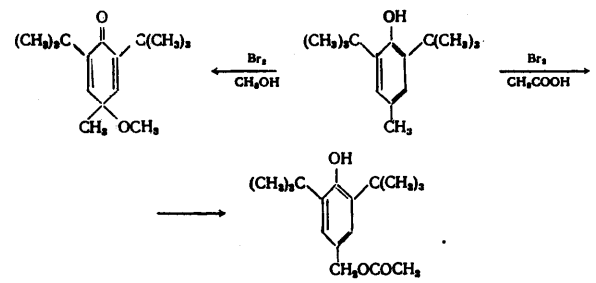
(XVII) (XVIII)

If the corresponding 2,6-dialkyl-*p*-cresols are brominated in the presence of water with two equivalents of bromine in a single operation, the hydroxy-aldehydes (XVIII) are obtained, the formation of which involves an intermediate quinobromide (XVII) stage. Dialkylhydroxy-aldehydes (XVIII) can also be obtained by the direct formylation of 2,6-dialkylphenols by means of hexamethylenetetramine[100].

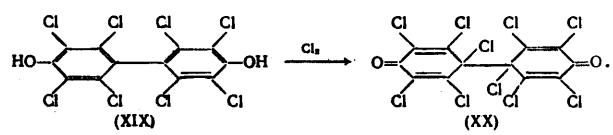


(XVIII)

Other examples are also known of the solvent reacting with the quinobromide which is formed, especially if the bromination of phenols is carried out at elevated temperatures. For example, the action of bromine on Ionol in methyl alcohol yields a quinol§ methyl ether, but in glacial acetic acid 4-hydroxy-3,5-di-t-butylbenzyl acetate is obtained[90].



The halogenation of substituted biphenyl-*pp'*-diols apparently also involves a phenol–dienone rearrangement. Thus chlorination of 2,3,5,6,2',3',5',6'-octachlorobiphenyl-4,4'-diol (XIX) yielded a compound (XX) to which a bis(cyclohexadienyl)dione structure was attributed[101]:



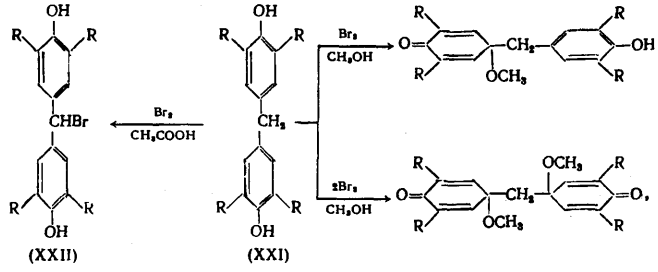
(XIX) (XX)

There is no doubt about the existence of this structure, especially as compounds having an analogous structure have been described several times in the literature[68,102].

The halogenation (bromination) of derivatives of diphenylmethane-*pp'*-diol is an interesting process. It was originally supposed[103,104] that replacement of one hydrogen atom

§ Hydroxy-derivatives of quinohalides (*i.e.* OH for halogen) are here described as "quinols" (Ed. of Translation).

by bromine yields a compound in which one of the rings has a cyclohexadienone structure. However, these hypotheses were not supported by sufficient experimental data. Subsequently, in 1957, it was shown[105] that, in the bromination of 3,5,3′,5′-tetra-t-butyldiphenylmethane-4,4′-diol (XXI), it was possible to isolate only the compound (XXII) in which the bromine was linked to the central carbon atom of the diphenylmethane system. When, however, the above compound was brominated in the presence of alcohol, ethers of the corresponding hydroxy-dienones (quinols) were obtained:



(XXII) (XXI)

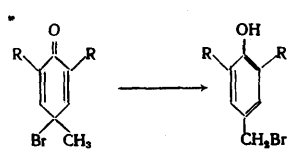
where R = $C(CH_3)_3$.

The formation of quinol ethers can be explained on the one hand as a result of the alcoholysis of quinobromides formed as intermediates, and on the other as a result of the addition of alcohol at the double bond of a methylenequinone, the latter having been produced by dehydrobromination of the bromide (XXII).

5. REACTIVITY OF QUINOHALIDE COMPOUNDS. PROBLEM OF METHYLENEQUINONE

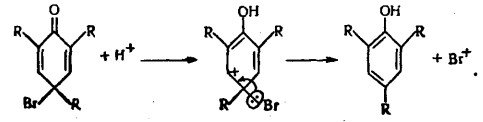
Quinohalide compounds obtained in the halogenation of substituted phenols are very reactive, this being due to the great tendency shown by *gem*-substituted cyclohexadienones to be converted into the aromatic phenol structure. On the other hand, their chemical properties are governed by the extreme lability of the carbon–halogen bond, which, depending on the conditions, can undergo either heterolytic or homolytic fission, and this sharply distinguishes quinohalides from other compounds having a quinolide structure. Almost all the properties of these substances have been studied only with quinobromide compounds. They are insoluble in alkalis, react readily with alcohols, amines, and acids, liberate iodine from potassium iodide in acetic acid solution, etc. Many reactions of these compounds depend on the structure of the initial quinobromide. For example, the reactions of the quinobromide obtained from dibromo-*p*-cresol very often differ markedly from the corresponding reactions of Ionol quinobromide.

The most general property, characteristic of all quinohalide compounds in which the halogen atom is located on a carbon atom linked also to a methyl group, is the "quino–benzylic" rearrangement, accompanied by migration of the halogen to the benzyl position with formation of an aromatic phenyl system. This rearrangement occurs during storage of the quinohalide[23,24,70], and especially readily at elevated temperatures[106]:



The speed of this rearrangement depends appreciably on the nature of the medium. When Ionol quinobromide is heated in different solvents at 59.5° for 2 h, yields of 9%, 44%, and 87% of 4-hydroxy-3,5-di-t-butylbenzyl bromide are obtained in cyclohexane, benzene, and bromobenzene respectively[106]. The velocity of the rearrangement is markedly increased in the presence of catalytic amounts of hydrogen bromide[23,94]. On the other hand, the ease of rearrangement is clearly linked with the bulk of the 2,6-alkyl substituents, and is sharply diminished with increasing steric hindrance at the carbonyl in the quinolide compounds[94]. The mechanism of the rearrangement has not been finally elucidated. Isolated facts indicate that it has a radical mechanism. However, kinetic investigations have shown it to be of first order, so that it most probably has an ionic mechanism[106].

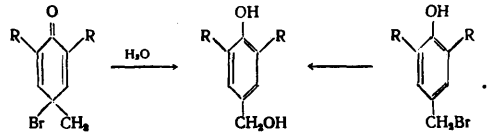
Sometimes, depending on the conditions, for example when Ionol quinobromide is heated in acetone at 60° for 3 h, debromination of the quinobromide takes place instead of the benzyl rearrangement, and the original Ionol is obtained[25]. If there is no possibility of the bromine passing to the benzyl position, the radical type of debromination can occur even when the quinobromide is just heated[91]. However, the most common type of debromination of quinobromide compounds is their behaviour in the presence of large concentrations of acid agents (hydrogen chloride and bromide, sulphuric acid)[107]:



This reaction sharply distinguishes quinobromide compounds from other quinolide derivatives, which under these conditions undergo the dienone–phenol rearrangement.

Very often (but not always) quinobromides and the *p*-hydroxybenzyl bromides formed by the quino–benzylic rearrangement give identical results on treatment with the same reagents. Whether these reactions are preceded by rearrangement of the quinobromide into the benzyl bromide is not considered at all in the literature. Moreover, many authors are inclined to suppose that the initial stage in many reactions of quinohalide compounds is the formation of the corresponding methylenequinone.

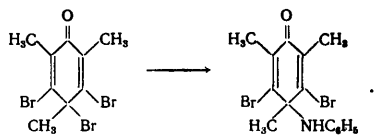
All quinobromide compounds react readily with water to form *p*-hydroxybenzyl alcohols[22,78,80,84,90]. This reaction is usually carried out in aqueous acetone medium. Exactly the same alcohols are obtained also from the corresponding *p*-hydroxybenzyl bromides[72,73,75,108]:



When formation of an alcohol is impossible (with the quinobromide of 3,5-di-t-butylbiphenyl-4-ol), the reaction yields the corresponding quinol[98].

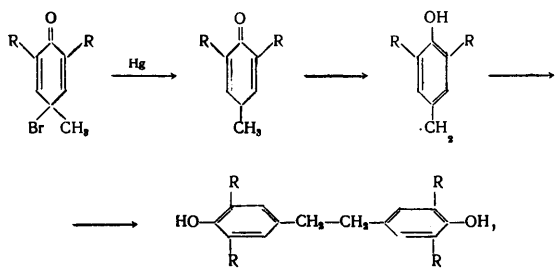
The reaction of quinobromides with alcohols is less clear-cut. Alcohols usually react with quinohalides to form ethers of *p*-hydroxybenzyl alcohol[69,78,80,83,89], which are also obtained by the action of alcohols on the corresponding hydroxybenzylbromides[25,73,108,109]. Quinobromides obtained from sterically hindered phenols, however, react with alcohols to form ethers of quinols, the dienone structure being preserved[33,90].

The reaction of quinobromide compounds with amines is less clear-cut. Early work on the simplest examples showed[78-84] that these compounds react with ammonia, primary and secondary aliphatic amines, and aniline with formation of *p*-aminomethylphenols, which can also be obtained from the corresponding benzyl bromides[23,73,75,77,84,86]. According to Fries[24,70], however, the action of aniline in alcoholic medium containing sodium acetate on the quinobromides of 2,6-dibromo-*p*-cresol and 3,5-dibromomesitol yields quinoamines, substances having a dienone structure which in acid medium can undergo rearrangement to ethers of the phenol:



Ionol quinobromide does not react in ethereal solution with aniline[25] or with tertiary amines (triethylamine, pyridine)[110], but it does react normally with secondary amines to form dialkylaminomethylphenols, which can also be obtained from 2,6-di-t-butylphenol by the Mannich reaction[111].

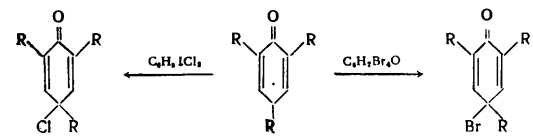
Very little work has been done on the reaction of quinohalides with organic acids and their salts. According to unverified data published in early papers, the action of sodium acetate in acetic acid on quinobromides yields quinol acetates[78,79,82,84,86], from which quinohalides are again formed by reaction with HCl, HBr, and HI.[78,79,82] Reaction of quinohalides with acetic anhydride or acetic acid yields benzyl acetates[82-85]. A similar reaction has been described also in a more recent paper[90]. The interaction of quinohalides with various metals is very interesting. For example, Ionol quinobromide does not react with sodium in ether, but treatment with metallic mercury yields 3,5,3′,5′-tetra-t-butyldiphenylethane-4,4′-diol[106], the reaction having a radical mechanism:



where R = $C(CH_3)_3$.

If it is impossible for the phenoxy-radical which is formed to isomerise into a benzyl radical, a stable phenoxy-radical may result from the reaction. Such a change takes place when mercury, copper, zinc, or especially silver acts on the quinobromide of 2,4,6-tri-t-butylphenol in the absence of oxygen[37,97,106].

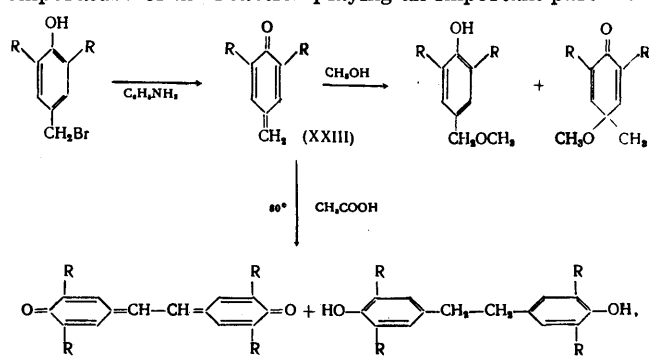
The action of a sodium–potassium alloy on the same quinobromide produces the 2,4,6-tri-t-butylphenoxide[33]. If, however, the quinobromide (quinochloride) of 2,4,6-tri-t-butylphenol is treated in alkaline alcoholic medium with 2,4,6-tri-t-butylphenol or even directly with its phenoxide, a quantitative yield of the 2,4,6-tri-t-butylphenoxy-radical is obtained[112], from which the quinochloride is again formed by the action of iodosobenzene dichloride[97], and the quinobromide is obtained by the action of tribromophenol bromide[113]:



where R = $C(CH_3)_3$.

It has been repeatedly emphasised above that many reactions of quinohalides and of the corresponding *p*-hydroxybenzyl halides give identical results. This is explained[90,114] by the possibility of methylenequinones being formed as intermediates, which can also occur with other compounds of analogous structure. Different workers have made many attempts to isolate a methylenequinone from the reaction mixture. Thus as early as 1898 Auwers supposed that he had obtained a methylenequinone by dehydrating the quinol of 2,4,5-tribromo-3,6-dimethylphenol[115]. Later Zincke[116] heated the quinonitrol¶ of 2,3,5,6-tetrachloro-*p*-cresol with methyl alcohol and obtained an alkali-insoluble substance, which reacted[116,117] with hydrogen bromide to form a nuclear-substituted *p*-hydroxybenzyl bromide, and on being boiled with methyl and ethyl alcohols and with acetic acid it formed the corresponding ethers and ester of benzyl alcohol. Reduction of this substance yielded a substituted *p*-cresol.

In 1905 Zincke[75] obtained, by the action of sodium acetate in absolute benzene on 2,3,5,6-tetrabromo-4-hydroxybenzyl bromide, an amorphous powder, which behaved in all the above reactions as a methylenequinone. Attempts were also made to prepare *o*-methylenequinone starting from *o*-quinonitrol[118,119] and from *o*-hydroxybenzylbromide[120,121]. However, subsequent work showed that the methylenequinone monomer had not been obtained in these cases, but instead dimeric and trimeric derivatives[24,120-122] possessing the properties of methylenequinone had been formed. A cyclic structure was adopted for the dimer of methylenequinone[123,124]. The trimer was obtained by the action of 2 *N* sodium carbonate solution on *p*-hydroxybenzyl bromide in ether[24]. Heating *p*-hydroxybenzyl bromides with caustic soda solution yields polymeric products[125] and stilbenequinones[25]. It was not until 1957 that it was finally reported[25,114] that one of the products of the action of an ethereal solution of aniline on 3,5-di-t-butyl-4-hydroxybenzyl bromide is monomeric 2,6-di-t-butylmethylenequinone (XXIII), obtained in the form of an amorphous powder, which reacts readily with several substances, the temperature of the reaction playing an important part[114]:

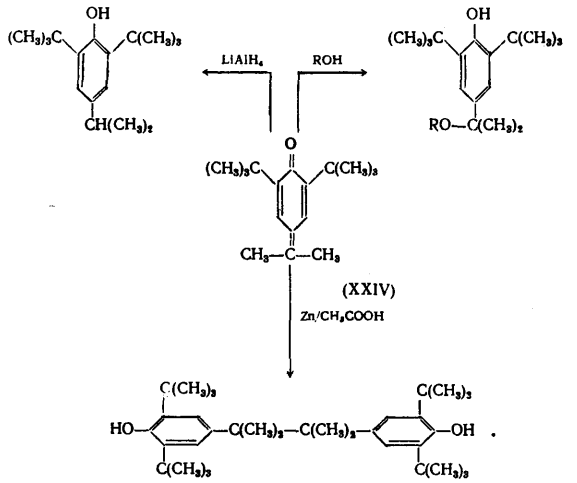


where R = $C(CH_3)_3$.

¶ Nitro-analogues of quinohalides (*i.e.* NO_2 for halogen) are here described as "quinonitrols" (Ed. of Translation).

In later work, however, it proved impossible[126] to isolate this methylenequinone (XXIII) in the free monomeric state. It was then shown that the methylenequinone (XXIII) is stable at a concentration 10^{-2} M in an inert solvent at 20°, 2% of the dimer being formed only after 72 h; whereas the corresponding methylenequinone in which methyl groups have replaced the t-butyl groups in both *ortho*-positions is less stable, and at the same concentration forms 60% of the dimer after only 140 min.

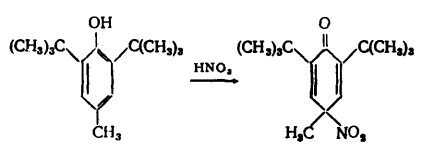
Homologues of methylenequinone are more stable[103,105,109,118,127-130], especially isopropylidenequinone (XXIV)[129], prepared by the oxidation of 2,6-di-t-butyl-4-isopropylphenol with lead dioxide in an atmosphere of nitrogen. The action of hydrogen bromide on this isopropylidenequinone yields a white substance which decomposes rapidly in air. With alcohols in acid medium, addition at the double bond takes place normally. Reduction with lithium aluminium hydride yields 2,6-di-t-butyl-4-isopropylphenol, but on reduction with zinc in acetic acid the corresponding substituted diphenylethane-*pp'*-diol (XXV) is obtained:



(XXV)

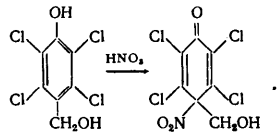
6. NITRATION OF PHENOLS

The nitration of phenols accompanied by phenol–dienone rearrangement has been less thoroughly studied than their halogenation. This is mainly because the nitration is a more complicated process, and is accompanied by several side-reactions, the chief of which is oxidation of the original phenols to the corresponding benzoquinones and biphenoquinones[26,131-136]. Furthermore, the nitration of phenols often involves replacement of a group in the phenol nucleus by a nitro-group[29-31,137]. However, there are grounds for assuming that in most of these cases both substitutive nitration[29] and many oxidation reactions[132,138] of phenols with nitric acid involve the intermediate formation of a cyclohexadienone structure. Nitration of substituted *p*-alkylphenols alone results in the formation of quinonitrols having a structure analogous to that of *p*-quinohalide compounds:



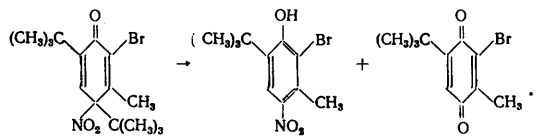
There are indications in the literature[139] also of cases of *o*-quinonitrol formation.

Nitration with the formation of quinonitrols is usually observed in the case of sterically hindered and polyhalogenated *p*-alkylphenols, *i.e.* in fact with those phenols whose structure to an appreciable extent favours the phenol–dienone rearrangement. Quinonitrols have been obtained chiefly from halogenated *p*-cresols[116,117,140,141], xylenols, mesitol[115,132], and *p*-hydroxybenzyl alcohol and its methyl ether[73].



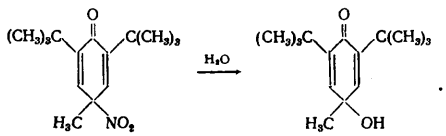
Quantitative yields of quinonitrols are obtained from Ionol[142] and from 2,4,6-tri-t-butylphenol[143]. In order to obtain quinonitrols, the nitration of phenols is usually carried out at a low temperature (0°) with concentrated nitric acid or with a mixture of nitric and acetic acids. At higher temperatures the phenols are oxidised. If, for example, nitration of 2,4,6-tri-t-butylphenol is attempted at 100°, 2,6-di-t-butyl-1,4-benzoquinone is formed instead of the quinonitrol[143].

A distinctive feature of the quinonitrols is their great instability. They are rapidly decomposed by acetic and sulphuric acids[144]:

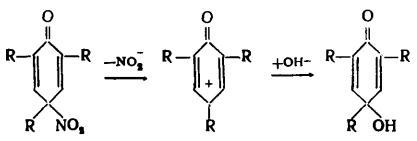


Thermal decomposition (at 90°) is accompanied by the evolution of nitrogen dioxide[91].

Another characteristic of quinonitrols is their ready conversion into quinols:



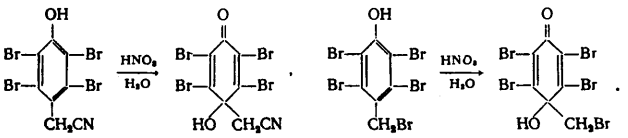
This reaction occurs readily on treatment of quinonitrols with hot water[142], aqueous acetone in the presence of caustic potash or acetic acid[134], sodium acetate in acetic-acid solution[144], etc. It was previously supposed that the formation of a quinol from a quinonitrol is accompanied by the elimination of a molecule of nitrous acid *via* a stage involving formation of a methylenequinone, followed by addition to it of a molecule of water[69,115,116,145,146]. Later, however, it was shown[91,143] that the corresponding quinol is also obtained even when the formation of a methylenequinone is impossible. The quinonitrol prepared from 2,4,6-tri-t-butylphenol, for example, is readily converted into a quinol, which can be explained by an ionic mechanism[143]:



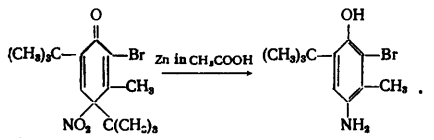
where R = $C(CH_3)_3$.

In this case *p*- and *o*-benzoquinones are formed as side-products.

The ease of formation of quinols is so great that the nitration of substituted *p*-alkylphenols very often does not stop at the quinonitrol stage, but yields the corresponding quinol immediately. Thus in the nitration of 3,5-di-t--butyl-4-hydroxybiphenyl (under conditions analogous to the preparation of the quinonitrol from Ionol) the quinol is formed at once. Direct formation of quinols takes place also during the nitration of substituted *p*-ethylphenols[147], *p*-hydroxybenzyl bromides[72,73,148,149] or chlorides[75], and 2,3,5,6-tetrabromo-4-hydroxyphenylacetonitrile[75]:



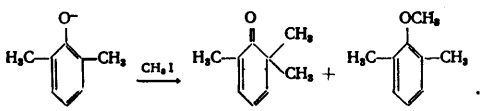
For a long time the structure of the quinonitrols remained a matter of dispute. Many writers were inclined to regard these compounds as nitrous esters. However, a direct bond between nitrogen and carbon in the quinonitrols is convincingly indicated by the formation of substituted *p*-aminophenols when several of them are reduced with zinc in acetic acid[144]. The reaction involves elimination of the alkyl group:



It seems that reduction may be preceded by decomposition of the quinonitrol, which, as mentioned above, takes place in acid medium with elimination of an alkyl group. A case is also known[117] in which reduction of a quinonitrol is accompanied by loss of the nitro-group, the corresponding substituted *p*-cresol being isolated as a product of the reaction.

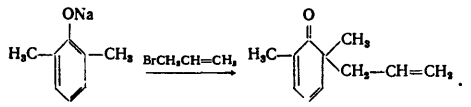
7. ALKYLATION OF PHENOLS

The alkylation of phenols and especially of the corresponding phenoxides also can lead to the formation of cyclic dienones. In contrast to the examples considered earlier, the cyclodienones obtained in this case contain only alkyl groups as *gem*-substituents. The formation of a new carbon–carbon bond affects also the characteristics of the accompanying phenol–dienone rearrangement. In the alkylation of phenoxides with alkyl halides, for example, formation of phenyl ethers is in several cases accompanied by that of cyclodienones having an *o*-quinolide structure. Such dienones are formed even in the alkylation of phenols containing no *p*-substituent[150]:

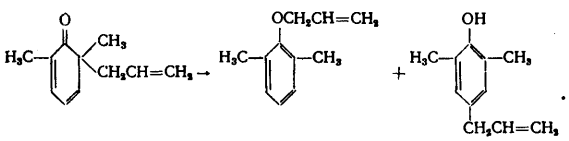


In the alkylation of phenoxides with alkyl halides dienones are usually formed in low yields, the main reaction products being the phenyl ethers. However, the proportions of cyclic dienone and phenyl ether among the reaction products may be varied considerably. The formation of a dienone structure is favoured in these cases[150] by the following factors: decrease in acidity of the initial phenol (for example in the sequence 4-bromo-2,6-dimethylphenol, 2,6-dimethylphenol, mesitol), presence of moisture, decrease in polarity of the solvent, and increase in concentration of the phenoxide during the reaction. If phenoxides of different metals are used, the total yield of reaction products increases in the sequence Li, Na, K. The yield also increases on passing from alkyl chlorides to alkyl bromides and iodides.

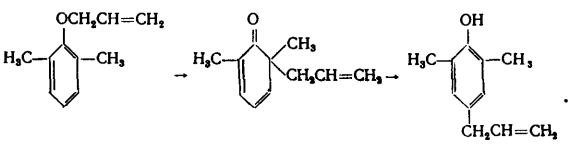
The ease of formation of cyclodienones in the alkylation of phenoxides is most affected by the nature of the alkyl halide. Dienones are formed to a considerably smaller extent when methyl iodide and propyl iodide are used than with benzyl bromide and allyl bromide[150,151]. In 1956 Curtin[152] was able to isolate a cyclohexadienone in 60% yield by the alkylation of sodium 2,6-dimethylphenoxide with allyl bromide at 15°:



The structure of the dienone was proved by the infra--red and ultra-violet spectra, and also by the formation of an adduct with maleic anhydride. On standing, the dimer of the dienone is formed (by a diene synthesis mechanism), and on being heated gives a 64% yield of 4-allyl-2,6-dimethylphenol. Heating the monomeric dienone above 70° yields a mixture containing 27% of allyl 2,6-dimethylphenyl ether and 73% of 4-allyl-2,6-dimethylphenol[153]:



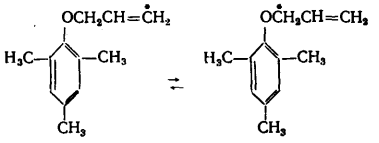
The alkylation of phenoxides with an allyl halide differs from the rearrangement of allyl phenyl ethers (the Claisen rearrangement), although the same final results may be obtained in the two cases. According to modern data[154,155], the Claisen rearrangement is a typical intramolecular rearrangement, which does not occur by an ionic mechanism. It is interesting that, when both *ortho*-positions of the phenol are already substituted, this rearrangement (the Claisen *para*-rearrangement), too, involves the intermediate formation of a quinolide structure. This was shown[156] in 1953 in the case of allyl 2,6-dimethylphenyl ether (the condensation product of maleic anhydride with the corresponding dienone was isolated).



Later this mechanism for the Claisen *para*-rearrangement was confirmed with other examples[157,158].

Allyl mesityl ether (in which the *para*- and both *ortho*--positions of the aromatic nucleus are substituted) gives under the conditions of the rearrangement a good yield of an adduct with maleic anhydride, which suggests that a dienone structure is formed, although it could not be detected by spectroscopic methods[158]. Later work[159] on

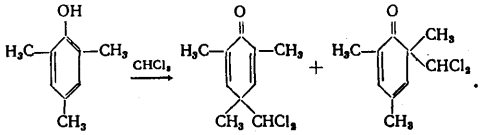
[3-^{14}C]allyl mesityl ether showed that in this case the reaction results in the establishment of equilibrium between two labelled allyl ethers:



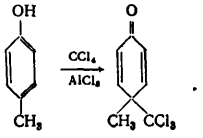
It was assumed that the process involves the intermediate formation of an *o*- or *p*-quinolide structure.

Another interesting example of a phenol–dienone rearrangement occurring in the alkylation of phenols is provided by the anomalous cases of the Reimer–Tiemann reaction†. As long ago as the end of the past century it was noted that *o*- and *p*-substituted phenols form cyclic ketones together with the expected phenolic aldehydes under the conditions of the Reimer–Tiemann reaction (the action of chloroform on a phenoxide). These compounds have a cyclohexadienone structure, and undergo reactions characteristic of ketones[160–164].

In the cast of mesitol, with which the formation of an aldehyde is impossible owing to the absence of vacant *ortho*- or *para*-positions in the phenol, this side-reaction becomes the principal reaction, and a good yield of a cyclic ketone is obtained[165]:

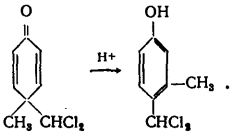


Zincke showed[166] that a ketone of analogous structure is obtained also by the action of carbon tetrachloride on *p*-cresol in the presence of aluminium chloride. This ketone readily forms an oxime and a phenylhydrazone, and sulphuric acid breaks it down into *p*-cresol and carbonyl chloride:

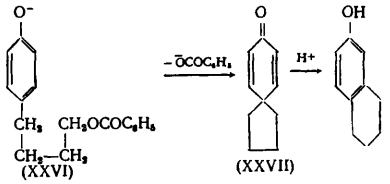


This reaction, occurring in the presence of aluminium chloride, was subsequently termed the Zincke reaction. In 1954 Newman[167] made a detailed investigation of this reaction in the case of *p*-cresol, and showed that it goes smoothly (yield 60%) only with carbon tetrachloride. Attempts to use $CHCl_3$, C_2Cl_6, $CH_2{=}CHCl$, CH_3Cl, or CH_3I in this reaction were unsuccessful. When, however, it was carried out with 1,1,1-trichloroethane, a substance having a dienone structure could be isolated as the 2,4-dinitrophenylhydrazone.

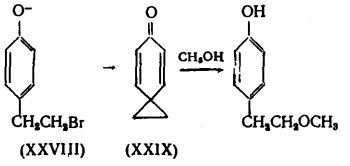
The 4-di(and tri)chloromethyl-4-methylcyclohexan-2,5-dienones resulting from these reactions behave normally in organomagnesium synthesis and the Reformatsky reaction, and in carbon tetrachloride solution are chlorinated (brominated) in the ring with preservation of the dienone structure; in the light halogen adds on at the multiple bonds[168,169]. Depending on the conditions, reduction of such dienones results either in the formation of *p*-cresol derivatives[170] or in reduction of the dichloromethyl group to methyl with preservation of the dienone structure[165,171]. In acid medium 4-dichloromethyl-4-methylcyclohexa-2,5-dienone undergoes dienone–phenol rearrangement[169]:



The alkylation of phenols leading to the formation of spirocyclohexadienones is a very interesting process. Thus 4-*p*-hydroxyphenylbutyl benzoate (XXVI)[172] in alkaline medium gives a 50% yield of a compound having a dienone structure, as has been confirmed by elemental and spectroscopic analyses. This compound can subsequently undergo dienone–phenol rearrangement with the formation of a tetrahydronaphthol:



Intramolecular alkylation occurs similarly also with *p*-2-bromo(or iodo)ethylphenol (XXVIII), which in alkaline medium splits off a molecule of hydrogen halide with closure of a cyclopropane ring and simultaneous phenol–dienone rearrangement[172]. Initially the structure of the resulting spirodienone (XXIX) was proved only by means of spectroscopic data, since it was not possible to isolate the pure material from the reaction products because of its rapid reaction with the methyl or ethyl alcohol used as solvent:



Later the dienone (XXIX) was obtained pure[173] by passing an ethereal solution of *p*-2-bromoethylphenol (XXVIII) through a column containing basic aluminium oxide. This spirodienone is extremely unstable. Even in minute concentrations it reacts with various substances at various pH values with ring-opening. The ring is opened especially rapidly, in acid medium, the period of half-decomposition of the substance in 10^{-5} M solution at 25° being in this case 10 sec. In ethereal solution the dienone can exist at a concentration 5×10^{-3} M for a week; in the solid form it is stable for not more than 20–30 min, after which it is converted into a polymeric ether.

Oxygen analogues of this spirodienone, in which the three-membered ring contains an oxygen atom instead of a methylene group, are more stable. These compounds are readily obtained by the action of alkaline reagents on *p*-bromomethylquinols[73,132,148].

† A fairly detailed survey has recently been published of the Reimer–Tiemann reaction[8].

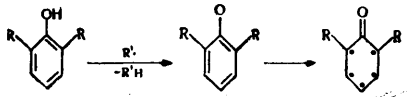
8. FORMATION OF DIENONES IN RADICAL REACTIONS OF PHENOLS

The conversion of phenols into cyclohexadienones in radical reactions must be considered in the light of the general laws of radical processes involving phenols, since those resulting in the formation solely of dienone compounds cannot be isolated as a separate group. It must be remembered firstly that the radical reactions of phenols are somewhat different in character from those of other aromatic compounds, and secondly that their mechanism has not yet been completely elucidated. A great amount of work has been published in this field during recent years, especially in connection with the use of phenols as inhibitors of free-radical oxidation processes in fats, oils, fuels, etc. A good review of the properties of various phenols in radical oxidations will be found in the recently published book by Emanuel' and Lyaskovskaya[174].

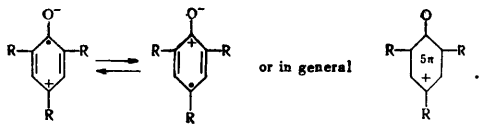
A distinguishing feature of radical reactions of phenols is the initial formation of phenoxy-radicals, which, depending on the structure of the original phenol, may be more or less stable, and may even exist for a long time in the free state. The initial formation of phenoxy-radicals is due to the considerably lower energy of rupture of the O–H bond in the phenolic hydroxyl than of a C–H bond in the aromatic nucleus, so that the rate of a radical reaction in which atomic hydrogen is split off from the hydroxyl will many times exceed the rate of loss of atomic hydrogen from the aromatic ring. From this it follows that, when any radical interacts with a phenol, formation of a phenoxy-radical (by the loss of atomic hydrogen from the hydroxyl) is practically the only process which occurs. Steric factors which impede radical attack on the phenolic hydroxyl should tend to prevent such a reaction. Increasing the bulk of the substituents in both *ortho*-positions of the phenol, for example, diminishes the rate of formation of the phenoxy-radical in the reactions of phenols with diphenylpicrylhydrazyl[175]. According to other workers[176], however, the rate of reaction of $RO_2^{\cdot}$ radicals is about the same with 2,6-dimethylphenol and with 2,6-di-t-butylphenol, since the two bulky *o*-substituents in the latter compound greatly disturb the coplanarity of the hydroxyl with the benzene ring, which in turn appreciably favours the formation of the phenoxy-radical, as this eliminates the non-coplanarity effect.

The existence of phenoxy-radicals has been demonstrated by various methods[174]. The formation of radicals from phenols by the loss of the hydrogen atom from the hydroxyl is indicated also by spectroscopic examination of some stable phenoxy-radicals, the infra-red spectra of which did not reveal absorption bands corresponding to the hydroxyl[33,97,113,134].

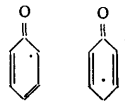
Phenoxy-radicals, which have an unpaired electron on the oxygen atom, usually have a very short life, and rapidly isomerise. This involves redistribution of the bonds with the formal creation of a cyclodienone structure, the unpaired electron being delocalised over the whole aromatic nucleus. With such a structure the phenoxy-radical preserves the π-electron sextet of the aromatic ring with coplanarity of the molecule as a whole. The presence of large, bulky substituents in the 2,6-positions of phenol substantially increases the stability of the resulting radicals:



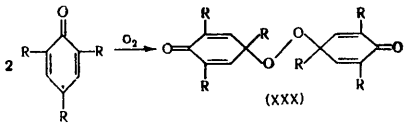
Since the infra-red spectra of several free phenoxy-radicals, especially in the solid state, are very similar to those of quinolide structures, Müller[177] suggested a dipolar ion quinolide radical structure for such radicals, for example:

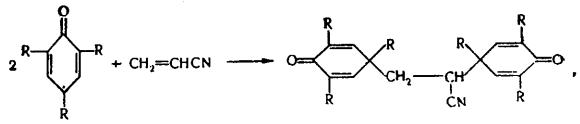


In the present paper we are unable to discuss the finer features of the structure and properties of such free radicals, which are known in the literature under the name of phenoxyls or aroxyls‡. The main peculiarity of phenoxy-radicals is that, depending on the structure of the original phenol, they can subsequently react in two different forms (α- or γ-ketomethyl), corresponding to the *o*- or *p*-quinolide structure:



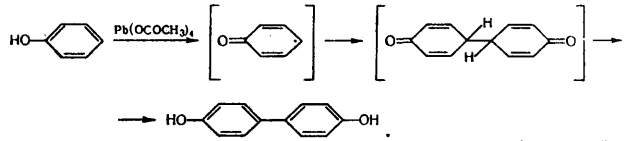
Thus, for example, the action of atmospheric oxygen on the 2,4,6-tri-t-butylphenoxy-radical yields the corresponding quinolide peroxide (XXX)[91], but in the presence of a diene or of acrylonitrile the phenoxy-radical can react at the double bond in these compounds[179]:





where R = $C(CH_3)_3$.

If the phenoxy-radical which is formed is unstable, and cannot be stabilised by addition of another radical at the free valence, recombination of the phenoxy-radicals takes place with the formation of bisphenols. Dimerisation of a phenoxy-radical usually occurs *via* the *p*-quinolide form. Thus the action of an equivalent amount of lead tetraacetate in benzene solution on phenol itself involves the formation of 4,4′-dihydroxybiphenyl[180]:



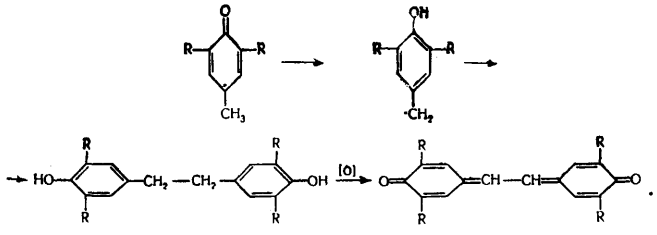
An intermediate compound having a biquinolide structure has been isolated in the oxidation of 2,6-di-t-butylphenol with potassium ferricyanide[142].

‡ The chemical properties of stable phenoxy-radicals (aroxyls) are being intensively studied at the present time by Müller[178].

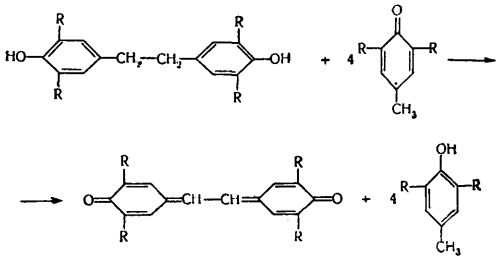
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If the *para*-position in a phenol is substituted, but a vacant *ortho*-position is available, dimerisation of the phenoxy-radicals takes place *via* an *o*-quinolide form[181]. Very often, especially in the presence of oxidising agents, the resulting bisphenols are oxidised to the corresponding biphenoquinones, which are usually isolated as the main products of the recombination of phenoxy-radicals[137,181,182].

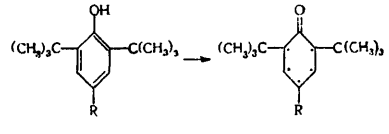
The recombination of 2,4,6-trisubstituted phenoxy--radicals is very interesting. In this case the radicals cannot be linked through unsubstituted *ortho*- or *para*--positions, and if active hydrogen atoms are present in the α-position of the alkyl substituent in the initial phenols, the phenoxy-radicals (probably their *p*-quinolide forms) are converted into benzyl radicals, which combine with the formation of 1,2-di(*p*-hydroxyphenyl)ethanes. These then usually oxidise to stilbenequinones[181-184]:



Stilbenequinones can be formed in radical processes[106] even in the absence of oxidising agents, by the reaction:

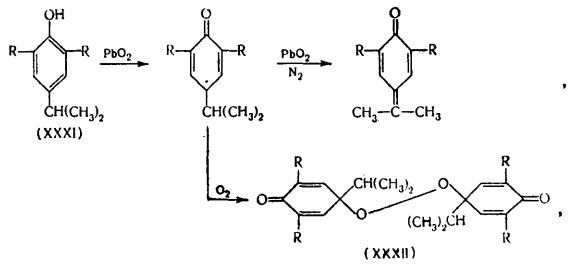


If a phenol contains a *p*-t-butyl group, as for example in 2-methyl-4,6-di-t-butylphenol, the corresponding phenoxy--radical is able to isomerise to a benzyl radical with subsequent recombination involving the hydrogen of the *o*-methyl group[181]. When isomerisation of the phenoxyl to a benzyl radical is made impossible by the absence of hydrogen atoms in the benzyl positions, the free phenoxy--radicals may be long-lived:



where R = $C(CH_3)_3$, OCH_3, $OC(CH_3)_3$, CN, C_6H_5, etc.

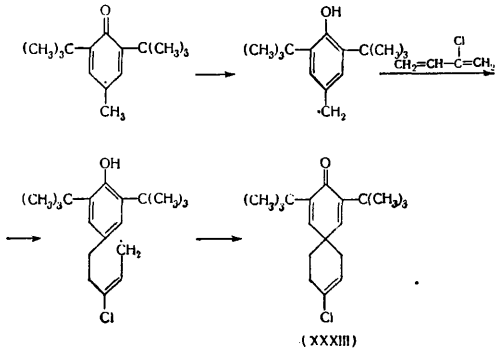
In some cases of the oxidation of phenols with lead dioxide or silver oxide stabilisation of the phenoxy-radical may involve formation of the corresponding methylene-quinone. This reaction is accomplished most smoothly by the action of lead dioxide on 4-isopropyl-2,6-di-t-butyl-phenol (XXXI) in an atmosphere of nitrogen[129]. In the presence of oxygen, however, the initially formed phenoxy--radical reacts with it to form a peroxide (XXXII):



where R = $C(CH_3)_3$.

This reaction has been extended[126] to other examples (mesitol, Ionol, 4-allyl-2,6-dimethylphenol, etc.), and at the present time is employed for the preparation of various methylenequinones.

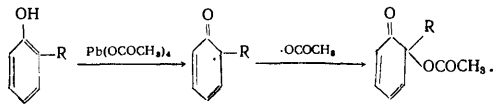
The action of the same oxidants (for example PbO_2) on Ionol and 4-isopropyl-2,6-di-t-butylphenol (XXXI) in the presence of chloroprene may involve reaction of the phenoxy-radical (probably in the isomeric benzyl form, in contrast to the other cases) with the diene to form a compound (yield 75%), which is assigned[185] a spirocyclodienone structure (XXXIII). The mechanism of this reaction has not been finally elucidated.



This reaction is accompanied by the formation of considerable quantities of the corresponding stilbenequinone, which can be assumed to result from dimerisation of the benzyl forms of the radicals.

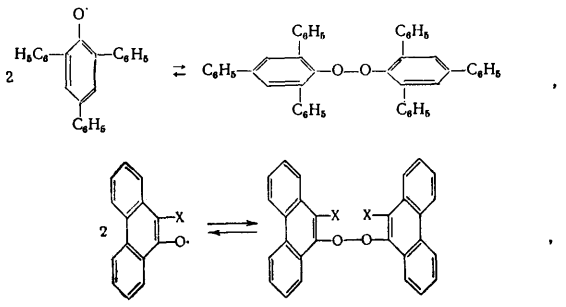
If other radicals are present in excess in the system at the instant of formation of the phenoxy-radical, dimerisation of the latter (itself or as its benzyl isomer) may not occur. The phenoxy-radicals are then stabilised by combination with other radicals present in the system (for example $RO_2^{\cdot}$ in the formation of peroxides, ROCO$^{\cdot}$ in the preparation of acyloxy-derivatives, etc.). A high concentration of such radicals in the system does not completely prevent dimerisation of the phenoxy- (or benzyl) radicals, These are usually competing processes, the main mode of the reaction depending both on the nature of the reactant radical ($RO_2^{\cdot}$, ROCO$^{\cdot}$, etc.) and on the relative stability of the phenoxy-radicals. The rate of recombination of phenoxy- (or benzyl) radicals usually falls with rise in their stability, and the latter increases appreciably with increasing size of *o*-substituents in the phenol.

Cyclodienones are formed in radical reactions of phenols if the phenol molecule already contains a substituent whose orientation (*ortho* or *para*) coincides with the form (*ortho* or *para*) of the phenoxy-radical which is reactive under the given conditions. In contrast to most electrophilic reactions, the *para*-position of the phenol may be unsubstituted[180] in this case:



Dienones are most readily obtained from 2,4,6-trialkylphenols. Even in these cases, however, recombination products of the phenoxy-radicals are very often formed as well.

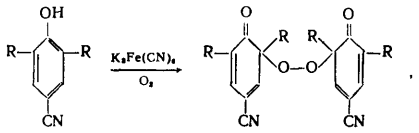
The most characteristic example of the conversion of phenols into dienone compounds in radical processes is the formation of quinolide peroxides by the action of oxygen on free phenoxy-radicals. As already noted, this usually involves formation of *p*-quinolide peroxides[91,129,134,184]. Only the radical obtained from 2,4,6-triphenylphenol is insensitive to oxygen, and this can dimerise *via* the oxygen atom to form a purely aromatic peroxide[186]. Similar properties are shown by the radicals from substituted phenanthren-10-ols[187,188]:



where X = Cl, OC_2H_5.

Such properties of these radicals probably indicate that their unpaired electron is localised on the oxygen atom, which is not usually observed in the monocyclic, non-polyphenylated phenols.

Quinolide peroxides can be obtained directly from the corresponding phenols by oxidation with alkaline potassium ferricyanide solution in the presence of oxygen[98,129,134,189]. Free phenoxyl is formed initially as a result of oxidation by the ferricyanide, and this then reacts with the oxygen to give the peroxide. Under these conditions *p*-quinolide peroxides are usually obtained, and it is probably only the oxidation of 4-hydroxy-3,5-di-t-butylbenzonitrile which results in the corresponding *o*-quinolide compound[32]:

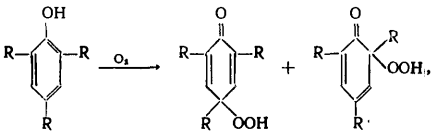


where R = $C(CH_3)_3$.

Silver oxide has been successfully employed[190] instead of potassium ferricyanide to obtain quinolide peroxides under the same conditions.

Quinolide peroxides are solids which darken in the light, are decomposed by sulphuric acid, and liberate iodine from a solution of potassium iodide in acetic acid. Reduction with lithium aluminium hydride yields the original phenol[97]. Thermal decomposition of the peroxide from 2,4,6-tri-t-butylphenol led to the isolation of 2,6-di-t-butylbenzoquinone, the reaction being accompanied by elimination of isobutene[133]. The peroxide obtained from 2,4,6-tri-t-pentylphenol behaves similarly, giving a quantitative yield of 2,6-di-t-pentylhydroquinone on being heated to 226°.[189]

Oxidation of sterically hindered 2,4,6-trialkylphenols in alkaline medium with oxygen alone (in the absence of potassium ferricyanide or silver oxide) gives quinolide hydroperoxides (phenol hydroperoxides)[142,191,192] instead of quinolide peroxides. Ionol, for example, yields Ionol hydroperoxide, which has a *p*-quinolide structure, and the oxidation of 2,4,6-tri-t-butylphenol leads to the formation of two isomeric hydroperoxides having a *p*- and an *o*-quinolide structure[191]:



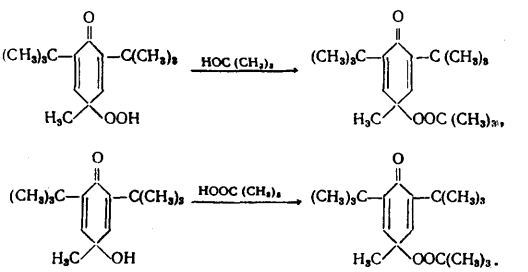
where R = $C(CH_3)_3$.

In alkaline medium *p*-quinolide hydroperoxides can break down to the corresponding quinol or the original phenols, or else may rearrange into the *o*-quinolide hydroperoxides[192].

The literature contains interesting indications[191] that the autoxidation of sterically hindered phenols in alkaline medium may not occur by a free-radical mechanism.

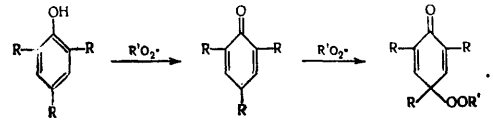
Quinolide hydroperoxides are also obtained by the oxidation of sterically hindered phenols with hydrogen peroxide in t-butyl alcohol in the presence of the ions Co^{2+}, Fe^{2+}, Fe^{3+}, Cu^{+}, and Cu^{2+}. The presence of oxygen does not interfere with this reaction. Reduction of the hydroperoxides with hydriodic acid[191] or with hydrogen in the presence of platinum[193] yields quinols. However, the *o*-hydroperoxide of 2,4,6-tri-t-butylphenol does not give the corresponding quinol on reduction[191].

Ionol hydroperoxide reacts with t-butyl alcohol to form the corresponding alkyl quinolide peroxide (phenol peroxide), which is also obtained by the oxidation of the quinol of Ionol with t-butyl hydroperoxide:



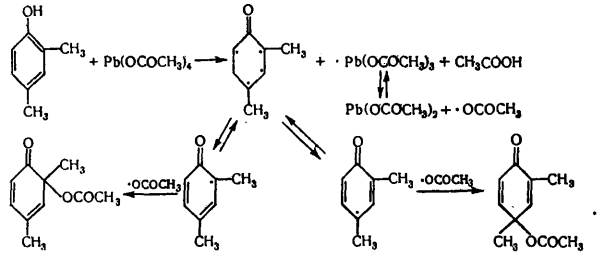
Analogous compounds are obtained also by the interaction of t-butyl hydroperoxide with the corresponding

phenols at the decomposition temperature of the hydroperoxide[194]. The formation of such peroxides of phenols, having a quinolide structure, usually occurs at the same time as the formation of recombination products of phenoxy-radicals in the inhibition by phenols of free-radical oxidation processes[174,195]:

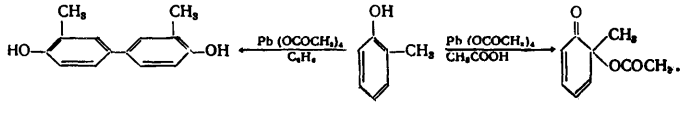


Both isomeric (*o*- and *p*-) quinolide peroxides of the phenols were isolated[183] in the oxidation of 2,6-dimethyl-4-t-butylphenol and 2-methyl-4,6-di-t-butylphenol with alkyl hydroperoxides. Reduction of Ionol t-butyl peroxide gives the theoretical yield of the quinol, but only a very low yield of the corresponding quinol is obtained[183] in the reduction of t-butyl 2,4,6-tri-t-butylphenol peroxide. 3,5-Di-t-butyl-4-hydroxybenzaldehyde is formed in the bromination of Ionol t-butyl peroxide with bromine in acetic acid[194].

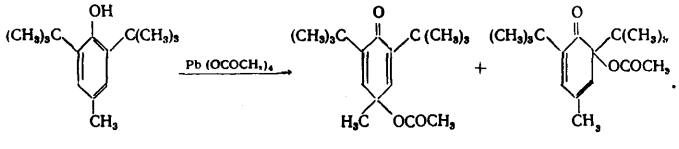
Another example of the formation of dienone compounds in radical reactions of phenols, which has been studied in some detail, is the formation of various acyloxy-derivatives of cyclohexadienones by the action of lead tetraacetate and acyl peroxides on phenols. The most thorough work in this field has been done by Wessely[196-203], who summarised his own results in a short review of quinol acetates[204].



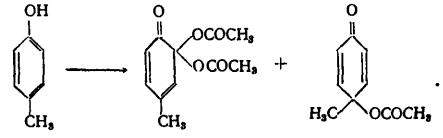
The nature of the substances obtained by the oxidation of phenols with lead tetraacetate depends to a considerable extent on the structure of the original phenol and on the solvent employed. When the reaction is carried out in benzene[180], for example, products of the dimerisation of phenoxy-radicals are usually formed, whereas in acetic acid[196,197] the reaction involves the formation of the isomeric *o*- and *p*-quinol acetates, the main product being the *o*-quinolide isomers:



The tendency of *o*-quinol acetates to be formed in this reaction is maintained with a wide variety of phenols: *o*-cresol, different xylenols, 2,4,6-trialkylphenols, etc. If, however, the phenoxy-radical obtained during oxidation of a trialkylphenol (Ionol, 2,4,6-tri-t-butylphenol) is sufficiently stable, both *ortho*- and *para*-isomers are formed[205]:

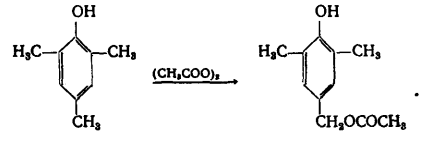


If both *ortho*-positions of the phenol are vacant, while the *para*-position is substituted, an *o*-(*OO'*-diacetyl)-quinone (6,6-diacetoxycyclohexa-2,4-dienone) can be formed in this case too, with a small amount of the *p*-quinol acetate as impurity[180,198]:



The action of lead tetraacetate on mesitol in propionic acid medium yields the quinol propionate[180] instead of the quinol acetate.

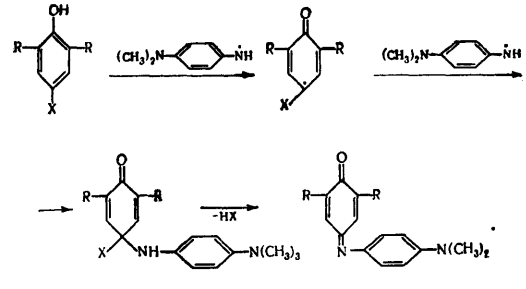
Completely different reaction products are obtained by the action on phenols of acetyl peroxide in acetic acid solution. Thus, for example, mesitol under these conditions gives an 80% yield of the acetate of the corresponding substituted benzyl alcohol[200]:



Mesityl methyl ether does not react with acetyl peroxide in acetic acid, which further confirms the formation of a phenoxy-radical in the course of the above reaction.

The reaction of benzoyl peroxide with phenols has its own peculiarities. It differs from those using lead tetraacetate and acetyl peroxide firstly in that *p*-quinol benzoates are obtained, and secondly in that it is usually accompanied by the formation of large quantities of dimers of the phenoxy-radicals (and of the benzyl radicals in the case of 2,4,6-trialkylphenols). Sometimes one of these reactions may predominate. In the oxidation of mesitol with benzoyl peroxide, for example, a 90% yield of the *p*-quinol benzoate is obtained together with the *p*-stilbenequinone[182]. In the oxidation of Ionol with benzoyl peroxide, a *p*-stilbenequinone derivative was isolated as the sole product of the reaction. 2,4,6-Tri-t-butylphenol reacts with benzoyl peroxide forming the phenoxyl[206].

In 1955 Hünig and Daum[207] published some very interesting work on the formation of quinoamines by the interaction of phenols with radicals obtained by the oxidation of *NN*-dimethylphenylenediamine with potassium ferricyanide. Formation of quinoamines occurs only when the original phenols contains a *p*-alkyl group. In the presence of other groups this radical reaction leads to their replacement by a *p*-dimethylaminoanilino-group. The process occurs as follows:



If X = H, Cl, Br, or even CH_2OH, these groups are eliminated. From mesitol (X = R = CH_3), a 30% yield of the quinoamine is obtained as a salt of perchloric acid. Its structure has been confirmed by elemental analysis and the infra-red and ultra-violet spectra. Reduction of this quinoamine yields mesitol. The quinoamine rearranges readily into 4-aminomethyl-2,6-dimethylphenol. Ionol [X = CH_3, R = $C(CH_3)_3$] and 2,4,6-tri-t-butylphenol [X = R = = $C(CH_3)_3$] form more stable quinoamines than does mesitol.

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The above examples of the formation of cyclohexadienones in electrophilic and radical reactions of phenols may prove useful for an understanding of many of the changes undergone by phenols and their derivatives.

Sterically hindered phenols exhibit an especially marked tendency to form cyclohexadienones. Such phenols display a very specific behaviour also in other reactions, a discussion of which may be of definite interest too.

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USE OF REAGENTS OF THE ARSENAZO–THORON GROUP IN ANALYTICAL CHEMISTRY

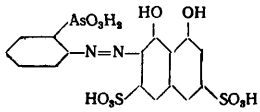
S. B. Savvin

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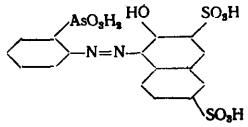
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1. GENERAL REVIEW OF APPLICATIONS

The reagents Arsenazo I [1] and Thoron I [1,2] synthesised by Kuznetsov in 1941 were the first of the general class of reagents of the arsenazo–thoron group:



Arsenazo I



Thoron I

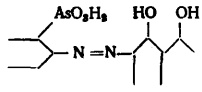
The main use of these reagents is in inorganic spectrophotometric analysis, but they are also used in complexometry, extraction, and coprecipitation methods. More than 40 elements can be detected by reagents of the arsenazo group, and quantitative methods have been developed for the determination of 20 of these in various materials.

Organic reagents containing the arsono-group AsO_3H_2 had previously been used widely in inorganic analysis, the best known being phenylarsonic acid. The presence of the arsono-group causes the formation of particularly stable complexes with several elements, such as zirconium, niobium, and thorium. The reaction products with phenylarsonic acid and many of its derivatives are colourless; the reagents are mainly used for the gravimetric determination of elements or for the removal of interfering elements.

The reagents of the arsenazo group are characterised by the presence of the arsono-group and also an azo-group in the *ortho*-position to it; almost always there is a

hydroxy-group *ortho* to the azo-group. Several dozen reagents of this type are now known, but only certain of them have been widely used.

The very convenient combination of the AsO_3H_2, OH, and azo-groups into a single complex functional group:



has provided a whole series of analytically valuable reagents. The presence of the salt-forming AsO_3H_2 group produces complexes of sufficient stability for complex-formation to take place even in acid solutions, the azo-group provides colour, and because of the hydroxy-group a second six-membered ring containing the cation can be formed, which not only substantially increases the stability of the complex, but also gives a deeper colour.

The relative complexity of the functional group means that reagents of the arsenazo group are not specific for any one element, but are group reagents; this is convenient in that a series of elements can be determined with a single reagent, but the necessary selectivity always requires special working conditions.

The exceptionally valuable analytical properties of arsenazo and its more recently developed analogues have caused them to be widely used in analysis; the relevant literature contains several hundred references, including reviews on the use of Thoron I [3], Arsenazo I [4,5], and Arsenazo III. [6]

The use of reagents of the arsenazo group is a successful complement to the use of dithizone, which is employed mainly for elements of the hydrogen sulphide group; satisfactory photometric methods have long been known for the determination of these elements and for certain others, *e.g.* those which have a chromophoric action or form ammines, but no convenient and sensitive methods were known for the determination of thorium, zirconium, hafnium, uranium, protactinium, beryllium, aluminium, the rare-earth elements, and several others, with a few exceptions [7]; arsenazo has proved to be useful for just these "difficult" elements.

The reagents of the arsenazo group are readily prepared by coupling diazotised *o*-aminophenylarsonic acid or its derivatives with any coupling component. Chromotropic acid is especially suitable as the latter; the resulting reagents are more sensitive than many described in the literature for the spectrophotometric determination of various elements.

2. MAIN PROPERTIES OF THE REAGENTS

Not all the reagents described in this section are equally widely used in analysis. The most widely used are Arsenazo I, Thoron I, and Arsenazo III.

The reagents of the arsenazo group are dark red powders, readily soluble in water to give a pink solution. The orange-red Thoron I and II dissolve to give an orange-yellow solution. Arsenazo I, II, and III form violet, blue, or even, with Arsenazo III, green complexes with elements. Complex formation with reagents of the thoron group, derivatives of R-salt, etc., produces less deep crimson colours.

Arsenazo I

The first studies of the properties of arsenazo [1,2,8] showed it to be a very valuable analytical reagent, primarily because it gives colour reactions with elements for which no convenient methods of determination had previously been known. The high sensitivity of these colour reactions (the molar extinction coefficients are of the order of several tens of thousands) enables micro-quantities of the elements (from 0.05 to 0.1 $\mu g\ ml^{-1}$) to be detected. Finally, the relatively high stability of the complexes enables elements to be determined even in acid solution, which is extremely valuable in analytical practice.

The high sensitivity of the reactions is due to the relatively large shift of the absorption spectrum of the complex in comparison with that of the reagent; Fig. 1 shows these spectra for the reagent and its thorium complex. The absorption spectra of other complexes resemble closely that of the thorium complex.

Methods have been developed for the determination, using Arsenazo I, of uranium [9-20], thorium [20-32], zirconium [33-38], scandium [39], lanthanum [40], cerium [41], total rare-earth elements [42-46], aluminium [47,48], beryllium [49-51], titanium [52], niobium [33,42,53], tantalum [54], vanadium(IV) [17], and indium [55]. Colour reactions also suitable for their determination have been described for tin, bismuth, gallium, copper, palladium(II), magnesium, and calcium.

One of the features of the use of Arsenazo I is the possibility of obtaining high selectivity by variation of pH, which is not always possible with other reagents, *e.g.* Thoron II. Examples are the selective determination of thorium in the presence of large amounts of rare-earth elements [21], of zirconium and thorium in the presence of UO_2^{2+}, and of UO_2^{2+} in the presence of rare-earth elements, calcium, and others [5,9,33]. The comparatively low stability of Arsenazo I complexes (in comparison with other reagents of this type) enables it to be used as an indicator in the complexometric determination of plutonium [56], thorium [57-59], total rare-earth elements [60-62], and fluoride (by titration with Th) [63-65].

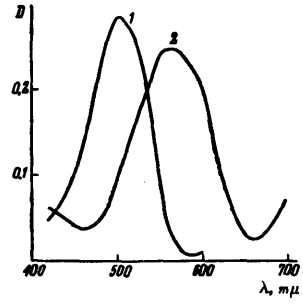
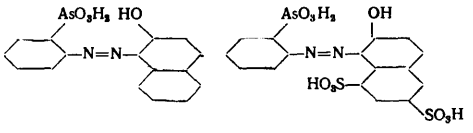


Fig. 1. Absorption spectra of 10^{-5} M solutions (at pH 2.0) of: 1) Arsenazo I; 2) Arsenazo I thorium complex.

Thoron I

Reagents of the thoron group are prepared from R-acid†, β-naphthol, or derivatives of β-naphthol as coupling component. As well as Thoron I [1,2] several analogues are known [4,5], *e.g.*:



extract thoron iso-thoron

Thoron gives somewhat less sensitive colour reactions than arsenazo; because of this, and because of the somewhat simpler analytically functional group, the number of elements which react with thoron is limited, *i.e.* thoron is more selective than arsenazo.

Thoron I has been most used for the determination of thorium [66-89]. The high reproducibility of results, the convenient working conditions (acid medium of pH 0.7–1.2) and the high selectivity make this a very efficient method; thus no interference in the determination of thorium is caused by the presence of more than 100- to 1000-fold quantities of rare-earth elements, UO_2^{2+}, and other elements. With the extraction-photometric variants of the determination described below, the tolerable ratio of thorium to certain other elements reaches 1 : 10^6.

Thoron I is used to a lesser extent for the photometric determination of plutonium [90], neptunium [91], total rare-earth elements [40], uranium(IV) [92,93], zirconium [94], beryllium [50,95,96], and lithium [97-100], and for the complexometric determination of thorium [101], uranium [102], bismuth [103,104], fluoride [105-107], and sulphate [108,109].

Table 1 gives the absorption maxima of various reagents and their thorium complexes, the shift of the maximum $\Delta\lambda$, which determines the contrast‡ of the reaction, and the working value of λ selected so as to reduce the effect of the excess of reagent as much as possible.

TABLE 1. Spectrophotometric data on reagents and their complexes.

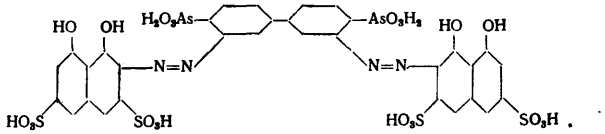
Reagent	Absorption maximum, mμ		Δλ	λ (working)
	reagent	thorium complex		
Arsenazo I	500	555	55	580
Thoron I	475	505	30	545
Arsenazo II	510	550	40	600
Thoron II	480	520	40	560
Arsenazo III	540	665	125	665

† 2-Hydroxynaphthalene-3,6-disulphonic acid (Ed. of Translation).

‡ The term "contrast" is used here apparently synonymously with selectivity (Ed. of Translation).

Arsenazo II

The reagent Arsenazo II [5] is an analogue of Arsenazo I in which the analytically functional group appears twice:



Arsenazo II

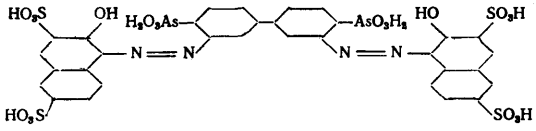
Its preparation has been described by Kuznetsov and Savvin [110]. A feature of the reagent is the substantially increased stability of its complexes, so that the optimum pH values for its reaction with elements is in the more acid region: thus Th and Zr can be determined in 0.1–0.6 *N* HCl. Interference due to masking anions (sulphates, phosphates, fluorides) is much reduced.

The selectivity of action of Arsenazo II is about the same as that of Arsenazo I; it reacts in acid solution with zirconium, hafnium, titanium, thorium, uranium(IV), and iron(III); in weakly acid and neutral solution with aluminium, indium, gallium, uranium(VI), rare-earth elements, copper, and beryllium; and in alkaline solution with calcium, magnesium, barium, zinc, cadmium, lead, and manganese.

Procedures have been developed for the determination of thorium in monazites [111,112], UO_2^{2+} in uranium ores [113], and scandium [39]. The reagent may apparently also be used for the determination of zirconium, hafnium, total rare-earth elements, vanadium(IV), beryllium, and gallium [5].

Thoron II

This is also the analogue of the corresponding monoazo-compound with two analytically functional groups [5]:



Thoron II

Its preparation has been described by Kuznetsov and Savvin [110]. An important feature of Thoron II, not shared by Thoron I, Arsenazo II, or many other reagents, is its ability to form with thorium, zirconium, uranium(IV), and the rare-earth elements very stable complexes which are not decomposed even in strongly acid solution. The reagent has been used to determine thorium [114], and its use for the determination of zirconium and certain rare-earth elements looks very promising [5,114]. A disadvantage of this reagent is the low contrast of the reaction.

Arsenazo III

Arsenazo III was prepared by Savvin in 1959 [115]; its properties have been described [6].

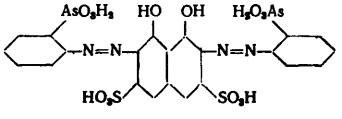


TABLE 2. Colour reactions of Arsenazo III.

Element	Colour of complex*	Reaction conditions	Conditions for maximum sensitivity		Molar extinction coefficient**
Th	green	0.01 – 10 *N* HCl	9 *N* HCl	665 λ, mμ	130 000
Zr	green	0.2 – 12 *N* HCl	9 *N* HCl	665 λ, mμ	120 000
Pa	green	1 – 10 M HCl or H_2SO_4	7 M H_2SO_4	660 λ, mμ	22 000
Hf	green	0.2 – 12 *N* HCl	9 *N* HCl	665 λ, mμ	95 000
U^{IV}	green	0.05 – 10 *N* HCl	4 *N* HCl	670 λ, mμ	100 000
UO_2^{2+}	green	pH 1 – 4	pH 2.0	665 λ, mμ	53 000
Sc	violet	pH 1 – 4	pH 1.7	675 λ, mμ	19 000
I	green	pH 3 – 4	pH 3.0	655 λ, mμ	55 000
La	green	pH 3 – 4	pH 3.0	655 λ, mμ	45 000
Ce	green	pH 3 – 4	pH 3.0	655 λ, mμ	47 000
Ca	blue	pH 4 – 5	pH 5.0	655 λ, mμ	10 000
Pb	blue	pH 4 – 5	pH 5.0	655 λ, mμ	10 000
Bi	violet	pH 1.5 – 4.5			
Fe^{III}	violet	pH 1.5 – 3			
Cu	violet	pH 4.5 – 5			
Ba	blue	pH 4.5 – 5			

* The reagent is pinkish crimson.

** Approximate data

Arsenazo III gives colour reactions with many elements, although with a smaller number than Arsenazo I. Its main distinguishing feature is the ability to form particularly stable inner complexes, so that elements can be determined in strongly acid media [*e.g.* thorium, zirconium, hafnium, protactinium, and uranium(IV) in up to 10 *N* HCl] and in the presence of complex-forming anions which normally interfere in the direct determination of the elements.

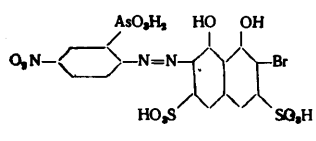
The sensitivity of the colour reactions can reach 0.01 – 0.05 μg of elements per ml. The most sensitive methods are those for the determination of thorium, zirconium, uranium, protactinium, scandium, and the rare-earth elements, and the least sensitive, those for lead, bismuth, iron, copper, calcium, and barium; methods with the greatest selectivity are those developed for the determination of thorium[97,116-125], uranium[115,126-128], zirconium[6,129-135], hafnium[131], rare-earth elements[136], and protactinium[137] in various materials. The analytical use of Arsenazo III and the mechanism of its reaction have been reviewed[6,139].

Table 2 lists the elements which give colour reactions with Arsenazo III, the resulting colours, the reaction conditions, and the sensitivity.

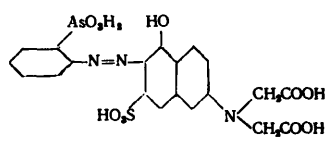
Other Arsenazo Analogues

A large number of derivatives and analogues of Arsenazo I, Thoron I, and particularly Arsenazo III have been prepared in recent years. Preliminary studies have shown many of these to be valuable analytical reagents[116,119].

Bromonitroarsenazo (I) has been recommended for the determination of lithium, and for the extraction-spectrophotometric determination of elements[138]. The reagent (II) prepared by Kuznetsov and Bol'shakova, has proved particularly useful for the determination of beryllium:

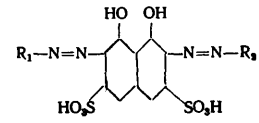


(I)

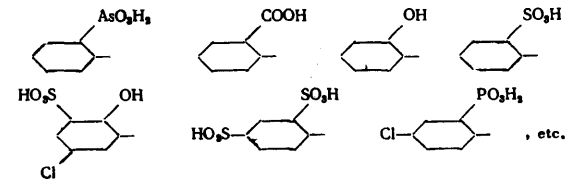


(II)

Arsenazo III analogues of analytical value are the bisazo-compounds obtained from chromotropic acid and various amines, of the general formula:

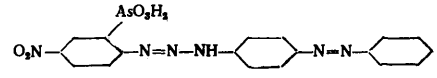


where R_1 and R_2 are the residues of the substituted anilines:



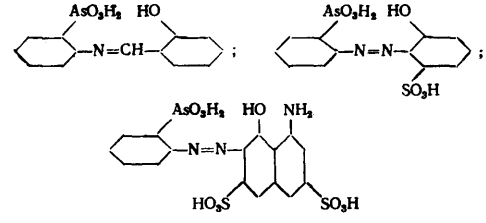
A general feature of these last reagents is that they form highly stable complexes with elements, and many have proved of interest for the determination of niobium, zirconium, hafnium, uranium, strontium, scandium, barium, and many other elements[140-145].

The use of "Arsazen":



has been suggested for the extractive determination of lead[146].

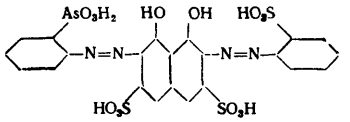
Many monoazo-compounds derived from *o*-aminophenylarsonic acid and various coupling components have been described, *e.g.* [2,147-149]:



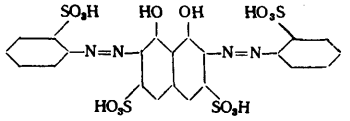
These all give colour reactions with thorium, zirconium, and several other elements in a near-neutral medium; the resulting complexes are relatively unstable and are readily decomposed by many masking complex-forming reagents (sulphates, phosphates, etc.). These reagents and others do not match up to those based on chromotropic acid and R-salt, and have not found wide analytical use.

Reagents which do not contain the AsO_3H_2 group do not belong formally to the arsenazo group of reagents (*i.e.* those containing arsenic and an azo-group), but a very close analogy in their analytical behaviour makes it convenient to consider them together with reagents containing the AsO_3H_2 group; the nature of the salt-forming group affects only the selectivity of the reagents, and not the mechanism of the complexing and colour reactions. We shall give a few examples.

The reagents (III) and (IV) are of use for the determination of barium and strontium in acid media (to pH 1)§ [142]:

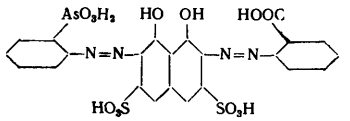


(III)

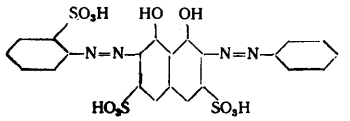


(IV)

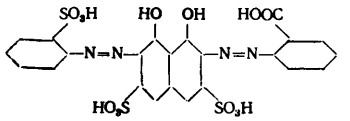
Reagents (III) and (V)–(VIII) have been used as indicators for barium ion in the volumetric determination of sulphate [142-143]:



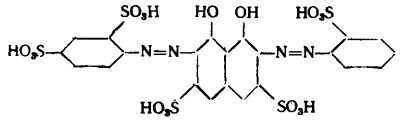
(V)



(VI)

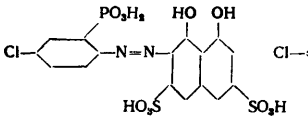


(VII)

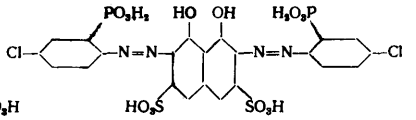


(VIII)

Reagents (IX) and (X) have been recommended for the determination of uranium [144,145]:

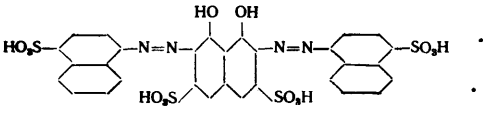


(IX)



(X)

Datta and other Indian workers have described a whole series of reagents based on chromotropic acid, which are useful for the photometric determination of thorium, zirconium, and others [140,141]. The best known is di-SNADNS, which is often used as an indicator for metal ions [150]:

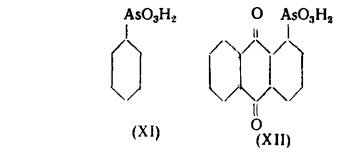


We cannot mention here all the reagents of this type, since the number derived from chromotropic acid, H-acid¶, and other naphthalene sulphonic acid coupling components described in the literature is so great that they would require a separate review.

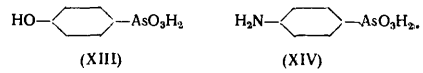
Other Reagents Containing the AsO_3H_2 Group

Colourless reagents containing the arsono-group are mainly used as precipitants for heavy metals and for their subsequent gravimetric determination or separation from other elements. We shall consider them here in less detail.

Phenylarsonic acid (XI) is the best known reagent of this group. It is used mainly for the precipitation of zirconium to separate it from other elements [151-153]; precipitates are also formed only with tin, titanium, niobium, tantalum, and cerium(IV), and the influence of these elements can be removed by adding hydrogen peroxide, after first removing tin. Phenylarsonic acid is also used for the detection of niobium and tantalum [154,155], tin(IV) [156,157], and thorium in monazite sands in the presence of rare-earth elements [158].



(XI) (XII)



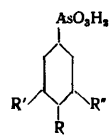
(XIII) (XIV)

Anthraquinone-α-arsonic acid (Anthraquas) (XII) is used to precipitate small amounts of tin(IV), zirconium, and titanium from dilute solutions [159]; because of the increased size of the molecule there is a certain increase in sensitivity as compared with phenylarsonic acid.

p-Hydroxyphenylarsonic acid (XIII) is used for the precipitation and gravimetric determination of titanium [160] and zirconium [161]. Arsanilic acid (XIV) is used for the detection of cerium by a colour reaction (appearance of a reddish-brown colour because of the chromophoric action of cerium) [162] and for the detection of zirconium (formation of a white precipitate) [163].

Propylarsonic acid, allylarsonic acid, and other alkylarsonic acids are used to precipitate zirconium [164,165].

A group of reagents of general formula:



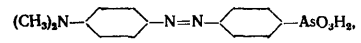
(where R is H, OH, NH_2, CH_3, C_6H_5, $NHCOCH_3$, or $NHCH_2$. .COOH and R′ and R″ are H, Cl, NO_2, or COOH) have been described; they are suitable for the precipitation of tin(IV), zirconium, and thorium [166-168], but have not found wide use.

§ In these compounds the grouping containing the AsO_3H_2 group does not take part in the reaction with barium and strontium.

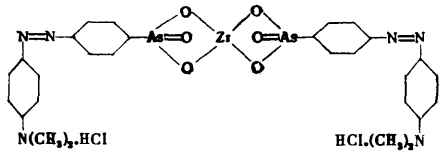
¶ 1-Amino-8-hydroxynaphthalene-3,6-disulphonic acid (Ed. of Translation).

This class of precipitating agents contains the coloured compounds having an arsono-group in a position other than *ortho* to an azo-group. In this case the reaction produces simple salts of the AsO_3H_2 group; there is no formation of inner complexes or any sharp colour change.

The most studied reagent of this type is *p*-dimethylaminophenylazophenylarsonic acid:

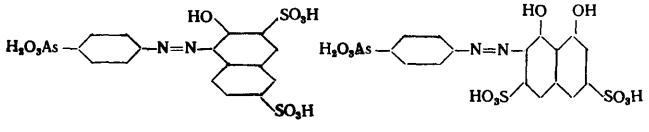


which forms with zirconium the brownish red salt[169-172]:



The sensitivity of the reaction is 10 μg ml^{-1}; many elements do not interfere.

Azo-dyes derived from arsanilic acid, with R-salt and chromotropic acid as coupling components[2,147-149]:



form simple salts with zirconium, thorium, and other elements, and may be used for their precipitation.

3. THE ATTAINMENT OF SELECTIVITY

The simplest method of increasing selectivity is by adjustment of the acidity of the solution, since the optimum pH for the reaction of a reagent with an element depends on the latter. For reagents of type ROH there is a definite correlation between colour reactions and hydrolysis[173]; thus colour reactions with coloured reagents are only given in strongly acidic media by elements whose cations are readily hydrolysed: zirconium, hafnium, uranium(IV), and thorium; in moderately acid solutions colour reactions are given, in addition to the above, by iron(III), aluminium, and UO_2^{2+}; in weakly acid and neutral solutions by rare-earth elements, iron(II), and copper; and in alkaline solutions by calcium, strontium, and magnesium. This series is not of course absolute in character, and applies only to reagents of type ROH.

The reaction conditions depend on the reagent used, but for each reagent the optimum pH depends on the element in the same way: readily hydrolysed elements react in a more acidic medium, and other elements in a less acidic medium.

Variation of the acidity is not the only method for increasing the selectivity. It is often recommended that the interfering elements present should be complexed as stable colourless complexes; this is only possible when under the given conditions (at a definite pH) the complexes formed by the complexing agent with the element to be determined and the impurity have greatly differing stabilities. A well-known example is the system UO_2^{2+}–Trilon B–other elements. When uranium is determined with Arsenazo II, aluminium is readily masked with sulphosalicylic acid†, and titanium with tartaric acid[113]. In the determination of uranium with Arsenazo III thorium is masked with fluorides[126]. In the determination of thorium with Arsenazo III zirconium is very selectively masked with oxalic acid[115]. Many other examples could be given.

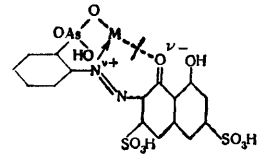
The so-called confirmatory reactions, when under the given conditions only the element to be determined is selectively masked, are sometimes very useful. By measuring the optical density before and after the addition of the masking agent, the interference due to the presence of other elements can be estimated. The use of hydrogen peroxide has been suggested in the determination of uranium with Arsenazo I,[9] sodium hexametaphosphate in the determination of thorium with Arsenazo III,[120] and phosphates in the determination of the rare-earth elements[42].

Another method for increasing selectivity is to use the so-called extraction–photometric procedure, which has only recently been described[138,174]; this combines extraction and photometry in one operation, and gives high selectivity with certain elements (thorium[116,119], UO_2^{2+} [126]).

In many cases a combination of these methods for thorium, protactinium, zirconium, hafnium, uranium(IV), plutonium, neptunium, and UO_2^{2+} will ensure a good selectivity in the determination. When materials of complex composition or of low content of the elements to be determined are analysed it is usually necessary to remove interfering elements before the determination.

4. NATURE OF THE COLOUR REACTIONS

The mechanism of the colour reaction has been discussed in many papers[21,95,136,175,176]. For example, the complex of arsenazo with bivalent elements may be represented:



With aluminium, copper, and certain other elements the hydroxy-groups of the naphthalene residue may participate in the formation of the complex.

In general, a colour reaction occurs if the element reacts with the dyestuff molecule in such a way that there is a direct effect on the atom or group of atoms of the reagent molecule which are responsible for its colour, *i.e.* on the chromophoric group[177,178]. In azo-dyes the –N=N– group is usually considered to be the chromophore, but it is more accurate to treat the molecule as a whole as a single conjugated system with π-bonds; therefore, if groups directly attached to the conjugated system (*e.g.* the OH group) take part in the formation of the complex, a colour reaction will occur. It is an established experimental fact, however, that direct action on the azo-group of a dyestuff molecule produces a larger optical effect than action on the peripheral part of the molecule; for instance, the aluminium complex of arsenazo is red-violet, while the UO_2^{2+} complex is blue. This has been established by studying the absorption spectra of the pure reagents in concentrated sulphuric acid, when the azo-group is protonated and deep violet,

† 2-Hydroxybenzoic-5-sulphonic acid (Ed. of Translation).

blue, and green colours are observed, corresponding to those of the complexes of UO_2^{2+}, Th, and other elements; and in alkalis, where the naphthalene hydroxy-groups are ionised and less deep red-violet colours are obtained, corresponding to the colours of aluminium and copper complexes.

The greatly increased depth of colour when complex--formation occurs is thus due firstly to the formation of a certain positive charge on the "chromophoric centre of the molecule" (the azo-group), and secondly to the formation of a certain negative charge on the residue of the naphthalene hydroxy-group. In order to indicate the partially ionic character of the $M^{\nu+}-O^{\nu-}$ bond, we here use the symbol M.../...O (intramolecular ionisation, after Kuznetsov[175,179-181]). The dipole formed at the ends of the system of conjugated bonds causes a sharp change in the colour of the reagent, *i.e.* it produces the corresponding colour reaction. The metal cation thus acts as an independent very strongly positive auxochrome, and at the same time the two six-membered rings which are formed, and which have almost aromatic properties, produce substantial stabilisation of the molecule.

Complex-formation with Arsenazo III shows a number of interesting features[115,136,139]. It has been shown that in the free state the Arsenazo III molecule is symmetrical but not planar, because of steric hindrance caused by the AsO_3H_2 groups. When complex-formation takes place, the planarity of the molecule may be partially restored, which is another factor producing a considerable deepening in colour[139].

The two analytically functional groups of the Arsenazo III molecule form part of two weakly interacting almost isolated conjugated systems, only one of which participates in complex-formation; this destroys the symmetry and creates two absorption bands in the complex in the visible region (Fig. 2). The reduced reactivity of the second analytically functional group when the first takes part in complex-formation may be related to the possible production of a certain positive charge on the second azo-group,

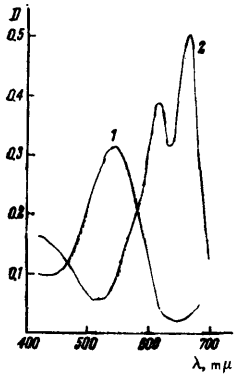


Fig. 2. Absorption spectra of 10^{-5} M solutions in 9 *N* HCl of: 1) Arsenazo III; 2) Arsenazo III thorium complex.

which hinders the formation of a second $M^{n+}-N$ bond. The longer conjugation system in Arsenazo III as compared with Arsenazo I, and the resulting possibility for the spread of the positive charge produced on the first azo-group, may be reasons for the increase in the stability of the M–N bond, which determines the stability of the whole complex[139].

Several studies have been devoted to the determination of the dissociation constants of Arsenazo I and Thoron I[182-184] and the instability constants of their complexes with a number of elements[176,185]. The very interesting quantitative data obtained require a special review.

5. FIELDS OF USE

Spectrophotometry is the main field in which the reagents of the arsenazo group are used. They show two typical features. The first is their ability to form stable complexes, which is of obvious interest for analysis, since it allows the use of strongly acid solutions, where there is no hydrolysis, conversion of the ions of the element into slowly reacting multinuclear ions, or other undesirable effect. The reproducibility of results and the reliability of the determination are greatly increased, there is no need for careful maintenance of the pH, and the experimental procedure is simplified; the influence of anions is reduced to the minimum. Particularly stable complexes are formed by the bisazo-derivatives of chromotropic acid, Arsenazo III and its analogues.

The second feature is the high sensitivity of the colour reactions: for some elements the determinable minimum concentration is 0.01–0.1 μg ml^{-1}, with molar extinction coefficient $100-150 \times 10^3$.[116,119] The high sensitivity is due to the nature of the absorption spectra of the complex and reagent, and to the high stability of the complexes formed, which enables the element to be completely complexed even at high dilution[119,187,188].

Arsenazo I has been employed as an ingredient in an *organic coprecipitant*, which can concentrate plutonium[189,190], americium[190], and rare-earth elements[191] from dilute solutions. The theory of the action of organic coprecipitants and the features of their analytical application have been discussed by Kuznetsov[192]. Methyl violet and certain other highly coloured basic dyestuffs have been used in the coprecipitants, but colourless organic coprecipitants may also be used; in this case the filtered precipitates can be dissolved in a small volume of organic solvent and the coprecipitated element determined directly by photometry of its complex with the reagent. In this way the element is simultaneously concentrated and determined. Ashing of the organic precipitate or its decomposition with acids are not required. These methods are exceptionally convenient for the determination of elements in extremely dilute solutions[138]. A method has been described for the coprecipitation of the diphenylguanidinium salt of the Arsenazo III complex of thorium with diphenylguanidinium anthracene-α-sulphonate as carrier, which can determine thorium at a dilution of 1 in 10^9.[119]

Another new use for reagents of the arsenazo group is in the so-called *extraction–spectrophotometric* methods of analysis[138,174]. The selectivity and sensitivity can be increased by combining spectrophotometry with preliminary extraction of the element; the spectrophotometry is best carried out directly in the organic phase, without re--extraction, but for this purpose only reagents soluble in organic solvents, such as dibenzoylmethane, can be used,

while the sulphonato-group-containing reagents of the arsenazo group are insoluble in non-aqueous solvents.

It has been shown that the hydrophilic action of the sulphonic acid groups and their anionic constitution, which hinder the extraction, can be removed by forming simple salts with heavy organic cations containing at least 10–12 carbon atoms; the most suitable is the diphenylguanidinium cation $[(C_6H_5NH)_2CNH_2]^+$.[138,174] When triply- and in some cases quadruply-charged cations are used for complex-formation with the reagent some of the cationic charge may be retained; this is compensated by adding an anion suitable for extraction. Thiocyanates, perchlorates, and chloroacetates can be used as hydrophobic anions. The hydrophilic action of the complex, caused by the partial charges distributed in different parts of the molecule, can be substantially reduced if the extractant molecules can replace water molecules in the solvates[193]. The most convenient solvents are butanol and pentanol, but hexanol, benzyl alcohol, cyclohexanone, and a solution of ethanol in chloroform can also be used[138,148].

The extraction of inner complexes has been considered from the point of view of the coordination saturation or unsaturation of the central atom[193]; extraction is thought to occur only when all the coordination positions of the central atom are saturated by the reagent used, by molecules of other substances present which can take part in coordination, by molecules of the organic solvent, and so on. These matters have been considered in detail in Zolotov's review (see p.107).

Examples of the extraction–spectrophotometric method are the determination of uranium[126] and thorium[116,119] with Arsenazo III.

The extraction of known reagents can be increased by using their bromo-, chloro-, or nitro-derivatives.

In the last few years the reagents of the arsenazo group have begun to be widely used as *metal-indicators* in the complexometric determination of elements; methods have been described for the volumetric determination of thorium[57-59,102], rare-earth elements[60-62], and plutonium[56]. For a high sensitivity and accuracy in the volumetric determination there must be a certain relationship between the stabilities of the complexes formed by the element with the indicator and with the complexing agent; this relationship depends on the element concerned, the pH conditions, the concentration, and other factors[60]. In this respect reagents of the arsenazo group show great possibilities. Of the large number of compounds described, it is always possible to select a series of reagents which will give a colour reaction with the given element but form with it complexes of different stabilities. The bisazo-derivatives of chromotropic acid are particularly useful, since by variation of the radical R_z it is possible to retain a colour reaction with the given element, but at the same time to provide reagents which produce complexes of greatly different stabilities[119]. The stabilities of the complexes in such cases can be determined most conveniently by the method of "particular instability indices"[194], which gives exceptionally rapid results. An example is the determination of the rare-earth elements, in which less than 1–2 μg of a particular element per ml can be determined with an accuracy of 1–2%.[60]

In the complexometric determination of readily hydrolysed elements — zirconium, thorium, uranium(IV) — or elements which tend to form oxo-ions (aluminium, chromium), the titration is preferably carried out in strongly acid solution. Certain bisazo-derivatives of chromotropic acid may prove useful here.

The reagents of the arsenazo group have not found wide application as *precipitants*. The precipitation of Zr with Arsenazo I has been described[195]. The separation of Th and Zr from other elements by adsorption of their complexes with Thoron I on activated carbon is of interest[196]. The most useful reagents for these purposes, as for co-precipitation with coloured or colourless precipitants, are those of higher molecular weight: Arsenazo II, Thoron II, and bromo- and nitro-derivatives of Arsenazo III.

The use of these reagents for the *chromatographic separation* of elements has been little studied, although it may reveal new possibilities.

6. QUANTITATIVE ANALYTICAL METHODS

Thorium

This element, which once presented serious difficulties analytically, can now be determined photometrically in almost any material, even in trace amounts. The use of Thoron I has been the most studied. After early work describing the colour reaction, the conditions for the determination and the selectivity[1,2], a series of independent papers appeared describing the determination of thorium in various materials[66-89].

Methods using Arsenazo I are somewhat more sensitive; the reaction has been studied in detail by Kuznetsov and Nikol'skaya[21]. The method has been described in Japanese[29-32] and other[22-28] papers. Zaikovskii and Gerkhard suggested the use of tartaric acid to mask Zr and Ti.[22,23]

The determination of Th with Arsenazo II is carried out in 0.2 *N* HCl under conditions such that the influence of many other elements is reduced to a minimum; zirconium and titanium are masked with phosphates. The determination of thorium in monazites[111], granites, and other minerals[112] has been described.

With Thoron II the determination can be effected in strongly acid media, where the influence of sulphates and phosphates is low; zirconium and titanium are masked with oxalic acid[114]. A method for the determination of micro-quantities of thorium oxide, ThO_2, has been developed[114].

The use of Arsenazo III appears to be the most promising[6,115]. The experimental conditions are: 3.0–9.0 *N* HCl, 1.5–2% oxalic acid to mask zirconium, and 0.002% Arsenazo III; the sensitivity is 0.05–0.1 μg of thorium per ml[6,115]. Sulphates, oxalates, and phosphates do not interfere. Methods have been developed for the determination of micro-quantities of thorium[119] and for the determination of thorium in zircons[117], metallic tungsten[124], products containing niobium and titanium[121], rocks[118,120], and other materials[97,121-123]. An extraction–spectrophotometric method using Arsenazo III has been developed, which can determine for example 1 μg of thorium in 1 litre of solution[119]. Methods have been described for coprecipitating thorium with Arsenazo III with colourless and inert coprecipitants[119,120].

In the absence of zirconium, thorium can be determined in 50% hydrochloric acid (~ 6 M) without adding oxalic acid. The sensitivity is a maximum in 8 M HCl. With a 5 cm photometric cell 0.01 μg of thorium per ml can be

determined[119]. Because of the high acidity, oxidants such as nitric acid and chlorine, which are sometimes found in commercial acids, must be absent. It is best to use distilled hydrochloric acid.

Various procedures have been described for use with specific materials; these differ mainly in the method used to decompose the sample and remove the base material, the photometry being carried out under practically the same conditions in each case. For rocks the following procedure may be used: 0.1–0.5 g of rock containing 0.0001% of thorium or more, *i.e.* assumed to contain 1–25 μg of thorium, is decomposed with hydrofluoric acid, the solution evaporated, the residue moistened with the same acid and treated with water, the filtered residue treated with perchloric–hydrochloric acid mixture, the solution evaporated, the residue dissolved in hydrochloric acid, the reagent is added, and the solution subjected to spectrophotometry[118].

To determine thorium in zircons, 0.1 g of the material is fused with potassium hydrogen fluoride at 800°–900°, the melt treated with sulphuric acid (1 : 1), and the solution evaporated to remove all the fluorine. The residue is dissolved in hydrochloric acid and the solution subjected to spectrophotometry[117].

In the determination of thorium in silicate rocks, zirconium, titanium, and the rare-earth elements are removed by ion exchange on cation-exchange resin KU-2‡ in the hydrogen-form. Titanium is not adsorbed from 1 M hydrochloric acid; the rare-earth elements are eluted with 2 M hydrochloric acid and zirconium with 0.5% oxalic acid, and then thorium is quantitatively eluted with saturated ammonium oxalate solution. The thorium is then determined with Arsenazo III in 5 M hydrochloric acid without removing the oxalates, which do not interfere. The sensitivity corresponds to 10^{-3}–10^{-4}% of thorium in the specimen[125].

The concentration of thorium from sea or river water has been described, with its subsequent photometric determination in the precipitates with Arsenazo III by "wet ignition" and with reprecipitation of the thorium to remove impurities present in the water. Quantities as low as 0.5–1 μg of thorium can be separated and determined from 20 litres of sea or river water[120].

Because of its high sensitivity combined with good selectivity, especially with respect to anions, the method using Arsenazo III is recommended for the rapid determination of micro-quantities of thorium present as ThO_2. The material is dissolved in sulphuric acid and the ThO_2 determined without removing the sulphates. Such determinations are required in the extraction and evaporation of solutions, and in the determination of thorium in aerosols, biological materials, blood and other cases requiring its determination for medical and health purposes.

Uranium

The highly sensitive reaction with Arsenazo I is most frequently used for the determination of uranium[1,9-20]; zirconium, thorium, titanium, aluminium, iron, the rare-earth elements, and some other elements interfere. With low contents of other elements their influence can be eliminated by adding Trilon B or by utilising the decomposition of the complex of UO_2^{2+} with arsenazo when hydrogen peroxide is added[9,197]. The determination is carried out at pH 4.5–6. A successful method for increasing the selectivity is to combine extraction with spectrophotometry[126,197,198]. Another method for greatly increasing the selectivity is to reduce the uranium to uranium(IV) and determine the latter in the same way as for thorium.

A complexometric method for the determination of uranium(IV) using Arsenazo I as metal indicator has been described. Methods for the chromatographic separation of uranium from impurities have been suggested[199]. An extremely useful method for determining uranium involves preliminary extraction of uranium(VI) with ethyl methyl ketone in the presence of Complexone III.[200]

Thoron I has been proposed for the determination of uranium(IV)[92,93] in 0.1–0.3 *N* HCl; many elements do not interfere.

A method for the determination of uranium in ores with Arsenazo II has been developed, using readily fusible extractants to separate uranium from impurities[113]; sulphates and relatively large amounts of phosphates do not interfere. Iron(III), vanadium(IV), copper, the rare-earth elements, and in part aluminium, titanium, and thorium are masked by adding the calcium salt of Trilon B; aluminium is readily masked with sulphosalicylic acid, titanium with tartaric acid, and thorium with fluorides[113].

Arsenazo III can be used to determine both UO_2^{2+} (pH 1.5–2) and uranium(IV) (4–10 *N* HCl)[115]. An extraction–spectrophotometric procedure has been developed for determining uranium in ores, comprising the extraction of the UO_2^{2+}–Arsenazo III complex with butanol from a solution saturated with Trilon B and containing potassium fluoride to mask thorium and other elements[126]. A highly selective method developed for the determination of uranium(IV)[127] comprises the reduction of uranium with zinc metal and ascorbic acid in one aliquot of the solution, addition of the reagent to this and a fresh aliquot, adjustment of the acidity to 4.5 *N* HCl, and measurement of the optical density of the second solution against the first. The influence of other elements is thus eliminated. Zirconium is masked with oxalic acid. Large quantities of thorium interfere. The determination of uranium in particularly complex materials requires the removal of at least the main mass of interfering elements. Methods for the separation of uranium, thorium, and plutonium have been reviewed[4].

A method for determining uranium in complex ores, minerals, and solutions comprises extraction of uranyl ion with a 20% solution of tributyl phosphate in carbon tetrachloride from a solution containing ammonium nitrate and Complexone III, re-extraction of the uranium with Arsenazo III solution, and photometry; the method can determine contents of uranium of 0.002 μg per ml or more of solution[128].

Zirconium and Hafnium

Zirconium is another element for which reagents of the arsenazo group are widely used analytically. Methods are known using Arsenazo I[33-38] and Thoron I,[94] and colour reactions with Arsenazo II and Thoron II have been described[5].

‡ KU-2 is a monofunctional, strongly acid cation-exchange resin with $-SO_3H$ active groups, prepared by treating a swollen styrene–divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

Good results have been obtained with Arsenazo III. The possibility of working in strongly acid media (2–11 *N* HCl), *i.e.* under conditions where there is practically no hydrolysis or formation of polynuclear zirconium ions, gives highly stable results and good reproducibility [6,129-135]. Many anions and cations, with the exception of thorium, hafnium, uranium(IV), fluorides, and oxalates, do not interfere. Therefore, in most cases, even in the determination of zirconium in complex materials (ores [130,133], alloys based on aluminium, copper, magnesium, and titanium [131,132], and other materials), other elements need not be removed nor the zirconium concentrated.

The optical absorption of the zirconium–Arsenazo III complex, and hence the sensitivity of the reaction, is greatly dependent on the acidity of the solution; the sensitivity is several times greater in 9 *N* than in 2 *N* HCl. [6]

Hafnium is determined under approximately the same conditions and with the same selectivity as zirconium. A slight difference in the behaviour of the zirconium and hafnium complexes with Arsenazo I [201] when the acidity is varied has enabled methods to be developed for the separate determination of zirconium and hafnium when both are present.

Hafnium can be determined with Arsenazo III under approximately the same conditions and with the same selectivity as zirconium. The variation of sensitivity with acidity is as great as with zirconium; the sensitivity is maximum in 6–11 *N* HCl.

The following method can be used to determine zirconium and hafnium when both are present: the combined solution is subjected to spectrophotometry at two pH values, such that the intensities of colour of the corresponding zirconium and hafnium complexes combine or show the greatest divergence respectively; it is then easy to calculate the contents of zirconium and hafnium from the results obtained. According to Elinson and Mirzoyan, in the case of Arsenazo III 1 *N* HCl and 4 *N* HCl should be used [131]; the procedure is as follows. Metallic hafnium (10–20 mg) is dissolved in hydrofluoric acid, the solution fumed with sulphuric acid, and the residue dissolved in 4 *N* HCl and made up to 500 ml. An aliquot of the solution (> 50 μg hafnium) is heated and cooled, 2 ml 0.05% Arsenazo III solution is added, and the solution made up to 50 ml with 4 *N* HCl and the extinction measured, with the reagent solution as comparison solution. The zirconium content is found from a calibration curve. Thorium, uranium(IV), and titanium interfere. The accuracy of the method is ±20% with 0.5% zirconium and ±10% with 1% zirconium.

Plutonium

The determination of plutonium(IV) with Thoron I in 0.05–0.25 *N* HNO_3 or HCl has been described; uranium(IV), thorium, zirconium, and to a lesser extent cerium(III), iron(III), and uranium(VI) interfere. The accuracy is ±1%. [90] Arsenazo I is used as metal indicator in the complexometric determination of 0.1–0.2 mg of plutonium(IV) per ml with Trilon B in 0.1–0.2 *N* HNO_3; up to 140-fold amounts of UO_2^{2+} can be tolerated [56].

A method for the coprecipitation of plutonium has been developed; coprecipitation is practically complete with the arsenazo–methylene blue system at pH 2–6.3 and a dilution of 1 in 2×10^9 (0.1 μg of Pu in 200 ml) [189].

Neptunium

In 0.3–0.5 *N* HNO_3 Thoron I forms with neptunium(IV) a coloured complex of molar extinction coefficient 14 500; 0.5–5 μg of neptunium can be determined to within ±2–4% with photometry at 540 mμ. [91] Neptunium(IV) can be determined with Arsenazo III in 4–6 *N* HNO_3; the molar extinction coefficient at 665 mμ is 100 000. Uranium, plutonium(IV), thorium, and zirconium are removed by extraction of their complexes with di-(2-ethylhexyl)orthophosphate in carbon tetrachloride [210]. The reactions of protactinium(V) with Arsenazo III [211] and Chlorophosphonazo III [212] have been described.

Americium

Traces of americium can be precipitated from dilute solutions by using coprecipitants containing reagents of the arsenazo group, especially Arsenazo I. [190] Basic dyes such as methylene violet are used to provide the heavy organic cations. The coprecipitation is carried out at pH 5–8, and is practically complete at a dilution of 1 in 10^{12} (0.00002 μg of americium in 200 ml). Each 200 ml portion of solution requires 200–400 mg of the coprecipitant components [190].

Protactinium

A highly selective reaction for protactinium has been described, using Arsenazo III, which gives a colour reaction with protactinium(V) over a wide acidity range: from weakly acid to 10 M or more sulphuric acid. The complex is green, and is stable for more than 24 h. The reaction can also be carried out by the extraction–photometric procedure. The complex of protactinium with Arsenazo III is fully extracted from sulphuric acid solutions (> 4 *N*) by isopentyl alcohol [137]; the molar extinction coefficient of the complex is 2.2×10^4 and Beer's law is obeyed over the concentration range 0.3–3.1 μg of protactinium per ml.

The possibility of extracting the complex of protactinium with Arsenazo III from strongly acid solutions makes the reaction highly selective; in addition to protactinium, the extract contains only traces of thorium, uranium(IV), and zirconium, and the influence of these elements can be completely eliminated by washing the extract with a solution of oxalic acid in 7 *N* H_2SO_4.

The procedure is as follows: 0.2–1 ml of the initial solution, containing 1–10 μg protactinium, is taken in a tube with a ground glass stopper, 0.8 ml 10^{-4} M Arsenazo III is added, and then concentrated sulphuric acid to give a final acid concentration of 7–8 *N*. The solution is extracted with 2 ml isopentyl alcohol saturated with 7 *N* H_2SO_4, the extract is transferred to a centrifuge tube, the extraction is repeated with 1 ml of the alcohol, and the extracts combined and centrifuged for better separation of the phases. The upper organic layer is transferred to a 10 mm cell and the extinction measured, against the reagent, at 660 mμ. If thorium, uranium(IV), and zirconium are present, before centrifuging the extract is washed with 1 ml of ~ 0.5 M oxalic acid in 7 *N* H_2SO_4. [137] The reaction of protactinium with Chlorophosphonazo III has been described [213].

Rare-Earth Elements

Arsenazo I and Thoron I have been proposed for the determination of the rare-earth elements in various materials. Arsenazo I is used at pH 6–8; the sensitivity is 0.2–0.4 μg ml^{-1}.[40-46,202,203] Many elements interfere; a confirmatory reaction is the immediate disappearance of the colour when phosphates are added[42]. Spectrophotometry at two different temperatures has been used for the direct determination of rare-earth elements in the presence of thorium; the optical density at 576 mμ of the thorium complex of Arsenazo I in a solution of pH 3.7 is the same at 20° as at 80°, while the optical density of the corresponding rare-earth complexes is greater at the higher temperature. By using a calibration curve 1.2% or more of rare-earth elements can be determined in thorium products[202].

A method for the determination of individual rare-earth elements with Arsenazo III has been developed[136]; the pH used is 1.5–3.5 and the sensitivity is 0.01–0.05 μg ml^{-1} of the element. Aluminium, iron, magnesium, sodium, potassium, sulphate, chloride, and dihydrogen phosphate do not interfere; many other elements greatly affect the determination. A method for the successive complexometric determination of thorium and total rare-earth elements has been described[204].

The spectrophotometric titration of rare-earth elements with Complexone III using Arsenazo I as indicator has been described[205]; 5–500 μg of rare-earth elements can be determined with an accuracy of ±6%.

Scandium

Scandium is determined with Arsenazo I at pH 6; the molar extinction coefficient is 11 500, and the sensitivity 0.04 μg of scandium per ml[39]. With Arsenazo II at pH 5.0 the sensitivity is 0.1 μg per ml[39]. With Arsenazo III more acid solutions can be used (pH 1.8), where there is no formation of polynuclear scandium cations; as with zirconium, this is of particular importance.

Scandium is determined spectrophotometrically by adding 0.5 ml of 0.1% Arsenazo III solution to ~9 ml 0.08 *N* HCl containing 5–30 μg of scandium, diluting to 10 ml, and measuring the extinction in a 1 cm cell at 680 mμ against water[208]. The use of Arsenazo III as complexometric indicator in the volumetric determination of scandium has been described. The use of an acid medium (pH ≃ 1) gives a rapid reaction and high selectivity.

The reaction of scandium with Chlorophosphonazo III has been described[214,215]. The colour is developed at pH 3–4; the molar extinction coefficient at 680 mμ is 9113.

Beryllium

Beryllium is detected with Arsenazo I at pH 6–6.5 (urotropine and hydrochloric acid); the sensitivity is 0.02 μg of beryllium per ml[49-51]. Many elements can be selectively masked: aluminium with tartrates or Trilon B; iron(III), rare-earth elements, and copper with oxalates; uranium with hydrogen peroxide; and thorium with tungstates[49]. Beryllium is determined with Thoron I at pH 12.4 (borate buffer mixture); methods have been developed for determining beryllium in aluminium alloys[95-97].

Aluminium

Arsenazo I has been used to determine aluminium[8,47,48]; the reaction is carried out at pH 4.3, with sensitivity 0.05 μg ml^{-1}. No interference is caused by iron(II), magnesium, manganese, alkali or alkaline earth metals, or sulphates. The experimental conditions are of great importance. Because aluminium tends to form oxo-ions and polynuclear ions, the pH must be adjusted by careful addition of sodium acetate or urotropine only after the reagent has been added. Certain *o*-hydroxy-diazo-derivatives of chromotropic acid can be used to determine aluminium in a more acid medium. Thermospectrophotometry can be used to determine aluminium in the presence of indium, gallium, and other elements[202].

Indium

The determination of indium with Arsenazo I has been described, at pH 4.8; 0.8–50 μg of indium per ml can be determined. Alkali or alkaline earth metals, ammonium, cobalt, nickel, zinc, cadmium, and palladium do not interfere[55].

Vanadium

Vanadium gives a typical colour reaction with Arsenazo I[17]; it is determined at pH 6. Complex-forming agents used for masking interfere. A colour reaction of vanadium(IV) with Arsenazo II has been described[113].

Niobium

Niobium can be detected with Arsenazo I[33,42,53] at pH 2, sensitivity 0.5–1 μg ml^{-1}. There is little colour contrast in the reaction.

Tantalum

A colour reaction of tantalum with Arsenazo I has been described[42,54]. A method has been developed for determining 0.5–30% of tantalum in titanium alloys. The sensitivity is 0.3 μg of tantalum per ml, in 1–2 *N* HCl.

Titanium

The determination of titanium in titanium and chromium borides with Arsenazo I at pH 2.5–3 has been described; the sensitivity is 0.01–0.25 mg of titanium in 100 ml[52]. The use of dichlorochromotropic acid offers better prospects[216,217].

Lithium

Thoron, nitrothoron, nitroarsenazo, and various other derivatives have been suggested for the determination of lithium[98]. The reaction is carried out in 2% potassium hydroxide solution, and the detectable minimum is 1 μg of lithium; calcium and magnesium do not interfere[99,101]. The determination of lithium in aluminium and copper alloys has been described. The best method is spectrophotometry of 0.1–0.7 mg of lithium in a volume of 50 ml at pH 14 in the presence of 0.7 ml of 0.1% thoron solution[100].

Barium and Strontium

Certain analogues of arsenazo — *e.g.* reagents (III) and (IV) — have been suggested for the determination of barium and strontium[142]. The determination is carried out at pH 1–2; the sensitivity is 0.04–0.1 μg of element per ml.

Bismuth

Methods have been described for the photometric[103] and complexometric determination of bismuth at pH 1.3 using Thoron I as metal indicator[104]. At pH 1.5–4.5 Arsenazo III gives a clear colour reaction[6].

Sulphates

Several methods have been described for the volumetric determination of sulphates by titration with barium chloride or barium perchlorate solution; Thoron I[108,109], reagent (V)[143], and reagents (VI) and (VII)[142] have been suggested as indicators for barium.

Fluorine

A number of methods are known for the volumetric determination of fluorine by titration with thorium salts; Thoron I[105,107] and Arsenazo I[63,65] have been suggested as indicators for thorium(IV) cation. The method with Thoron I has been most widely used. Several methods are based on the masking of fluorides with elements other than thorium, *e.g.* aluminium in the presence of Arsenazo I[208,209].

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Reagents of the arsenazo group occupy a foremost place in inorganic photometric analysis, by virtue of the scale of their use, their universality, and the efficiency of their analytical action. A feature of these reagents is their high sensitivity (to 0.01 μg of element per ml) and the high stability of the complexes formed; because of the latter, strongly acid media can be used for the determinations. The determination of elements producing highly charged cations (palladium, thorium, zirconium, hafnium, plutonium, neptunium, and certain others) with Arsenazo III is highly selective. In many cases these elements can be determined without removal of other elements, and several methods have accordingly been used for rapid process control determinations. In addition to photometry, the reagents are widely used as coprecipitant components in the concentration of elements from dilute solutions, as metal indicators in volumetric complexometric determinations, and in the extraction–photometric determination of elements.

The ready synthesis of the basic reagents (Arsenazo I, Thoron I, and Arsenazo III) and their derivatives and the availability of the necessary starting materials favours an even wider use of the reagents of the arsenazo group in inorganic analysis. The wide choice of readily-prepared compounds ensures that in each particular case the determination of the elements in the given combinations can be carried out with the most suitable reagent in respect of selectivity, ease of extraction, completeness of precipitation, or required stability of the complex.

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HYDRATION AND SOLVATION OF ACIDS AND SALTS UNDERGOING EXTRACTION

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Recent experimental investigations of the mechanism of the extraction of iron from chloride solutions and also of some simple inorganic acids by oxygen-containing solvents[1-5,70-72] have led to conclusions extending insignificance beyond these systems. The results obtained, combined with existing data, gave an orderly picture of the mechanism of the extraction of simple and complex acids (partly in relation to the hydration and solvation of the compounds extracted). It has also been found that in several cases the extraction of salts, too, has much in common with that of acids. An attempt is made below to present this picture as a whole.

1. SOME EXPERIMENTAL DATA

It might be supposed that tervalent iron is extracted from hydrochloric-acid solutions by oxygen-containing solvents (ethers, esters, ketones, alcohols) in the form of compounds of general formula $HFeCl_4.nH_2O.mS$, where S represents a molecule of the organic solvent. Examination of the infra-red spectra of the iron compounds extracted from hydrochloric-acid solutions by esters (ethyl, butyl, and isopentyl acetates) has enabled several conclusions to be drawn concerning the character of the hydration and solvation of these compounds[1,3-5].

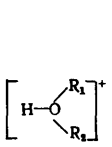
The extracts containing iron showed shifts in the band due to stretching vibrations of the C=O group of the esters by 30–40 cm^{-1} compared with the spectra of the pure solvents and those of solutions of water in these solvents, where hydrogen bonds may be formed between the water and solvent molecules. These shifts indicate combination of the solvent, *i.e.* that it forms part of the extracted compounds.

The changes in the spectra of extracts containing iron do not differ in character from those observed in extracts containing hydrochloric acid alone, and also in solutions of hydrochloric acid in organic solvents. The spectra of extracts of iron show no changes other than the above shift in the C=O band and the associated shift in the C–O band. The spectra of solutions of $KFeCl_4$ in anhydrous organic solvents show no displacements of the C=O band. These

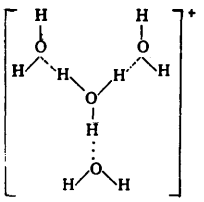
results indicate that the organic solvent, and probably water, do not add on to the anionic portion of the complex acid which is extracted, *i.e.* to the $FeCl_4^-$ ion; hence they can be located only in the cationic portion.

It has also been shown that the extracted compounds do contain water[1,4]. In the region of the OH-stretching vibrations, the infra-red spectrum of water in the extracts shows a displacement towards lower frequencies compared both with the spectra of gaseous or liquid water and with those of solutions of it in the corresponding organic solvents, where ordinary hydrogen bonds can be formed. It must be stressed that water is bound more strongly in the extracts than in solutions of it in the organic solvents.

Cole soon established that the compounds which are extracted contain both the organic solvent and water (but not in the anionic portion), and it was necessary to "stow" the proton, water, and organic solvent in the cationic portion. Two hypotheses exist in the literature concerning the structure of the cationic portion of extracted strong acids. One of them, known as the oxonium mechanism[6,7], is based on the assumption that the proton of the acid adds on directly to the oxygen atom of the organic solvent to form a "solvonium", or substituted oxonium cation (I). This hypothesis postulates that water does not take part in the process of extraction, that it even interferes with extraction, and that extraction can occur only from solutions of high hydrogen-ion concentration; it is also implied that only monosolvates should be extracted:



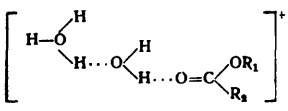
(I)



(II)

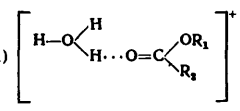
The second hypothesis[8-11] is based on the postulate that the proton of the acid adds on, not to the oxygen of the organic solvent, but to the oxygen atom of the water with the formation of a simple oxonium cation, which is in turn hydrated with three water molecules (II). The organic solvent adds on to the water molecules which are polarised in the field of the simple oxonium ion.

The above data suggest that the organic solvent is combined in the cationic portion of the extracted compounds with water molecules which are polarised in the field of the proton or the simple oxonium ion. Actually, if the water were not polarised, the changes in the spectrum of the solvent in the extract would not differ from those observed in solutions of water in the solvent and produced by an ordinary water–solvent hydrogen bond. On the other hand, the water can be polarised in this case only by being located in the field of the cation, proton, or simple oxonium. This hypothesis is supported by data on the change in spectrum of the water, which is greater than in hydrogen-bond formation with the solvent. In such a case it seems most natural to represent the cationic portion in the form $[H_2O^+ \ldots (H_2O)_{n-1} \ldots S_m]$ or (an individual fragment of this)



(III)

or (for $n = 1$)



(IV)

But this represents only the minimum data required. A further fact which probably indicates that the solvent is combined *via* water[4,5] is that the spectrum of a solution of anhydrous $FeCl_3$ in an anhydrous solvent contains a band due to a very strongly bound carbonyl group (displacement of 80 cm^{-1}). This indicates the direct addition of solvent to the iron, which is expected under these conditions. The spectrum of the hexahydrate of $FeCl_3$ in the solvent contains no bands due to the strongly bound C=O group, but there is a band due to more weakly combined carbonyl (displacement of 30–40 cm^{-1}). The coordination sphere of the iron is probably filled with water molecules, while molecules of the organic solvent add on to the water of hydration. The shifts in the C=O band are the same in this spectrum and in those of our extracts. Vdovenko and Suglobov[12] observed a similar shift in the C=O band of esters with the hydrates of uranyl nitrate, and with this system it was definitely proved that the link is effected *via* water. The nature of the cation binding the water obviously does not influence the solvent–water bond sufficiently for this to be noticeable in the spectrum.

But the most important result is that, if water is polarised in the field of the proton, the spectrum should contain bands due to strongly bound water, in other words oxonium bands[1,4]. If the simple oxonium ion appears in the spectrum, the problem is finally solved. In several experiments the presence of the simple oxonium ion is clearly revealed in the region of the O–H deformation vibrations. Thus an oxonium band has been found in the spectrum of an extract of sulphuric acid in isopentyl acetate (conditions were chosen such that the extraction of H_2SO_4 was considerable); the broad band observed represented the sum of a band due to carbonyl stretching vibrations and a band due to simple oxonium. In order to avoid such superimposition of bands, ethers were used, as they have only a weak overtone in this range. Distinct oxonium bands were obtained in the spectra of the extracts with perchloric acid and with iron[4].

Bands due to strongly bound water are observed also in the region of the O–H stretching vibrations. This is especially noticeable if, instead of extracts, solutions of the extracted substance are taken in the anhydrous solvent, to which known amounts of water are gradually added. Such experiments have been carried out with hydrochloric acid. Anhydrous pentyl acetate was saturated with dry hydrogen chloride, the quantity of which was determined by titration. The calculated quantity of water was added to the resulting solution. At a certain ratio of water and HCl, the spectrum contains only a band (3200 cm^{-1}) which can be assigned to strongly bound water.

These results lead to the conclusion that water plays an important part in the extraction of strong acids, and suggest that the main process is addition of the proton of the acid to water with formation of a simple oxonium ion. The latter is probably hydrated and solvated. We shall term this mechanism of extraction, involving the formation of a hydrated and solvated simple oxonium ion, the hydrate–solvate mechanism.

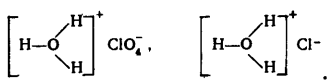
2. HYDRATION OF THE PROTON AND SOME CHARACTERISTICS OF THE MECHANISM OF THE EXTRACTION OF STRONG ACIDS

The above results enable us to regard the hypothesis of the addition of the proton to a water molecule as proved.

Let us examine the hydrate–solvate mechanism in greater detail.

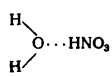
The oxygen atom in the small and strongly polarised water molecule is usually more basic than the active oxygen atoms in the solvents used for the extraction of acids. The high proton-acceptor capacity of water indicates that, in its presence, the proton should combine preferentially with water molecules and not with the organic solvent. This involves formation of a simple oxonium ion, a feature of which is the great strength of the O–H bonds. Actually, each O–H bond in the water molecule has an energy of about 110 kcal,[13] while the affinity of the proton for the water molecule is 180 kcal. Thus the total energy of formation of the H_3O^+ ion is 400 kcal. Since the O–H bonds in this ion are equivalent, each of them is associated with 133 kcal, a higher energy than in the water molecule. This great energy is responsible for the great stability of the H_3O^+ ion in solutions of strong acids. Such favourable conditions are not created by the addition of the proton to the oxygen atom of the organic solvent.

The H_3O^+ ion is more likely to be formed the stronger the acid (under otherwise identical conditions). Simple oxonium ions are formed, for example, by such acids as perchloric and hydrochloric:



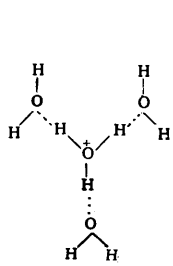
(V) (VI)

Nitric acid, which is of intermediate strength, shows less tendency to form H_3O^+ ions; it is characterised rather by hydrates in which the O–H bonds are not equivalent:

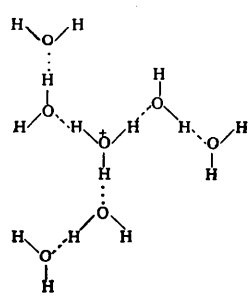


(VII)

In aqueous solution the simple oxonium ion is hydrated. Numerous data indicates that the hydration number of the proton is 4; Eigen *et al.*[14–17] supposed that the H_3O^+ ion forms the centre of three strongly bound water molecules, constituting by means of hydrogen bonds the pyramidal complex $H_9O_4^+$ (VIII). A few more weakly bound water molecules may be present in the outer hydration layer (IX):



(VIII)

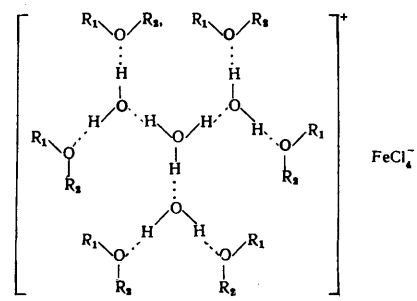


(IX)

The H_3O^+ ion differs from spherical monatomic ions, for example, the potassium ion, which is of the same size, in having three definite points for the addition of water molecules. The positive charge on the ion is concentrated at these points (hydrogen atoms); in spherical monatomic ions, however, the charge is uniformly distributed over the whole surface. The energy of hydration of simple oxonium is ~100 kcal mole^{-1}.[18,19] The complex consisting of four water molecules and one proton, *i.e.* $H_9O_4^+$, or $H_3O^+.3H_2O$, is stable in aqueous solution. In concentrated solutions even of strong acids the hydration number of the proton may be less than four; it is assumed, for example, that a change in concentration of sulphuric acid from 10 M to 20 M is accompanied by a change in hydration number from 4 to 2.[18]

It is further supposed that the proton is not fixed in the H_3O^+ ion, which constitutes the nucleus of the $H_9O_4^+$ complex, but migrates within this complex[9,15,18]; in time each of the four water molecules becomes the simple oxonium ion. The life of each H_3O^+ is of the order of 10^{-13} sec.

Since, as already noted, the ion usually interacts more strongly with water than with the organic solvent, it is more advantageous during extraction for the ion to pass into the organic phase together with its primary hydration shell, when the losses in energy of solvation will be a minimum[9]. In the organic phase the hydrated simple oxonium ion is solvated by molecules of the organic solvent, which add on to the water molecules by hydrogen-bond forces. Since each of the water molecules periodically becomes the oxonium ion, the organic solvent forms more stable bonds than in the water–organic solvent system. A structure of type (X) results:



(X)

This scheme is, of course, to a considerable extent arbitrary. Some of the sites in the second layer may be occupied also by water molecules; in systems in which there is a deficiency of water, solvent molecules may displace water also from the first layer ($n < 4$). The nature of the solvent plays an important part here, primarily its coordinating power, which is determined by the basicity and steric accessibility of the active oxygen atom. The degree of hydration or solvation depends on the degree of dissociation of the acid in the organic phase, which is determined both by the strength of the acid and by the nature of the organic phase (the dielectric constant).

The acidity of water in the equilibrium aqueous phase plays a great part. A hydration number of 4 (or above) may be optimum in relatively dilute solutions of strong acids. The activity of water diminishes with increase in concentration of the acid in the aqueous phase, and the degree of hydration of the proton should also decrease. It is therefore to be expected that the hydration numbers of the extracted compounds will not be constant, but may fall with rise in the equilibrium concentration of acid in the aqueous phase. At high acid concentrations the hydration

number may drop even to unity, *i.e.* unhydrated oxonium may remain. The mechanism under consideration envisages that the solvation numbers may, of course, be greater than unity and may vary under the influence of different factors. The solvation numbers should be linked firstly with the hydration numbers: it is probable that, the smaller the number of water molecules hydrating the oxonium, the fewer the sites for the addition of solvent. Therefore the solvation numbers also may, for example, diminish with increase in the equilibrium concentration of acid in the aqueous phase.

The above structure for the cationic portion indicates that solvation and hydration numbers are variable quantities, depending on many factors, while the cationic portion as a whole is a quite labile structure.

3. PUBLISHED DATA ON THE EXTRACTION OF STRONG ACIDS IN RELATION TO THE HYDRATE-SOLVATE MECHANISM

Experimental data on the extraction of strong acids agree well with the ideas reported above.

Let us examine published data on hydration and solvation numbers. We shall suppose that strong acids are extracted in the form of compounds of general formula $HA.nH_2O.mS$, where A is the anion of the acid, and S is a molecule of the oxygen-containing organic solvent.

Information in the literature indicates that the extraction of strong acids by oxygen-containing solvents is accompanied by combination of the acid molecule in the organic phase with a few molecules (more rarely with one molecule) of the organic solvent ($m \geq 1$). In several cases at least, the solvation number diminishes with rise in the equilibrium concentration of acid in the aqueous phase. In an absolute majority of cases the extraction of strong acids is accompanied by the withdrawal of water into the organic phase ($n > 0$), the number of moles of water per mole of acid in the equilibrium organic phase also diminishing with rise in the equilibrium concentration of acid in the aqueous phase.

Let us cite some examples. According to Siekierski and Gwozdz[11] the hydration number in the extraction of perchloric acid from dilute solutions with 100% tributyl phosphate (TBP) is 4. This gradually decreases with increasing concentration of $HClO_4$ in the aqueous phase. The solvation number also depends on the acid concentration (it is determined from the slope of the plot of the logarithm of the partition coefficient against the logarithm of the TBP concentration in the organic phase). At low $HClO_4$ concentrations the slope is about 3, and at higher concentrations it is unity. Similar results were obtained for the same system by Kertes and Kertes[20], who showed that, with rise in the concentration of $HClO_4$ in the initial and hence in the equilibrium aqueous phase, the solvation and hydration numbers diminish (they were determined by methods of physicochemical analysis using density, viscosity, volume changes, and electrical conductivity). Thus according to these results[20] the hydration number falls from 4 to 1. Similar results were obtained by Shevchenko *et al.*[21], according to whom the solvation number of $HClO_4$ in TBP diminishes with rise in concentration of acid in the aqueous phase (from 3.4 to 1 with a change in acid concentration from 0.1 M to 3 M). Analogous data on the solvation of perchloric acid in TBP were obtained by Fomin and Maiorova[22] ($m = 4$ and diminishes with rise in acid concentration).

Values of $n > 0$ and $m \geq 1$, and also a decrease in degree of hydration and solvation with increase in acid concentration, have been shown for the systems $HCl-TBP-H_2O$,[23] HCl–diisopropyl ether–H_2O,[24] and $HBr-TBP-H_2O$.[25] In the case of the strong complex acid $HFeCl_4$ and diisopropyl ether, the hydration number is also greater than zero and, according to Myers *et al.*[26], diminishes with rise in concentration of hydrochloric acid in the aqueous phase. A decrease in the solvation number in the $FeCl_3-HCl-TBP-H_2O$ system is probably indicated by the results of Specker and Cremer[27]: at hydrochloric acid concentrations in the aqueous phase of 4 M, 5 M, 7 M, and 9 M, the respective solvation numbers are 2.9, 2.4, 2.1, and 1.9.

Diamond and Tuck[8,9] pointed out the regular hydration number of 4 in the extraction of strong acids (simple oxonium hydrated with three water molecules). Actually, this number is frequently met; the results already quoted can be supplemented by data on a hydration number of 4.0–4.5 for $HClO_4$, HCl, and HBr in dibutyl Cellosolve, diisopropyl ketone, and TBP,[28] and for $HFeCl_4$ in diisopropyl ether[29-31,34]. However, it is essential to stress yet again the variability of the hydration number (as a more important fact), which is indicated in particular by the data cited here.

The labile character of the cationic portion of the extracted compounds is indicated also by other data, for example, the results of experiments[5] on the influence of several factors on the infra-red spectra of extracts with iron and hydrochloric acid. When extracts are heated or exposed to ultra-violet radiation, the spectra indicate a decreased degree of binding of the organic solvent, whereas the water is combined to a greater extent. This appears in diminished absorption in the band due to the combined C=O group, while the band due to free C=O becomes more intense; the bands assignable to free and combined water (the range of stretching vibrations) vary in corresponding fashion. With time, changes of a different type probably occur: the solvent is bound to a greater extent (the data for water do not enable a definite conclusion to be reached).

The instability of the cationic portion is indicated also by some data on the formation of three-phase systems. In several cases, especially when highly concentrated solutions of acids are used, the organic phase separates into two layers, one of which contains a greater proportion of the extracted substance.

Two organic phases are formed, for example, in the extraction of iron with diisopropyl ether[26,32-34]. The phases differ in the number of molecules of water per atom of iron, but are otherwise identical[33]. Laurene *et al.*[34] showed that it is the water which is the decisive factor in the formation of two ether phases; they regard the extraction system with two ether phases as analogous to the $HFeCl_4$–ether system, which contains insufficient water for a homogeneous solution to be formed. Two ether phases arise at high concentrations (above 8 M) of hydrochloric acid in the aqueous solution; under these conditions there is practically no longer any "free" water, the whole of the water being used up in the hydration of ions; the hydrochloric acid acts as a dehydrating agent. The degree of hydration of the proton is thus lowered, and different hydrates are formed, yielding the layers which separate out. According to these workers[34] two phases are formed also when sodium chloride is added to the isolated extract (diisopropyl ether–iron), the salt acting as a dehydrating agent.

In several cases three phases are formed also in the

extraction of simple acids. An example is the extraction of hydrochloric acid with undiluted TBP.[23] The homogeneous equilibrium extract, separated from the equilibrium aqueous layer, divides after several days into two layers. It was found that after some time dehydration occurs[35]: during extraction from 12.15 M HCl, the complex $HCl.3H_2O.TBP$ is first formed, and on standing $HCl.2H_2O$. .TBP appears. Three phases arise in the extraction of perchloric acid with solutions of TBP in "kerosene" (a mixture of saturated hydrocarbons of high boiling point, distilling over the range 182°–222°, $d^{25} = 0.743$).[36] The $HClO_4$ concentration used was 0.49 M, with a wide range of TBP concentrations; it is interesting that a third phase is not formed when benzene is used as diluent. Three phases have been observed in the HNO_3–TBP–H_2O mepazine system[37]; in this case, however, other causes are probably operative. Formation of the anhydrous complex $3HNO_3.TBP$, soluble neither in the aqueous nor in the organic phase, plays a part here.

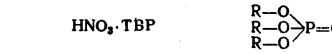
Let us now examine the dependence of extraction on the hydrogen-ion concentration. Since we are dealing with the extraction of acids, *i.e.* of extracted compounds containing the hydrogen ion, the partition coefficients should, in conformity with the law of mass action, increase with increasing concentration of hydrogen ions in the equilibrium aqueous phase. Monobasic acids are usually extracted, and hence there should be a linear relation, of unit slope, between $\log D$ (where D is the partition coefficient) and $\log [H^+]$. Vdovenko and Krivokhatskii[38] showed, for example, that such a relation is observed in the extraction of iron from hydrochloric-acid solutions with diisobutyl sulphide, and Horrocks and Voigt[39] found a similar relation in the extraction of thallium(III) with diisopropyl ether. The second factor of significance here is the decrease in activity of the water with increasing equilibrium concentration of acid in the aqueous phase (caused by combination of the water with protons). In the case of complex acids, the decrease in activity of the water favours in particular the formation of extractable complex anions, for example $FeCl_4^-$. This fact definitely tends to increase the partition coefficients.

There are no grounds for ascribing the fact that extraction depends on the hydrogen-ion concentration to increasing stability of substituted oxonium cations. It is assumed that the latter should be stable only in solutions of very high hydrogen-ion concentration, whereas extraction of acids takes place quite often also from weakly acidic solutions. This does not contradict the two factors noted above, but is inconsistent with the substituted oxonium mechanism. Tervalent thallium, for example, is extracted by ethers from hydrochloric-acid solutions at HCl concentrations below 1 M. With complex acids in general, the position of the ascending portion of the extraction curve is determined to a considerable extent not only (or even, perhaps, not so much) by the hydrogen-ion concentration but also by conditions favouring the formation of a complex anion (stability constant, concentration of ligand, nature of solvent). The chloro-complexes of thallium or gold are probably extracted at lower HCl concentrations than, for example, the gallium or iron complexes, primarily because their chloro-complexes of the type MCl_4^- are considerably more stable. Incidentally, if the formation of substituted oxonium compounds did play a decisive part, stronger acids should, under otherwise identical conditions, be extracted better, as Grinberg and Lozhkina[40] noted. However, this is not altogether so.

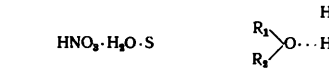
This mechanism explains the insolubility of anhydrous $HFeCl_4$ in anhydrous ethers, a fact established by Laurene *et al.*[34] and confirmed by Fomin and Morgunov[41] (dissolution occurs only after the addition of about five molecules of water per atom of iron). $HFeCl_4$ dissolves in anhydrous ketones[42]; in spite of this, the extraction of $HFeCl_4$ by ketones involves the participation of water.

4. EXTRACTION OF ACIDS OF MODERATE STRENGTH

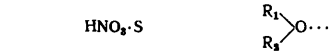
Acids of moderate strength do not always form the simple oxonium ion even in the aqueous phase, and the probability of this ion existing in the organic phase is still smaller. Water is linked to such acids by the hydrogen bonds, and some solvents readily displace this water† (especially under conditions such that the activity of water in the system is low). For example, nitric acid is extracted, by such an exceptionally basic solvent as tributyl phosphate, in the form of anhydrous solvates even at low acid concentrations (at any rate if addition takes place *via* the phosphoryl oxygen atom of the TBP). There is a vast literature on this question (see for example Tuck[43] and Alcock *et al.*[44]). Less basic solvents may not displace the water, and hydrated solvates are then extracted. The extractable compounds formed with nitric acid can be represented by the formulae (XI)–(XIII)

$HNO_3 \cdot TBP$ 

(XI)

$HNO_3 \cdot H_2O \cdot S$ 

(XII)

$HNO_3 \cdot S$ 

(XIII)

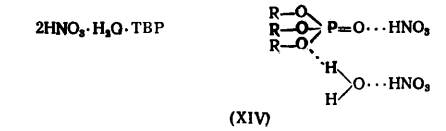
Let us cite some examples. According to Fomin and Maslova[45,46] nitric acid is extracted (at not very high concentrations) in the form of hydrated and partly as anhydrous solvates in the cases of ethyl propyl, dipropyl, and dibutyl ethers. The concentration of the anhydrous solvates becomes appreciable only at concentrations above 6 M and above 4 M with the ethyl propyl and dipropyl ethers respectively; in the case of dibutyl ether, both solvates are already extracted simultaneously at low HNO_3 concentrations. The complexes always contain at most one molecule of ether and of water. A decrease in degree of hydration with increase in acid concentration can be understood from all that has been said above. Similar data have been obtained for the HNO_3–H_2O–dibutyl ether system by Vdovenko *et al.*[47,48]. They showed in particular that the degree of hydration of nitric acid in the ether phase is 0.6 molecule of water per molecule of HNO_3 over the concentration range 0–1.5 m HNO_3 and 0.15 molecule in the range 3–6 m. Fractional values of the hydration number indicate the simultaneous extraction of anhydrous solvate and monohydrate.

Vdovenko and Alekseeva[49] showed that the degree of hydration of nitric acid in the phase formed by the dibutyl ether of diethylene glycol (dibutyl Carbitol) is 1.75 at low HNO_3 concentrations (up to 1.5 M), and that it depends on the concentration of HNO_3 in the aqueous phase. Tuck[50] found that nitric acid is extracted by the dibutyl ether of ethylene glycol (dibutyl Cellosolve) as a monohydrate (probably up to 7 M HNO_3 in the equilibrium aqueous phase). He

† See Tuck and Diamond[28].

suggested that a complex of the type (XII), produced by hydrogen bond formation, is formed between the acid hydrate and the solvent.

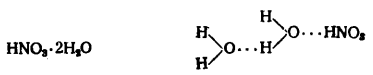
It is interesting that, although nitric acid adds not only to the phosphoryl oxygen atom of tributyl phosphate but also to the considerably less basic ester oxygen, these additional acid molecules probably add *via* water. This occurs at sufficiently high concentrations of nitric acid in the equilibrium organic phase, only after the phosphoryl oxygen atoms of the TBP molecule have been completely saturated‡. The complexes which are thus formed may be represented by the following formula:



(XIV)

Polish workers[37] have found that the TBP molecule may add up to four molecules of HNO_3 (all the oxygen atoms being occupied). A similar phenomenon probably occurs also with other solvents.

It is obvious that no hydrates of nitric acid exist (in the extracts) which could contain more than one molecule of water. This can be readily explained by the weak bond between water and the acid: the only water molecule which can add to the hydrogen atom of the acid is feebly polarised, and is unable to form stable bonds with other water molecules. But even if one of them is formed (formula XV), such compounds can hardly be extracted, since they cannot be stably solvated by the organic solvent. Actually, the water molecules in the second hydration layer should be practically unpolarised, and here, of course, there is no migration of the proton, because the proton as such is absent:



(XV)

Strong acids may sometimes occur under conditions such that they will behave like acids of intermediate strength. Hydrochloric acid, for example, can probably be extracted as an anhydrous solvate from highly concentrated solutions with not very basic solvents of comparatively low dielectric constant. This occurs in the case of dibutyl ether[42,52]. However, it is rare with strong acids.

The direct bonding of the organic solvent to the hydrogen atom of the acid, which is achieved in a small number of anhydrous solvates, is readily seen to have little in common with the formation of a substituted oxonium cation. Actually, we cannot speak here of the addition of a proton, which is essentially absent in this case; compounds of molecular type are formed.

Summing up, we must note that, in the vast majority of cases, the extraction of acids is accompanied by that of water. This water is simultaneously combined with the cation (proton or simple oxonium) and molecules of the organic solvent. The latter are located in a layer which is more remote from the cation than are the water molecules. Thus the decisive factor involving the organic solvent is its interaction with the hydrogen atom of the water of hydration.

‡ There is also another explanation for this phenomenon (see Pushlenkov *et al.*[51]).

Comparatively rarely, the solvent adds to the hydrogen atom of the acid. This occurs when the acid is feebly dissociated in the organic phase (weak acids or an organic phase of low dielectric constant) and/or when the activity of water is very low, for example, as a result of combination with ions present in the system. Molecular compounds in which the bonds are of the hydrogen type are then formed.

5. METHOD OF DETERMINING SOLVATION NUMBER FROM DISTRIBUTION DATA

A method often used to determine the solvation number of extracted compounds is based on a study of the dependence of partition coefficients on the concentration of active solvent in an inert diluent. This method was probably first employed by Peppard[53]. It consists essentially in the application of an expression which can be derived on the basis of the law of mass action: $D = A[S]^m$, where D is the partition coefficient, [S] the equilibrium concentration of free active solvent in the organic phase, m the solvation number, and A a constant. Since this expression represents an equation to a straight line ($\log D = \log A + m \log [S]$), the value of m, numerically equal to the slope of the straight line, is usually found graphically. A necessary condition for application of the method is that all other conditions should be constant, primarily the composition of the equilibrium aqueous phase. Use of this procedure presupposes that the activity coefficients of solvent and solvate are equal to unity.

Difficulties often arise in applying this method. It is usually applicable only at comparatively low concentrations of active solvent. Deviations from linearity ($\log D = f \log [S]$) at high solvent concentrations are ascribed[54] to a deviation from ideal behaviour (variation of activity coefficients of solvent and solvate).

Sometimes deviations from linearity are observed even at low solvent concentrations. This was observed, for example, by Zvyagintsev and Zakharov-Nartsissov[55] in a study of the solvation number of hydrogen cyanoaurate(I) in the system water–cyclohexanone (or pentanol)–benzene; as the concentration of cyclohexanone in the benzene was changed from 0.3 M to 5 M the "solvation number" increased from 1 to 6. Kertes and Kertes[20] noted that the concentration of TBP in the diluent affected the solvation number of several acids, and Goroshchenko and Babkin[56] that the solvation numbers of the acids $HNbF_6$ and $HTaF_6$ were influenced by the cyclohexanone concentration. According to Fomin and Morgunov[42] $HFeCl_4$ is extracted by undiluted octan-2-one from a hydrochloric-acid solution of a definite concentration in the form of a pentasolvate, and by a solution of the octanone in benzene in the form of a trisolvate (or a tetrasolvate).

Maslova and Fomin[45] observed deviations from additivity in the systems HNO_3– ethers–C_6H_6–H_2O. Dilution of ethyl propyl and of dipropyl ethers with benzene somewhat lowers their "specific extractive capacity" (the amount of substance extracted per mole of active solvent).

The "slope" often depends also on the nature of the diluent. This applies, for example, to the system $HClO_4$–TBP–diluent–H_2O, studied by Schevchenko *et al.*[21] Casey *et al.*[57] studied the composition of the solvates formed by iron during extraction with 2,4-dimethylpentan-3-ol, and showed that the "slope" differs with the diluent (heptane, benzene, CCl_4).

The difficulties in applying the slope method to determine the solvation number of strong acids (simple and complex) seems to be fully explicable in the light of the ideas examined above on the mechanism of extraction. Furthermore, acceptance of the hydrate–solvate mechanism as fundamental in the extraction of strong acids leads to the conclusion that this graphical method is not strictly applicable at all to the study of the solvation number of the extracted acids.

Let us examine this in greater detail. If the organic solvent adds on *via* water, the solvation number should be linked with the hydration number. The above data on the variation in hydration and solvation numbers with rise in acidity probably confirm this. But does the hydration number remain constant with change in concentration of the active solvent? General considerations and available experimental data indicate that the hydration number should depend on the concentration of the solvent.

In fact, as was noted above, the degree of hydration depends on the degree of dissociation of the acid in the organic phase. For a given acid the degree of dissociation is in turn determined by the properties (composition) of the organic phase, increasing with increasing dielectric constant of the latter. An increase in concentration of an active solvent in an inert diluent is accompanied by an increase in dielectric constant and in degree of dissociation of the acid in the organic phase. This should lead to an increase in the hydration number. It is also possible that the hydration number is linked with the total content of "free" water in the organic phase, and will vary with increase in concentration of the acid in the organic phase, *i.e.* ultimately with increase in concentration of the active solvent. Thus the degree of hydration may vary with increase in concentration of the active solvent. The nature of the diluent should also, of course, influence the degree of hydration.

Let us refer to some data, indicating the correctness of the above considerations concerning the variation in degree of hydration. Maslova and Fomin[45] showed that, with increasing concentration of ethyl propyl and dipropyl ethers in benzene, the proportion of hydrated solvates rises; the opposite situation is observed with the less active dibutyl ether, which dissolves water less well[46]. Fomin and Morgunov[42] showed that hydrochloric acid is extracted from 7–8 M HCl by octan-2-one in the form of $HCl.3H_2O.S$; on dilution of the ketone with benzene, however, the degree of hydration is diminished; in extremely dilute solutions of the ketone, extraction takes place without water. A similar situation occurs in the extraction of $HFeCl_4$ with octan-2-one: the pure ketone extracts $HFeCl_4.4H_2O.5S$ (at a definite acidity, of course), and a solution of the ketone in benzene removes $HFeCl_4.3H_2O.3–4S$.

The change in degree of hydration with increase in concentration of active solvent may lead to a change in the solvation number, as is evident from the last example. It is this variation which explains the inapplicability of the method in some of the cases cited at the start of this section.

Acceptance of the hydrate–solvate mechanism as the main mechanism enables us to suggest that numerical values of the solvation and hydration numbers themselves are to some extent devoid of meaning. In any case, these numbers characterise the system only under certain concrete conditions (concentration of acid and active solvent, nature of diluent, etc.).

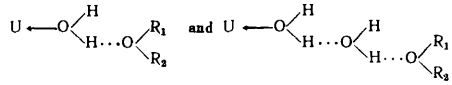
6. EXTRACTION OF SALTS

This section deals with salts formed by anions of simple and complex acids with metal cations. The question of the extraction of salts of complex acids has been discussed in part by Diamond[8].

It has already been mentioned that, since the ion–water interaction is stronger than that between the ion and the organic solvent, the ion can more advantageously pass into the organic phase together with its primary hydration shell. In the organic phase the hydrated ion would be solvated by molecules of the organic solvent. It is probable that sometimes water can be displaced by the organic solvent with the formation of a structure in which the solvent is directly coordinated to the metal atom.

A mechanism involving bonding of the solvent with the metal through water has been established for the extraction of uranyl nitrate with not too basic organic solvents. The data on this well-studied system are worth detailed consideration.

Glueckauf and McKay[58] put forward the idea that, in the extraction of uranyl nitrate with ether, a hydrogen bond may be formed between the hydrogen atom of the water of hydration and the oxygen atom of the organic solvent. This hypothesis was later proved by the work of Ryskin *et al.*[59] and especially of Vdovenko and his collaborators[12,60–65], which showed that two molecules of water enter the inner sphere of the complex (are directly coordinated with the uranium). To these water molecules, which are strongly polarised in the field of the uranium, molecules of the organic solvent are attached by means of hydrogen bonds. In several cases the hydration number exceeds 2, but the "extra" water molecules are present in the second hydration layer, and organic solvent is already attached to them. The structures thus formed are:



(XVI) (XVII)

As Vdovenko and Suglobova[60] noted, the water molecules entering the inner sphere are strongly deformed, and acquire acidic properties. The solvent molecules possess the properties of a base, and can therefore interact with the coordinated water.

The degree of hydration of the uranyl nitrate depends, as Vdovenko and Smirnova showed[62], on the nature of the organic phase, *i.e.* the nature of the active solvent, its concentration in the diluent, and the nature of the diluent. The "specific extraction capacity" of the solvent decreases on dilution with an inert diluent, the decrease varying in the sequency $C_6H_6 < CCl_4 < CHCl_3$; these workers link this with a change in degree of hydration of the salt. The hydration number decreases with decreasing concentration of active solvent, the nature of which plays an important part. In the case of solvents having appreciable proton-acceptor properties, in which water is soluble, this decrease is greater than in the case of feeble proton-acceptors, in which water is sparingly soluble. The degree of hydration in undiluted solvents is also linked with the nature of the solvent; the hydration numbers with diethyl ether, methyl butyrate, ethyl butyrate, and dibutyl ether are 4, 4, 3.3, and 2.5 respectively. It is readily seen that the degree of hydration depends on the proton-acceptor capacity of the solvent.

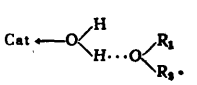
Anhydrous uranyl nitrate is insoluble in ethers, but dissolves in ketones, esters, and alcohols[63]. Thus direct attachment of solvent to the uranium atom is obviously possible, but under the actual conditions of extraction, addition takes place only *via* water. We are dealing with a system resembling in its behaviour one containing $HFeCl_4$.

Very active solvents displace water from the inner sphere of the uranyl ion. Tributyl phosphate extracts anhydrous uranyl nitrate, two TBP molecules entering the positions usually occupied by two water molecules — composition of solvate $UO_2(NO_3)_2.2TBP$. However, uranyl perchlorate is extracted[66] as a dihydrate with two or more TBP molecules. A possible explanation of this is that perchlorate ions create steric hindrance to TBP molecules but not to water. It is also possible that substitution of the anion results in a change in charge density on the central atom of the uranyl ion, and hence in a change in the extent of bonding of water. In the perchlorate the organic solvent is again linked apparently through water.

Tervalent iron is extracted quite well not only from hydrochloric-acid solutions but also from lithium-chloride solutions in the almost complete absence of hydrochloric acid, the Fe : Li ratio in the extract being close to unity. Iron is extracted, although not as well, also from $MgCl_2$, $CaCl_2$,[27] and $AlCl_3$ solutions. According to Specker and Cremer[27] the Fe : Ca ratio in the organic phase, in the extraction of iron with TBP from $CaCl_2$ solutions in the absence of acid (in order to eliminate competition by $HFeCl_4$), is close to 2 at low and intermediate $CaCl_2$ concentrations, and to 1 at high concentrations. Iron is present in the extracts in the form of $FeCl_4^-$. It may be assumed that mainly $Ca(FeCl_4)_2$ is extracted in the former case, and a mixture of $Ca(FeCl_4)_2$ and $CaCl_2$ in the latter.

More detailed study has been made of $FeCl_3$–LiCl–ester systems[3-5]. The infra-red spectra of the extracts show practically the same shift in the band due to stretching vibrations of the C=O group of the solvents as in the case of hydrochloric-acid solutions. This indicates that the organic solvent is combined in the extract. The spectrum of the solutions undergoes the same changes with time as in the case of hydrochloric-acid solutions: the spectrum undergoes analogous changes on being heated and exposed to ultra-violet radiation. Thus in the case of LiCl solutions, too, the organic solvent probably forms part of the compounds extracted. Since, as has been shown, water is also combined, the mechanism of the addition of the organic solvent can be regarded as analogous to that considered above.

The mechanism of the extraction of acids and uranyl nitrate, and also apparently of salts of $HFeCl_4$, shows common features. It is obvious that in all cases a structure is formed of the general type



(XVIII)

In some (comparatively rare) cases water is absent.

A mechanism of this type should not be peculiar to the cations considered above. It can obviously operate when the cation combines quite firmly with water, while the total amount of water in the system is not sufficiently large for it to form second, third, etc., hydration layers. The latter is achieved in systems having a high concentration of cations combining with water. Another condition is the ability of the organic solvent to form hydrogen bonds with the water molecule.

It is quite possible that compounds containing "intermediate" water may be extracted, under otherwise identical conditions, even more readily than anhydrous compounds. The size of the cation is an important factor. Passage from the aqueous to the organic phase proves to be easier with large ionic structures, among which are the hydrated forms. It is also noteworthy that these forms, in which the water is screened by organic molecules, have to a considerable extent lost their hydrophilic character.

Considerations of size are especially important in connection with the anion of the extracted ion pair. For a given cation (with anions of equal charge) a salt should be extracted more readily the larger the anion§. Anions are weakly hydrated. This is associated with the fact that the water molecule is bent; it is oriented with its oxygen atom towards a metal cation, and here is concentrated the negative pole of the molecular dipole, so that ion–dipole interaction is supplemented by donor–acceptor interaction. However, the water molecule is oriented with its hydrogen atoms towards the anion, and in this case only ion–dipole interaction is present. This interaction is intensified by increasing charge on the anion. As a result, only singly charged anions are extracted well, double charged anions are already feebly extracted, while triply charged anions are hardly extracted at all by oxygen-containing solvents.

Thus it would appear in principle that any salts should be extracted provided that the cation can firmly bind water, the anion has a small charge and is not too small in size, while the organic solvent possesses sufficient donor capacity. Salts containing large ions can be extracted in non-coordinating solvents having a high dielectric constant. Two opposite tendencies exist: when solvents with coordinating ability are used, salts with small cations capable of considerable solvation should be extracted better (for example Li > Cs); with non-coordinating solvents of high dielectric constant, on the other hand, extraction should improve with increase in size of the cation (Li < Cs).[9] In practice the two factors operate simultaneously, but sometimes these tendencies are very clearly expressed. An example is provided by Boyd and Larson's results[67] on the extraction of septivalent technetium from 1 M nitrate solutions with tributyl phosphate and from 1 M chloride solutions with nitromethane (Table).

Let us cite some other experimental data on the extraction of salts. The extraction of sodium chloride by TBP is very poor, but sodium perchlorate is extracted from 3 M solution by a 2.3 M solution of TBP in benzene with a partition coefficient of 0.068;[21] lithium perchlorate will probably be extracted still better. Baldwin *et al.*[68] studied the distribution of a series of alkali-metal halides between an aqueous solution and tributyl phosphate, and determined the equilibrium amount of water in the organic phase. It was shown that all the halides carry water along with them on passing into the organic phase. The quantity of water in the organic phase depends on the nature of the cation, diminishing in the sequence H > Li > Na > K. The hydration number depends also on the anion. The sequence of extractability is HI > HBr > HCl; LiI > LiBr > LiCl; HX > LiX > NaX > KX > CsX. The extent of extraction

§ The dielectric constant of the organic phase plays an important part here. For a more detailed account, see Diamond[9].

TABLE. Extraction of technetium from 1 M salt solutions with tributyl phosphate and with nitromethane.

TBP, 1 M nitrate solutions of Tc	D	Nitromethane, 1 M chloride solutions of Tc	D
H	28.3	Li	0.55
Li	14.7	Na	1.2
NH_4	4.6	H	1.6
Na	2.2	K	2.1
K	1.1	Rb	2.5
Ca	15.6	Cs	3.7
Cu	5.4		
Al	4.4		

increases with increasing halide concentration in the aqueous phase; even LiCl, when its concentration in the aqueous phase is 13 m, is extracted in amount corresponding to a concentration of it in the equilibrium organic phase (TBP) of the order of 1 m (*i.e.* with a partition coefficient close to 0.1). So that there may be no doubt whether the extraction of salts can be considerable, we stress that LiI is extracted by TBP even better than is hydrochloric acid. It is readily established that these results correlate fairly well with the views set out above.

When basic oxygen-containing solvents are used (with which we are mainly concerned here), salts are usually extracted less well than the corresponding acids¶. The reason is that molecules of the water of hydration are usually more weakly bound to the metal cations than in the extraction of acids (the positive charge of the cation is diffuse, and there is no migration of the proton in the hydrates).

It is interesting that long ago Werner also gave expression to the thought that several coordination spheres can form around a positive ion. He argued that when water molecules form a coordination sphere around a positive ion, a negative charge is induced on the inner surface of the sphere, so that the outer surface bears a positive charge, just as the metal ion itself does. This enables it to attract another sphere of water molecules, which will likewise bear an induced charge. The process may be repeated several times (quoted from Bailar and Busch[69]).

If the salt is extracted together with "intermediate" water, the "slope method" for determining the solvation number may not give a satisfactory result. The reasons are the same as in the case of acids considered above. Determination of the solvation number by the slope method encounters less difficulty with the anhydrous solvate formed by uranyl nitrate with TBP than with hydrated uranyl perchlorate. Shevchenko *et al.*[21] showed that the slope method is inapplicable to the system $UO_2(ClO_4)_2$–TBP–H_2O–diluent. As already mentioned, the work of Vdovenko and his collaborators has shown that the degree of hydration of uranyl nitrate on extraction with ethers and esters varies with the concentration and nature of the diluent. It must be supposed that the solvation number, too, will vary.

In the investigation of the extraction of acids as a function of hydrogen-ion concentration, a constant ionic strength (*i.e.* concentration of chlorides, for example) is sometimes maintained by means of lithium salts. This apparently should not be done, since lithium itself can be extracted by basic solvents to a greater extent than, for example, sodium or potassium. As a result, the data obtained do not reflect the relation under investigation. Deviations would be especially large at low hydrogen-ion concentrations; at higher concentrations, the acid will be extracted preferentially (for example, $HFeCl_4$, not the salt $LiFeCl_4$), and the relative error will diminish.

¶ The position may change when non-coordinating solvents of high dielectric constant are used, as Diamond[9] has shown.

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COLLOID-CHEMICAL MECHANISM OF THE SEPARATION OF SOME ELEMENTS BY EXTRACTION

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Extraction processes are of very great value in radiochemistry, inorganic and analytical chemistry, and also for the fissile materials industry and in chemical technology. Establishment of the mechanism of the extraction of various elements is therefore of great theoretical and practical interest, since it will make possible a systematic choice of extractants and determination of the optimum conditions for the process. In some cases a colloid-chemical mechanism is possible for the extraction of a series of elements. Some elements on passing into the organic phase may be extracted in the form of highly disperse colloidal particles (submicroscopic sols).

The extraction of elements by a colloid-chemical mechanism is due to the diminution in free surface energy of the system when hydrophobic colloidal particles pass from the aqueous phase into the organic phase, and is governed to a first approximation by the difference in surface tension at the aqueous medium – disperse phase boundary of the sol and at the disperse phase – organic solvent boundary.

Thus good extractants should generally have a comparatively low surface tension (γ = 15 – 25 erg cm^{-2}). In fact, however, this relation is more complex in character.

The process of extraction consists in the vigorous stirring of aqueous solutions with the organic solvent in the presence of air. The aqueous solution and the organic solvent are divided up into fine droplets, and unstable emulsions are formed, which break down rapidly. At the same time the air which is present also forms fine bubbles, and to some extent affects the process of extraction. Highly disperse colloidal particles, on passing into the extractant layer, may be stabilised by the adsorption on them of an oriented monolayer of organic solvent molecules. Sometimes stabilisation requires the use of some ionogenic surface-active agents.

An important role in extraction processes is played by thin layers and films formed at the surface of separation of the two liquid phases. Various physicochemical processes take place in these films, and these play a considerable part in extraction processes (formation and stabilisation of emulsions, etc.).

The interfacial tension in the interphase film at the surface of separation of two liquids is diminished as a result of the increased adhesion between the two liquid phases[1]. Theoretical calculations show that a 1000–3000-fold concentration of a substance is sometimes possible in the surface film[2]

Adsorbed layers, resembling surface gels in structure, form interphase films having considerable elasticity and mechanical strength. Molecules in these layers possess some mobility[3,4].

Some soluble inorganic colloids can form films at the surface of separation of two liquid phases, and act as stabilisers for emulsions[5]. In most cases the formation of colloidal solutions involves the initial formation of globular or shapeless amorphous particles, which then disintegrate, in the process of crystallisation, into finer crystalline particles[6], so that sols have their maximum reactivity at the instant of formation of colloidal solutions. Colloidal solutions may result from hydrolysis, and also from the formation of sparingly soluble compounds in the presence of certain electrolytes. It is also possible that some elements may be adsorbed on sols of substances present in the solution as impurities. Some solutions also show an increased quantity of sols with increasing time of storage.

Elements (W, Mo, Nb, Ta, Ru, Zr, Po, Ce, La, Pb, Th, Sn, Ti, Y, etc.) present in solution in low concentrations tend to form colloidal solutions, and can therefore be extracted by a colloid-chemical mechanism. "Carrierless" radioisotopes may be extracted as a result of the formation of true colloidal solutions of the radioisotopes or may even be adsorbed on foreign colloidal carriers, after which they are extracted.

It has previously been ascertained[7] that thin films are formed on the surface of colloidal solutions of hydrosols of the hydroxides of iron, chromium, and aluminium. It has been suggested[8] that these films are formed as a result of surface coagulation of the sols, and it has been established that the surface of aqueous solutions is negatively charged as a result of orientation of the water dipoles and preferential adsorption of anions in the surface layer[9].

As a result of Brownian motion, positively charged colloidal particles of the sol escape to the surface, where they are partly discharged and are coagulated with the formation of a surface film. The hydration sheath of the colloidal particle is lost together with its charge[10,11].

At the hydrosol–organic solvent interface the colloidal particles are more firmly attached, this being associated with interfacial tension at the colloidal particle–liquid surface[12,13]. It has also been established that the use of an organic solvent is accompanied by a change in stability of the sol, resulting in its rapid coagulation[14].

It had already been ascertained long ago that sols are coagulated under the influence of those non-electrolytes which diminish the dielectric constant of the medium[15]. The coagulating action of a non-electrolyte is stronger the greater the diminution in dielectric constant produced by the non-electrolyte at the interface.

Colloidal particles will concentrate at the interface between liquids if the polarities of the liquids are different[16]. Thus the greater the difference in dielectric constant between the aqueous solution and the non-aqueous phase, the more are colloidal particles concentrated at the boundary with the organic solvent.

Depending on the coagulating power of organic solvents, a film of varying thickness is formed at the surface of separation of the liquids, non-polar liquids giving the thickest films. When colloidal particles pass into the organic phase, the electrical repulsion decreases, the density of packing of the micelles increases, and also the structure of the micelles becomes more compact owing to the expulsion of water from them. Finely ground powders (quartz, glass, Al_2O_3, etc.) form both stable and unstable suspensions in some ketones[17]. Stable suspensions of some compounds (TiO_2, ZnO) can be formed also in organic solvents (toluene, butyl acetate, etc.)[18]. Stable colloidal solutions of Rhodamine B can be obtained in benzene.

It is to be assumed that an increase in the degree of dispersion of a sol will result in a more complete transfer of the extractable substance to the organic phase. Addition of some substances (starch, etc.) sometimes promotes extraction by stabilising the sols in the aqueous and organic phases.

Several inorganic compounds present in colloidal solution can be extracted by various organic solvents. Study by electrophoresis, electrolysis, and diffusion methods of the properties of the coloured thiocyanato-complexes of iron (obtained by the interaction of $FeCl_3$ and NH_4SCN) has shown that the complex is present in solution in the colloidal state and carries a positive charge; the degree of dispersion of the particles increases in acid medium[19]. It may be supposed on the basis of these investigations that the good extraction by organic solvents of several thiocyanato-complexes (of W, Nb, Ta, Co, etc.) is due to their being present in the aqueous solution in the colloidal state. It is possible that iodine is extracted by various organic solvents (chloroform, etc.) also in the colloidal state.

Some metal halides can form stable sols[20] in concentrated solutions (sulphuric and phosphoric acids, concentrated $CaCl_2$ solution, etc.); perhaps it is this which explains the good extraction of these salts ($FeCl_3$, etc.).

Increase in the HCl concentration up to a certain limit (6–7 *N*) produces an improvement in the extraction of the chlorides of several elements (Ga^{III}, Fe^{III}, Mo^{VI}, As^{III}, Sb^{V}, Te^{IV}). A similar situation occurs in the extraction of bromides (of Fe^{III}, Ga^{III}, and In^{III}). This observation can be explained by the increasing quantities of salts passing into the colloidal state as the acid concentration increases. When the concentrated solutions are diluted with water, the colloidal particles break down, and extraction of the elements ceases.

It has also been found that elements are poorly extracted from dilute solutions of nitric acid (0.5–1 *N*); increase in the nitric acid concentration to 8 *N* produces a marked improvement in the extraction (of Au^{III}, Th^{IV}, U^{VI}, Ce^{IV}), which can also be explained by the formation of sols of the nitrates of these metals in the comparatively concentrated nitric acid. The use of salting-out agents in extraction processes favours the formation of colloidal solutions, since an increasing salt content in the solution is accompanied by the formation of the corresponding sols[21].

It must be assumed that some heteropoly-acids, which are readily extracted, also can form colloidal solutions[22,23]. Readily extractable compounds are formed by the interaction of microquantities of various elements with some organic reagents (cupferron, 8-hydroxyquinoline, 1-nitroso-2-naphthol, dimethylglyoxime, etc.) These reactions result in the formation of sparingly soluble compounds of the elements in the colloidal state, which usually pass readily into the organic phase. A colloid-chemical mechanism can explain the absence of appreciable specificity in the isolation of these compounds by extraction.

Nitrates of lanthanides, actinides, and zirconium form compounds with tri-n-butyl phosphate (TBP), their formulae being $M(NO_3)_3.3TBP$, $M(NO_3)_4.2TBP$, and $MO_2(NO_3)_2.2TBP$. In the tributyl phosphate the nitrates of these metals are solvated and occur in an unionised form[24].

TBP extracts molecular compounds of other elements as well[25]. Numerous investigations have been made of the extraction of uranium and other elements in the form of various compounds, in which a tendency has been observed in some cases for polymeric forms to be produced[26,27]. It must be assumed that these compounds, too, form on extraction colloidal or semi-colloidal solutions, and pass into the organic solvent in the form of sols.

Several dyes (Methylene Blue, Methylene Violet, Congo Red, Benzopurpurin, etc.) form colloidal solutions in aqueous solution[28,29]; therefore the extraction by organic solvents of these dyes and their reaction products with certain elements also can be explained by a colloid-chemical mechanism. Use of surface-active agents makes it possible to extract with various solvents several non-extractable colloidal dyes and the sparingly soluble reaction products which they form with elements.

The possibilities must be noted of the extraction of microquantities of various elements which form sparingly soluble compounds with organic reagents. In most cases these compounds dissolve well in the appropriate organic solvents, and therefore should be readily extracted by a colloid-chemical mechanism. Research on these lines will probably yield a considerable number of methods for the separation of microquantities of various elements by extraction.

Associated molecules are sometimes formed in solution under the influence of cohesive forces.

At the present time a considerable number of molecular compounds are known, formed both by inorganic and by organic molecules. Several substances form polymeric compounds, among which are silver and gold cyanides, silver thiocyanate, and hydrargillite $[Al(OH)_3]_n$. The hydroxide, carbide, sulphide, and silicide of iron[30] also can form polymers.

In the formation of the thiocyanato-complex of molybdenum, Mo^V undergoes reaction in dimeric forms[31].

It has been suggested that ferric chloride occurs in the form of dimers $[FeCl_3]_2$ in benzene, as also in aqueous solution[32,33]. Polymerisation of iron is possible in an ether layer, with formation of the compound $[HFeCl_4]_n$.[34] It is also possible that similar associated molecules of ferric chloride and other halide salts can exist in some other organic solvents, and under the influence of the organic solvents can then form colloidal solutions.

The extraction of associated molecules can be represented as their interaction with the organic solvent to form a sol, which then passes into the organic phase. The extraction of elements present as ions in the solution can also be represented as interaction with the organic extractants, yielding associated molecules which subsequently aggregate and form sols capable of extraction. It can be assumed that an equilibrium between simple molecules, aggregated molecules, and colloidal particles is sometimes established in extraction processes.

Extraction can take place at very high temperatures. At 1150°–1200° molten metallic magnesium can be used to extract plutonium from molten metallic uranium containing up to 1% of Pu. Plutonium can be extracted also from a U–Cr alloy melting at a lower temperature (860°).

The extraction is carried out with vigorous agitation of the two immiscible phases either mechanically or by an induction method. The partition coefficient is 2. The process takes place very slowly in the absence of stirring[35,36]. Colloidal particles of plutonium must be assumed to pass into the metallic magnesium. Other similar processes are also known[37].

It has previously been established that colloidal solutions can be formed in two-phase metallic alloys[38]. Various radioisotopes can occur in solution in a colloidal state[39–43].

Study of the adsorption of microquantities of some radioisotopes (Zr, Po, etc.) on hydrophobic non-ion-exchange surfaces (paraffin wax, Floroplast 4) shows that these radioisotopes may be present in solution in molecular form[44].

It has been found that ^7Be at concentrations below 10^{-9} M in 0.01 *N* HNO_3 is present in the solution in the form of a radiocolloid. From the Einstein–Stokes equations the mean radius of the aggregates was calculated as 7 Å at pH 2[45] and 22 Å at pH 10. It has also been found that some radioisotopes can be adsorbed on other colloidal particles present in the solution[46].

Methods of centrifuging, ultrafiltration of the solutions, and adsorption on activated charcoal have been used to study the radioisotopes ^{90}Y and ^{125}Sb at concentrations of $\sim 10^{-8}$ M. It was found that the yttrium isotope forms radiocolloids and is poorly adsorbed on colloidal impurities. The antimony isotope is present in solution in the form of radiocolloids, and also as chloro- and chlorohydroxo-complexes.

At a concentration of $\sim 10^{-7}$ M in nitric-acid solution ^{111}Ag forms a truly colloidal solution, and is not adsorbed on impurities[47]. The state of the radioisotopes ^{65}Zn and ^{90}Y in solution has also been studied[48].

At the present time extraction methods are employed with various radioisotopes at extremely low concentrations.

A study has also been made of the extraction with tributyl phosphate of fission rare-earth radioisotopes[49,50]. All these results show that some radioisotopes can be

extracted in the colloidal state by themselves, or else are adsorbed on colloidal impurities and are extracted together with the latter.

Extraction by a colloid-chemical mechanism can be represented as follows: if the element to be separated is present in solution in the form of highly disperse sols (submicroscopic sols and semi-colloids), these sols pass into the organic phase as a result of the decrease in free surface energy of the system. If, however, the element to be separated is present in the form of ions in the solution, extraction involves the formation of an unstable emulsion with the production of a very large surface of interaction between the extractant and the aqueous solution. Associated molecules of the extractable compound then arise in the interfacial film, and these aggregate to particles of a sol, which subsequently pass into the organic phase.

When the sol passes into the organic phase it may completely dissolve with the formation of a true solution. There may be cases in which a sol becomes uniformly distributed in the organic solvent, when colloidal solutions are formed; in most cases the degree of dispersion of the sol is then diminished.

Finally, it is possible that, after the sol has passed into the layer of organic solvent, it will probably aggregate and separate in the interfacial film (and also at the organic solvent–glass interface) as a suspension.

It is seen from the above that particles of various sols can be formed and pass from the aqueous medium into the organic solvent. When a hydrosol is shaken up with an organic liquid, it sometimes happens that after some time the particles collect at the interface between the two liquids. At low concentrations of the sol, however, this process is slowed down, and it is therefore possible to isolate the element together with the organic phase.

We have carried out experiments on the extraction from colloidal solutions of various elements and compounds with organic solvents (Table 1).

These experiments show that diverse compounds can be extracted from colloidal solutions formed by sparingly soluble compounds.

The most stable sols are formed in chloroform, those obtained in diethyl ether being less stable. It is advisable to separate the organic solvent rapidly from the aqueous solution after extraction, since in some cases unstable colloidal solutions can be formed in the organic solvent. When the sol is readily soluble in the organic solvent, a comparatively large amount of substance can be extracted.

As a practical result of the ideas which we have developed on the colloid-chemical mechanism of extraction, we have worked out a method for the extraction of microquantities of many elements in the form of sparingly soluble compounds.

Table 2 illustrates the application of this method to several elements. It can be seen that a colloidal solution of gold containing 0.1 μg of Au is extracted comparatively well (20–25%). Microquantities of zinc (20 μg) in the form of carbonates are extracted to the extent of 20–25%. Lead chromate is extracted well (75–90%); if $BaCrO_4$ is used as carrier, unweighable amounts of lead (RaD) are extracted to the extent of 75%.

An interesting phenomenon is observed in the extraction of unweighable amounts of RaD (Pb) in the form of sulphate when different carriers are used. In the absence of carrier, RaD is poorly extracted; use of $PbSO_4$ and $SrSO_4$ as carriers also gives unsatisfactory results. With $BaSO_4$ as carrier, however, extraction is increased to 30%. This difference probably depends on the solubilities of the sulphates of these compounds, and also on their chemical composition.

TABLE 1. Extraction of some elements from colloidal solutions.

Chemical compound	Organic solvent	Chemical compound	Organic solvent
Au	$CHCl_3$ and CCl_4	$BaSO_4$	ether and $CHCl_3$
Ag	ether and $CHCl_3$	Ag_2CrO_4	ether and $CHCl_3$
S	ether and $CHCl_3$	$PbCrO_4$	$CHCl_3$
CoS	$CHCl_3$	SiO_2	ether and $CHCl_3$
Ag_2S	$CHCl_3$	$Co(OH)_2$	$CHCl_3$
AgCl	$CHCl_3$	$Co(AlO_2)_2$	$CHCl_3$
AgI	$CHCl_3$ and CCl_4	$Ag_2C_2O_4$	$CHCl_3$
$SrSO_4$	ether and $CHCl_3$	Ag_2CO_3	$CHCl_3$

TABLE 2. Extraction of microquantities of some elements in the form of sparingly soluble compounds.

Radio-isotope	Amount of carrier, μg	Precipitant	Extractant	Radio-isotope extracted, %	Remarks
Au^{198}	Au 0.1	ascorbic acid*	$CHCl_3$	18.6	3 ml of aqueous soln. and 3 ml of extractant taken for all expts.
Au^{198}	Au 0.1	quinol*	$CHCl_3$	25.1	
Au^{198}	Au 0.1	»	ether	14.3	
Zn^{65}	Zn 20	Na_2CO_3	$CHCl_3$	16.7	
Zn^{65}	Zn 20	$K_4Fe(CN)_6$	$CHCl_3$	8.6	
Zn^{65}	Zn 20	Na_2CO_3	CCl_4	20.1	
Pb^{210} (RaD)	Pb 200	K_2CrO_4.	$CHCl_3$	88.0	2 extractions
Pb^{210}	Ba 23	K_2CrO_4	$CHCl_3$	76.0	measurements made after equilibrium reached between RaD and RaE
Pb^{210}	Pb 20	K_2CrO_4	$CHCl_3$	58.2	3 ml 0.1 *N* KCl taken
Pb^{210}	Pb 20	Na_2SO_4	$CHCl_3$	0.0	
Pb^{210}	Sr 90	Na_2SO_4	$CHCl_3$	0.6	
Pb^{210}	Ba 22	Na_2SO_4	$CHCl_3$	30.0	
Pb^{210}	none	H_2SO_4	$CHCl_3$	5.5	
Pb^{210}	Pb 20	H_2SO_4	$CHCl_3$	0.5	
Pb^{210}	Sr 90	H_2SO_4	$CHCl_3$	0.6	
Pb^{210}	Ba 22	H_2SO_4	$CHCl_3$	30.6	
Ag^{110}	Ag 19	KCl	$CHCl_3$	48.7	
Ag^{110}	Ag 19	K_2CrO_4	$CHCl_3$	53.0	
Ag^{110}	Ag 19	K_2CO_3	$CHCl_3$	20.6	
Ag^{110}	Ag 19	$H_2C_2O_4$	$CHCl_3$	35.3	
Co^{60}	Co 20	K_2CO_3	$CHCl_3$	21.0	
Co^{60}	Co 20	Na_2S	$CHCl_3$	56.0	3 extractions
Co^{60}	Co 20	NaOH	$CHCl_3$	26.6	
Co^{60}	Co 20+Al 80	NaOH	$CHCl_3$	80.5	3 extractions[81]
Sr^{90}	Sr 85+Ba 44	H_2SO_4	$CHCl_3$	30.8	
Sr^{90}	Sr 85	K_2CO_3	$CHCl_3$	23.1	
Pb^{210} (RaD)	Pb 26	Na_2S	$CHCl_3$	45.6	3 extractions
In^{114}	In 23	NaOH	$CHCl_3$	13.2	
In^{114}	In 23	K_2CrO_4	$CHCl_3$	34.4	3 extractions
In^{114}	In 23	KNO_3	$CHCl_3$	12.4	
Tl^{204}	Tl 63	Na_2S	$CHCl_3$	12.1	
Tl^{204}	Tl 63	Na_2S	CCl_4	25.8	
Tl^{204}	Tl 63	NaOH	$CHCl_3$	3.0	
Tl^{204}	Tl 63	NaOH	CCl_4	15.3	
Tl^{204}	Tl 63	KI	$CHCl_3$	27.3	3 extractions
Tl^{204}	Tl 63	KI	CCl_4	98.6	3 extractions
Tl^{204}	Tl 63	$K_4Fe(CN)_6$+NaOH	$CHCl_3$	12.1	
Tl^{204}	Tl 63	$K_4Fe(CN)_6$+NaOH	CCl_4	69.8	3 extractions

* Colloidal particles of Au separated.

Thus the coprecipitation of microquantities of a substance can be studied by using the colloid-chemical method of extraction. Minute quantities of a substance ("carrierless" radioisotopes) can be isolated by extraction with the use of a microcollector (20–100 μg of M) for coprecipitation.

It is interesting that very small amounts of sparingly soluble compounds of elements are not extracted; this can be explained by the impossibility of a solid phase being formed; employment of an appropriate microcollector (10–100 μg of M) results in the formation of colloidal solutions, which can then be extracted. Microquantities of silver are relatively well extracted in the form of AgCl 50%, Ag_2CrO_4 50%, $Ag_2C_2O_4$ 35%, and Ag_2CO_3 20%. Cobalt is extracted well in the form of cobalt aluminate $Co(AlO_2)_2$ 80%, CoS 56%, and $Co(OH)_2$ 25%.

The efficiency with which sols are extracted depends on the relative volumes of extractant and of aqueous phase.

Additional work which we have carried out has shown that good results are obtained in the extraction of microquantities of several other elements in the form of sulphides and various sparingly soluble compounds. An advantage of this method is the rapid separation from solution (5–10 min) of the element to be determined and the simplicity with which the precipitated compound is converted into a soluble state without the introduction of foreign impurities. The method makes it possible to isolate microquantities of various elements in the form of sparingly soluble compounds.

The mechanism of the transfer of elements to the organic phase can be represented as follows: (*a*) a sol present in the aqueous solution passes into the organic solvent; (*b*) the compounds to be extracted form, under the influence of the organic solvent, associated molecules, which aggregate to sols, the latter then passing into the organic solvent. Elements may be present in the solvent in the following states: particles of hydrosol which pass into the solvent and dissolve in it; particles of the sol which pass into the solvent and exist in it in the form of a colloidal solution, when the particle size may even increase; particles of the sol which pass into the organic solvent, then rapidly aggregate, and separate in the interfacial film in the form of a coarse suspension.

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ADVANCES IN THE SYNTHESIS OF PERFUMES POSSESSING AN ISOPRENOID STRUCTURE

V.N.Belov and N.I.Skvortsova

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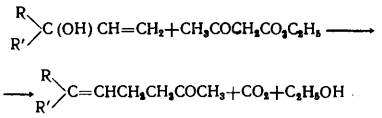
1. INTRODUCTION

Compounds of isoprenoid structure are known to occupy a special position in the chemistry of perfumes. This group includes a large number of natural compounds having valuable scents, as well as synthetic compounds which are not found in Nature.

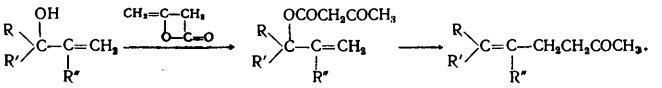
The evolution of scientific research in this field has been characterised during recent years not only by a continuation of the intensive search for new perfumes but also by considerable advances in developing industrial methods for the synthesis of many important compounds of this type from the simplest chemical raw materials. This work is examined in the present review.

2. TERPENOID AND SESQUITERPENOID COMPOUNDS

The direction of research on the synthesis of compounds of isoprenoid structure was greatly affected by the work of Carroll, who in 1940 proposed an elegant method for preparing unsaturated ketones by the treatment of tertiary allylic alcohols with acetoacetic ester in the presence of sodium ethoxide or of other alkaline reagents[1,2]:



This method†, subsequently developed by several other chemists, opened up wide possibilities for the preparation of the most important intermediates of isoprenoid structure. One of the most promising variants of Carroll's method is the use of diketen instead of acetoacetic ester. In this process the unsaturated ketone is obtained by condensation of the corresponding unsaturated vinylmethanol with diketen followed by pyrolysis of the resulting acetoacetate:



Among the compounds obtained in this way, 6-methylhept-5-en-2-one (I)[3] was described as early as 1943. A little later 5,6-dimethylhept-5-en-2-one (Ia) was obtained in a similar manner from 2,3-dimethylbut-1-en-3-ol (IIa)[5] (see Scheme 1, p.122).

During recent years various aspects of these reactions have been studied. A detailed investigation has been made of the conditions for the conversion of tertiary allylic alcohols into unsaturated ketones by the Carroll reaction[6-13]. Dreux and Colonge[7] suggested the use of aluminium isopropoxide as catalyst, and also studied the effect of the

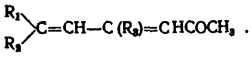
† For the reaction mechanism, see Refs. 1, 3, and 4.

structure of the initial alcohols on the yield of the unsaturated ketones. Nazarov and his collaborators[9-11] established that the alcohols can be made to react with acetoacetic ester even in the absence of a catalyst, if reaction is carried out under pressure or in high boiling solvents; high yields can be achieved if the ethyl alcohol formed is distilled off during the reaction (using a fractionating column)[9].

Results have been obtained showing that, during the reaction of acetoacetic ester with an unsaturated tertiary alcohol, formation of an unsaturated ketone involves the intermediate formation of an acetoacetate[11]; on the other hand, it has been shown that unsaturated ketones can be obtained from substituted vinylmethanols by the "diketen" method in a single stage without isolation of an acetoacetate[9,14].

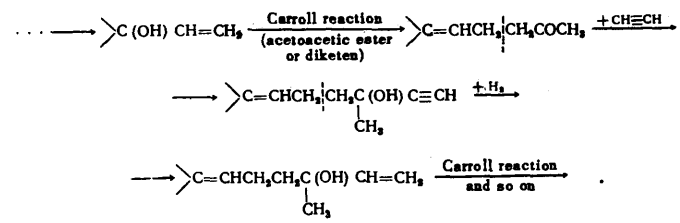
Amines — piperidine, pyridine, triethylamine, and several others[9-11] — are among new catalysts suggested for the formation of acetoacetate by the "diketen" method.

An interesting extension of the method was found in 1953 by Kimel and Sax[15], who showed that tertiary ethynylmethanols can be converted in this way into dienones. This allowed for the first time the transition to be made from dehydrolinalool (III), a product of the condensation of 6-methylhept-5-en-2-one (I) with acetylene, *via* its acetoacetate (IV) to pseudoionone (V), and also from dehydromethyllinalool (IIIa), obtained in a similar way from 5,6-dimethylhept-5-en-2-one (Ia), to pseudoirone (Va). Kimel and Sax's method was soon developed by Lacey[16,17] and applied to the synthesis of various dienones of general formula:



During subsequent years this method was subjected to a thorough and comprehensive investigation, special attention being paid to the development of various modifications of the synthesis of pseudoionone (V) and pseudoirone (Va). The possibility was noted of obtaining (V) and (Va) by the direct reaction of (III) and (IIIa) respectively with acetoacetic ester[4,11,12,18-24] or even by condensation with diketen followed by pyrolysis of the resulting acetoacetate (IV) or (IVa) respectively[8,11,15,25-27].

The elaboration of new methods for obtaining dienones of the type of pseudoionone and pseudoirone from acetylenic alcohols has played an extremely important part in the further development of the synthesis of compounds of terpenoid structure. At the present time an isoprenoid chain of any desired size can be constructed by repeated introduction of an acetonyl radical followed by condensation of the resulting ketone with acetylene and selective hydrogenation of the triple bond to a double bond:

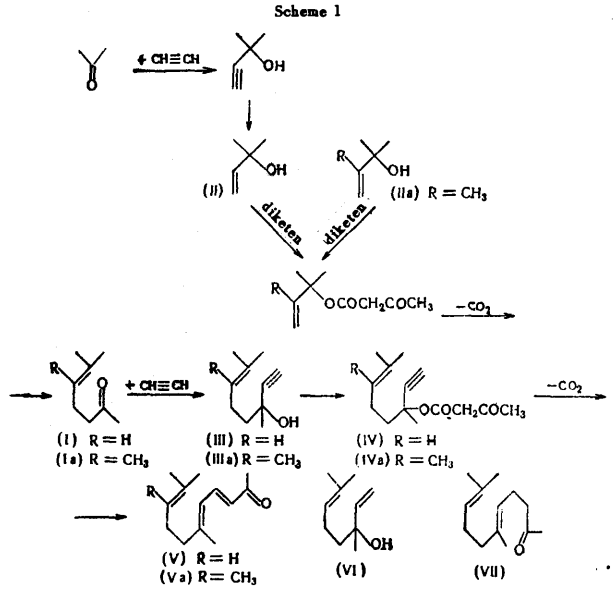


The condensation of acetylene with ketones in the presence of alkalis, leading to the formation of the corresponding ethynylmethanol, was discovered by Favorskii‡ as early as 1900.[28,29] Thanks to the detailed elaboration of this method by Nazarov and his coworkers[30-33], who studied the condensation of acetylene with many carbonyl compounds, no appreciable difficulty was encountered in carrying out the reaction under industrial conditions. Data on the condensation of acetylene with acetone (influence of solvents, nature and amount of alkaline agent, and added alcohols) have recently been reported in a paper by Japanese chemists[34], and also in Lacey and Jowitt's patent[35]. This reaction can also be carried out in solution in liquid ammonia in the presence of metallic sodium[6,8].

There is no difficulty in converting the ethynyl alcohol to the corresponding vinyl alcohol, the selective hydrogenation of the acetylenic to an ethylenic bond, under industrial conditions. This reaction has been quite well studied on many examples[30,33,36-43].

The above scheme for synthesising a terpenoid molecule has already found practical application in the USA, where Hoffmann-La Roche have constructed large works near New York for the synthesis of linalool, citral, and a group of isoprenoid vitamins[44-47]. From the general scheme for the production of terpenoid compounds in these works, we give below only that part which relates to the synthesis of pseudoionone (V) and pseudoirone (Va) (Scheme 1).

Scheme 1



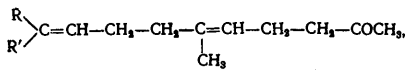
The yield of (V) is 35% based on the initial acetone and acetylene.

The above authors note the wide possibilities for the synthesis of terpenoid compounds opened up by the application of this method: thus linalool (VI) and dihydrolinalool can be obtained by the partial hydrogenation of dehydrolinaloool; condensation of linalool with diketen and subsequent decomposition of the resulting acetoacetate yields geranylacetone (VII), from which sesquiterpenoid alcohols and their ethers,

‡ For the significance of this work and also of other investigations by Favorskii on the synthesis of isoprenoid compounds see the recently published review by Yanovskaya and Kucherov[48].

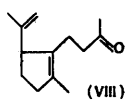
etc. can be obtained. The method can, of course, be extended to the synthesis of the most varied isoprenoid alcohols, aldehydes, ketones, and their derivatives, homologues, and analogues differing in chain length, substituents, or position of double bonds. In a detailed paper Kimel *et al.*[6] reported a considerable number of substances synthesised in this way, but unfortunately they did not describe the odour of previously unknown compounds.

A series of homologues and analogues of pseudoionone of general formula



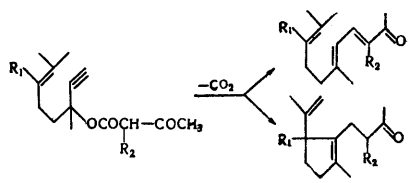
where R = CH_3 and R′ = H, Cl, CH_3, C_2H_5, iso-C_3H_7, and t-C_4H_9 and R = R′ = iso-C_3H_7, have recently been synthesised by Nazarov *et al.*[49,50] by the reaction of homologues and analogues of dehydrolinalool with acetoacetic ester, and also by condensation with diketen followed by pyrolysis of the resulting acetoacetates.

Pyrolysis of the acetoacetates of tertiary ethynyl alcohols is accompanied by a series of side-reactions, which considerably lower the yield of the desired dienones. This was responsible for the appearance of a large number of papers aimed at seeking better conditions for carrying out this stage[8,9,11,26,27,51], and also on the side-products which are formed. It was established that the most important side-products in the pyrolysis of dehydrolinalyl acetoacetate is a ketone§ (VIII) isomeric with pseudoionone and containing a cyclopentene ring[52-56]:



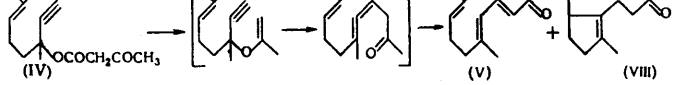
(VIII)

A similar formation of ketones having a cyclopentene group was noted also in the pyrolysis of substituted dehydrolinalyl acetoacetates[55]:



The ketone (VIII) was also detected as a side-product in the preparation of pseudoionone by the reaction of dehydrolinalool with acetoacetic ester[53].

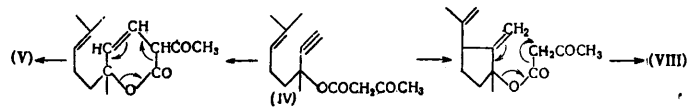
Possible schemes for the formation of pseudoionone and its isomeric ketone (VIII) by the pyrolysis of dehydrolinalyl acetoacetate have been discussed in several papers[54,56,57]. It is assumed, for example[26,55,56], that an allenone is formed as an intermediate product, and this undergoes further changes, *e.g.*[55]



(IV) (V) (VIII)

§ The formation in this reaction of a ketone isomeric with pseudoionone was noted also in a paper by Samokhvalov *et al*[27].

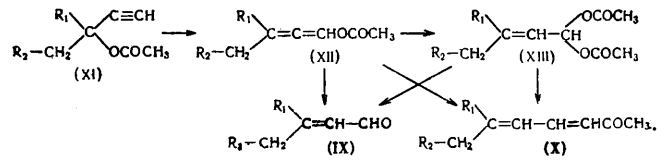
The following scheme has also been suggested[55]:



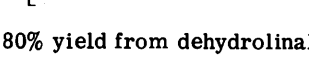
Nazarov and Krasnaya[58] studied the pyrolysis of acetoacetates prepared from tertiary enynyl and dienyl alcohols.

An interesting process, analogous to the Carroll reaction, was described by Daev and Dashunin, who showed that 5,6-dimethylhept-5-en-2-one (Ia) is formed by the reaction of pinacol with acetoacetic ester[59] or with diketen[60]. In the latter case the diacetoacetate of pinacol was obtained, which was subjected to pyrolysis at 200°.

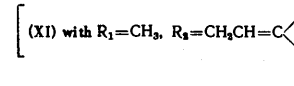
An extremely promising new possibility of passing from tertiary ethynyl alcohols to unsaturated aldehydes (IX) or the corresponding dienones (X) has been reported in recently published papers by Isler and his coworkers[61-63]. According to them, acetates of tertiary ethynyl alcohols (XI) isomerise, on being heated with acetic acid in the presence of copper or copper or silver salts, into allene acetates (XII), which then add on acetic acid to form diacetates (XIII). Alkaline hydrolysis of (XII) and (XIII), and also acid hydrolysis of (XIII) yield $\alpha\beta$-unsaturated aldehydes (IX). The simultaneous action of alkali and acetone, however, converts (XII) and (XIII) into $\alpha\beta\gamma\delta$-unsaturated ketones (X).



By this method Isler obtained citral:



in more than 80% yield from dehydrolinalool (III) *via* its acetate:



and also methylcitral, farnesal, and several other aldehydes from the corresponding ethynyl alcohols. From dehydrolinalool and methyldehydrolinalool (IIIa), pseudoionone and pseudoirone can be prepared, also in yields exceeding 80%, by esterification and rearrangement into allene acetates and diacetates followed by treatment with alkali in acetone.

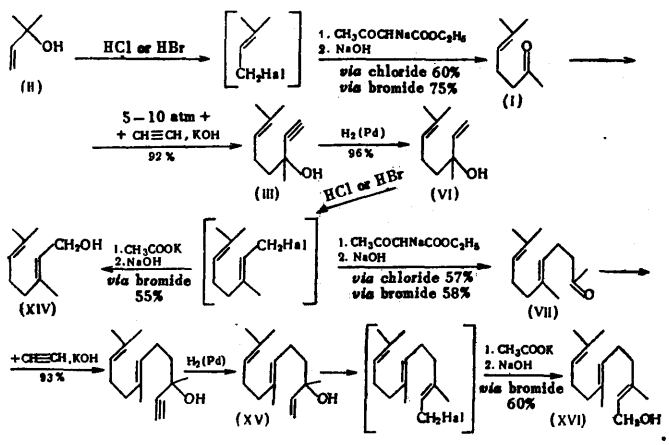
The simplicity and elegance of this route for converting tertiary ethynyl alcohols into unsaturated aldehydes or the corresponding dienones have attracted the interest of other chemists as well[51,57].

In order to obtain the unsaturated ketones which are intermediates in the synthesis of perfumes of the terpene and sesquiterpene series, much of the work published during recent years has also used the old, classical method of condensing halogeno-derivatives with the sodium derivative of acetoacetic ester followed by ketonic hydrolysis of the resulting substituted acetoacetic esters. In this way

methylheptenone (I) [9,14,64-66] and dimethylheptenone (Ia) [67] have been obtained from 3-methylbut-2-enyl halides $CH_3.C(CH_3):CR.CH_2Hal$, and geranylacetone (VII) [14,43,64,68-70] from geranyl halides $CH_3.C(CH_3):CH.CH_2.CH_2.C(CH_3):CH.CH_2Hal$.

By successive repetition of acetonylation, condensation of the ketones with acetylene, selective hydrogenation of the ethynyl alcohols to vinyl alcohol, and conversion of the tertiary alcohols *via* the halogen derivatives into primary alcohols, Nazarov *et al.* [14,64] synthesised a series of isoprenoid alcohols according to Scheme 2.

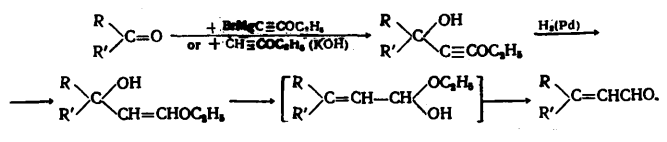
Scheme 2



The change from (II) to (I), from linalool (VI) to geraniol (XIV) or geranylacetone (VII), and also from nerolidol (XV) to farnesol (XVI), can be accomplished in one step, without isolation of the intermediate products.

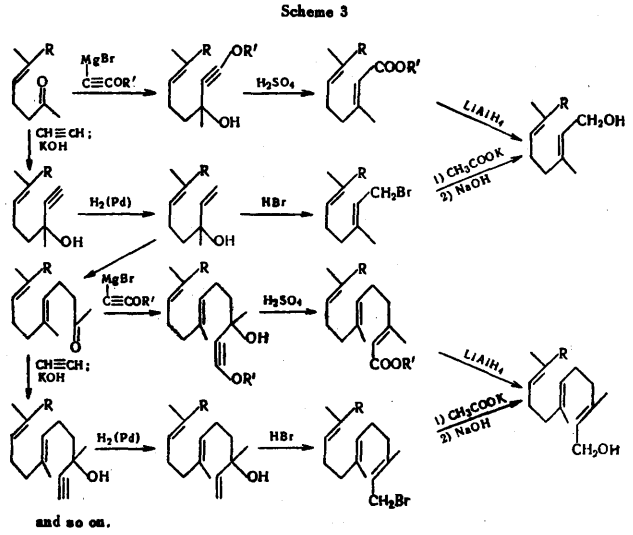
Starting from 4-bromobut-2-ene, Nazarov *et al.* [71] synthesised analogues of linalool and nerolidol containing one methyl group instead of the *gem*-dimethyl grouping.

Nazarov and his collaborators, in another synthetic route to isoprenoid compounds, have condensed the ketone with ethoxyacetylene instead of acetylene. This method of passing from a ketone to an unsaturated aldehyde containing two extra carbon atoms in the chain, which had been employed earlier in syntheses of terpenoid compounds [36,72-76], was used by Nazarov and his coworkers in two ways. In one of them the ethoxyacetylene was used in the form of its bromomagnesium derivative, and in the other the condensation with ethoxyacetylene was effected in the presence of caustic potash. The resulting ethoxyethynyl alcohols were hydrogenated to ethoxyvinyl alcohols, which were then converted into $\alpha\beta$-unsaturated aldehydes, probably *via* the intermediate formation of hemiacetals as a result of an allylic rearrangement [77]:

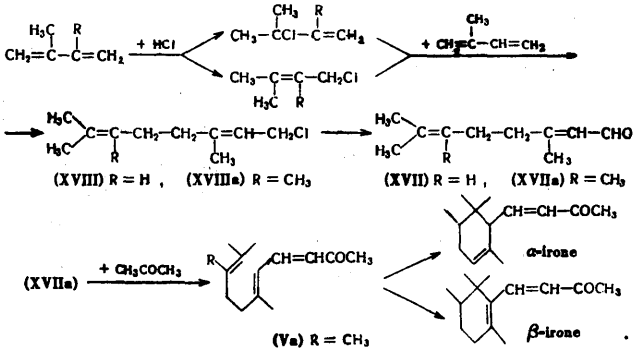


Use of methylheptenone (I) as starting compound gave a high yield of citral, and several of its homologues and analogues have been synthesised in the same way. This reaction has been employed also for the synthesis of analogues of geraniol, farnesol, and some other alcohols of isoprenoid structure [50,78] (see Scheme 3).

Scheme 3



A fundamentally new route for the synthesis of citral (XVII) [79-82] and 3,6,7-trimethylocta-2,6-dien-1-al (methylcitral) (XVIIa) [83,84] is based on the construction of a terpene skeleton by the treatment of the hydrochlorides of isoprene and dimethylbutadiene respectively with isoprene in the presence of a catalyst; the geranyl chloride (XVIII) and 1-chloro-3,6,7-trimethylocta-2,6-diene (XVIIIa), which were respectively obtained, were further converted into aldehydes by the Sommelet reaction¶. In the case of 3,6,7-trimethylocta-2,6-dien-1-al (methylcitral) (XVIIa) condensation with acetone was then carried out, followed by cyclisation of the pseudoirone (Va) into a mixture of α- and β-irones with a considerable preponderance of the former [83,84]:



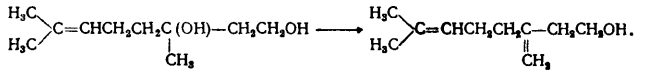
The dependence of the yield of geranyl chloride, and also of other terpene chlorides formed at the same time, on the

¶ Recently Swiss chemists [85] suggested a noteworthy new possibility for converting halogenated allyl derivatives into the corresponding unsaturated aldehydes by the action of nitroalkanes; among other examples, they give the preparation of citral from geranyl bromide; when the potassium salt of 2-nitropropane is used, the yield of citral reaches 75%. Nazarov *et al.* [86] employed the potassium salt of nitrocyclohexane for this purpose.

nature of the catalyst and the solvent, the temperature, and other conditions has been studied in a series of special investigations[87-90].

From a study of the infrared spectra of specimens of citral obtained by the Sommelet reaction from mixtures of terpene chlorides formed by the reaction of isoprene with its 1,2- and 1,4-hydrochlorides, Petrov *et al.*[91,92] established that such specimens consist of a mixture of geranial and neral, the content of the latter being higher than in natural citral[92]. This synthetic scheme for citral and methylcitral is attractive since it allows the carbon skeleton of the terpene compound to be constructed in a single step, by the direct combination of isoprene with its hydrochloride (or, in the case of methylcitral, with the hydrochloride of dimethylbutadiene), which are now readily available. Another extremely valuable feature is that the compound obtained in this way contains an active chlorine atom, which readily undergoes reactions leading to the formation of the corresponding oxygen derivatives (the alcohol by hydrolysis and the aldehyde by an oxidative change). All this distinguishes the method favourably from others. The processes which are assumed to form the basis of this scheme for constructing an isoprenoid chain have been worked out in detail in a series of investigations by Petrov and Leets and their collaborators[93-95].

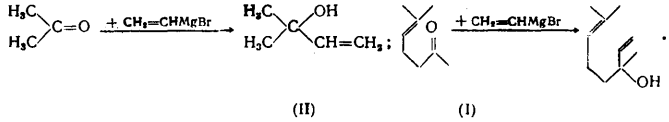
The formation of aliphatic terpene alcohols by the action of acidic reagents on 2-methylbut-3-en-2-ol (II) was studied by Lebedeva and Almashi[96]. They investigated the effect of pH on the composition of the mixture of products formed; the total yield of linalool and geraniol did not exceed 13–14% with a low recovery of the original methylbutenol. Subsequent work[97] established that, when aqueous $KHSO_4$ solution acts on (II), several reactions occur, including hydration of the geraniol formed during the reaction to geranyl hydrate (XIX), elimination of water from which in the presence of $KHSO_4$ yields an alcohol (XX) isomeric with geraniol:



(XIX) (XX)

Noteworthy work has also been done on the synthesis of terpenoid compounds using the method developed recently by Normant[98,99] for preparing organomagnesium compounds of vinyl type and using them in condensations with carbonyl compounds. The simplicity of the method (reaction is effected in tetrahydrofuran or tetrahydropyran solution) and the good yields of the reaction products make this an extremely attractive process, and have been responsible for its rapid introduction into laboratory practice†.

The change from acetone to methylbutenol (vinyldimethylmethanol) and from methylheptenone to linalool (yield 83%) was accomplished by Normant by treating these ketones with vinylmagnesium bromide[101-103]:

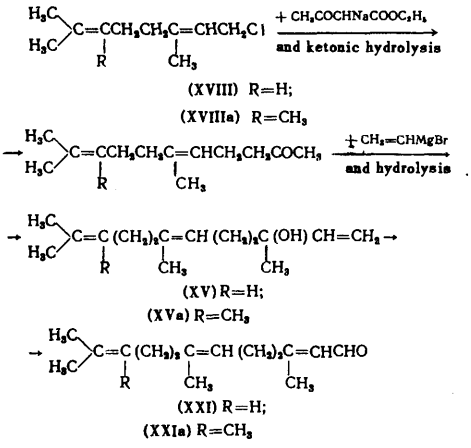


(II) (I)

Somewhat later other chemists reported the preparation of linalool in approximately the same yield by the reaction of methylheptenone with vinylmagnesium chloride[104].

† The vast literature on this reaction is quoted in a review by Ioffe[100].

Skvortsova *et al.*[84,105] utilised the Grignard reaction with vinylmagnesium chloride for the synthesis of nerolidol (XV), methylnerolidol (XVa), farnesal (XXI), and methylfarnesal (XXIa). The geranylacetone and methylgeranylacetone required for this were obtained by reaction of the corresponding chlorides, geranyl chloride (XVIII) and methylgeranyl chloride (XVIIIa), with the sodium derivative of acetoacetic ester. These syntheses made use of the chlorides obtained as intermediates in the synthesis of citral and irone by schemes discussed previously (see above):



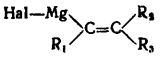
(XVIII) R=H;
(XVIIIa) R=CH_3
(XV) R=H;
(XVa) R=CH_3
(XXI) R=H;
(XXIa) R=CH_3

The transition from tertiary alcohols (XV) and (XVa) to aldehydes (XXI) and (XXIa) was accomplished by an allylic rearrangement and oxidation with chromic acid, the method which is customary for oxidations of this type.

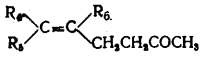
Subsequently, in the development of work on the use of terpene chlorides to obtain valuable perfumes of the sesquiterpene series, nerolidol and methylnerolidol were converted by a previously known method[84] into the corresponding primary alcohols, farnesol and methylfarnesol, by treatment with phosphorus tribromide, conversion of the resulting primary bromides into acetates, and saponification of these acetates[106]. The preparation of nerolidol by the reaction of geranylacetone with a vinylmagnesium halide has also been described by other chemists[107].

Normant's method has been successfully used also in syntheses of many other compounds, several of which, judging from their structure, may be of interest as perfumes. Unfortunately, in by no means all cases are the odours of the compounds obtained indicated in the papers.

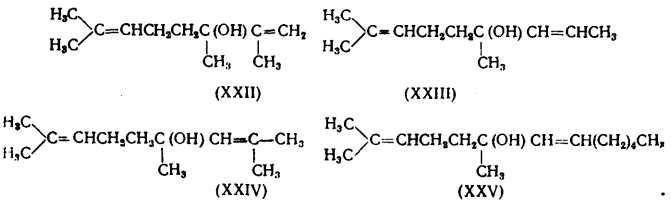
The reaction of magnesium halide derivatives of the type



with unsaturated ketones of general formula

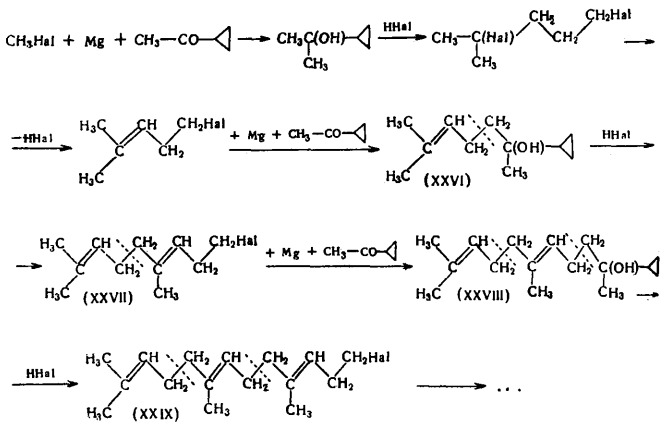


yields the diene tertiary alcohols (XXII)–(XXV)[103] possessing the odours of bergamot and lavender.



(XXII) (XXIII) (XXIV) (XXV)

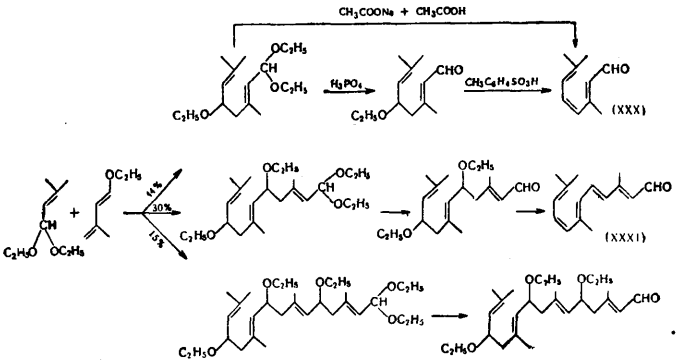
An extremely original new method for the successive building up of isoprenoid chains was suggested recently by French investigators[108], who utilised the Grignard reaction with cyclopropyl ketones for this purpose. The resulting cyclopropyl alcohols are converted by halogen hydracids into dihalogenated derivatives with opening of the ring, and these are then converted by partial dehydrochlorination and reaction with magnesium into organomagnesium compounds, which with the original cyclopropyl ketones give cyclopropyl alcohols containing five additional carbon atoms. Four of these form a straight chain, while the fifth is attached to the penultimate carbon atom. Repetition of these processes results in the formation of a chain of isoprene groups containing one double bond in each "isoprene" link:



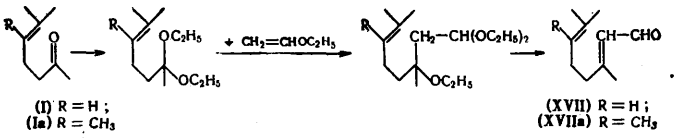
This method has yielded the tertiary cyclopropyl alcohols (XXVI) and (XXVIII), which differ from linalool and nerolidol in containing a three-membered ring instead of the vinyl group; reaction of (XXVII) and (XXIX) with sodium acetate followed by saponification gives primary alcohols which are the immediate homologues of geraniol and farnesol respectively. The alcohols (XXVI) and (XXVIII) have a very pleasant odour.

A recently developed method for passing from a carbonyl compound *via* an acetal to an $\alpha\beta$-unsaturated aldehyde containing two extra carbon atoms in the chain[109-113] has also been successfully employed for the synthesis of perfumes of terpenoid structure. This method, based on the reaction between acetals and vinyl ethers discovered by Müller-Cunradi[114] as early as 1939 (see also Ref. 115), has been developed during recent years by Soviet chemists[116-129]. We shall note only those papers which are most closely related to the synthesis of perfumes‡.

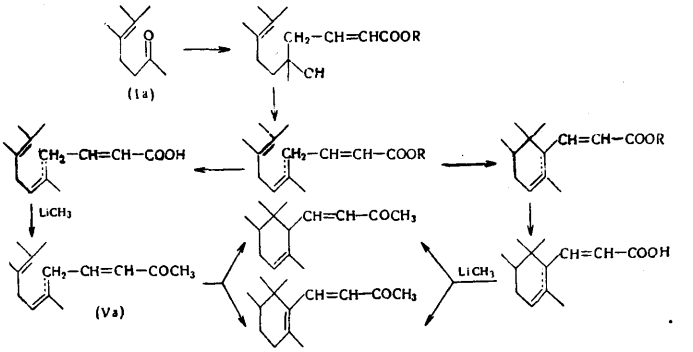
Nazarov and Krasnaya[123,125] studied the reaction of acetals with ethoxyisoprene (for the preparation of the latter, see Ref. 131). In the presence of zinc chloride or boron trifluoride, an acetal reacts with one, two, or more molecules of the ethoxyisoprene to form $\alpha\beta$-unsaturated alkoxy--acetals, which can then be readily converted into alkoxy--aldehydes and polyenals. The main synthetic products obtained when the acetal of dimethylacrylaldehyde is used are 3,7-dimethylocta-2,4,6-trien-1-al (XXX) and 3,7,11-trimethyldodeca-2,4,6,8,10-pentaen-1-al (XXXI).



Preobrazhenskii *et al.*[126,127] employed this reaction to convert methylheptenone (I) into citral (XVII), and Nazarova and Torgov to convert dimethylheptenone (Ia) into methylcitral (XVIIa):[124]



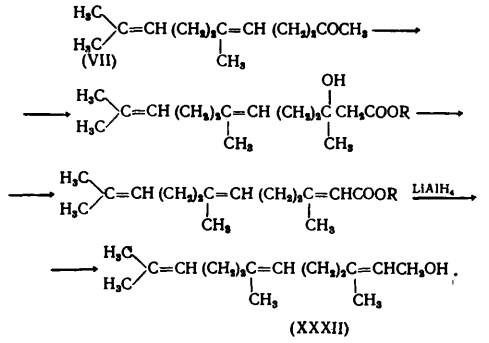
In a series of papers Preobrazhenskii and his collaborators used the well-known Reformatsky reaction to build up the carbon skeleton of perfumes of terpenoid structure. In a previous review we noted[132] their syntheses of pseudoionone (V) from methylheptenone (I) *via* its condensation products with esters of halogenated acids[133,134]. During recent years Preobrazhenskii, Samokhvalov, and their coworkers have studied the individual stages in these syntheses[135,136], and also the analogous conversion of dimethylheptenone (Ia) into pseudoirone (Va), which on cyclisation forms a mixture of isomeric irones. In another variant the ester of methylgeranic acid was cyclised, and then the product saponified and the acid converted into irone by the action of methyllithium in dry ether[137,138]:



The sesquiterpene alcohol farnesol (XXXII) was synthesised in Preobrazhenskii's laboratory by the reaction of geranylacetone (VII) with chloroacetic ester, followed by

‡ A detailed review of work on this reaction has recently been published by Yanovskaya[130].

dehydration of the resulting hydroxy-ester and reduction with lithium aluminium hydride[69]:



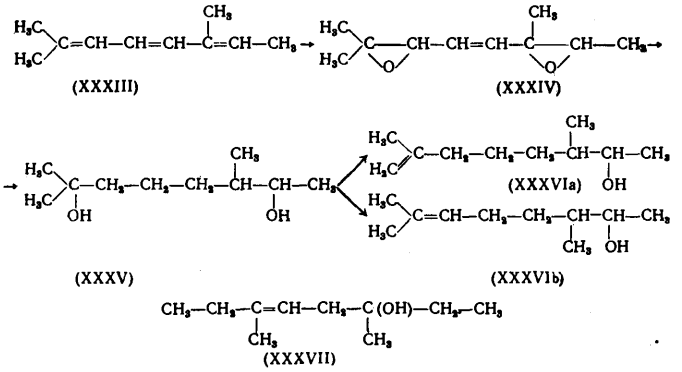
(XXXII)

A disadvantage of this synthesis is its clumsiness and the low yields at several stages. On passing from geranylacetone through the hydroxy-ester to the unsaturated ester, for example, the yield is only 8.5%.

The method of obtaining polyenecarboxylic esters by condensing $\alpha\beta$-unsaturated ketones with 4-halogenocrotonic esters was improved by Dorp *et al.*[139], who suggested treating the unpurified mixture of esters, before saponification, with dehydrating agents (PBr_3, P_2O_5, and several others).

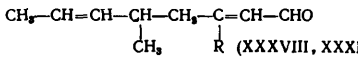
Apart from the new compounds considered above, several others have also been obtained during recent years, these being homologues or analogues of the terpene and sesquiterpene compounds. Some of them possess a pleasant odour and may find application as perfumes, while the preparation of others is of interest in elucidating the relation between odour and structure.

Several new compounds of this group having an interesting smell have been synthesised by Naves and his collaborators[140] using alloocimene (XXXIII) as starting material. Oxidation of (XXXIII) yielded the dioxide (XXXIV), hydrogenation of which gave the saturated diol (XXXV); dehydration of the latter resulted in unsaturated alcohols isomeric with citronellol, which were termed α-elgenol (XXXVIa) and β-elgenol (XXXVIb):



There are indications of the possibility of the use in perfumery also of another isomer of citronellol, 3,6-dimethyloct-5-en-3-ol (XXXVII).[141]

An aldehyde (XXXVIII) isomeric with citral was obtained by Petrov *et al.*[142] and reported as having an odour resembling that of citral. The citral analogue (XXXIX), which contains chlorine and was synthesised by the same chemists, possesses the same type of odour[143].



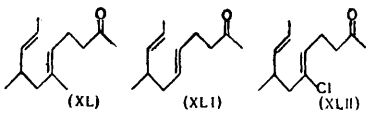
where in (XXXVIII) R = CH_3, and in (XXXIX) R = Cl.

A series of homologues and analogues of citral were obtained from the corresponding bromides or chlorides by Nazarov *et al.*[50,86] These compounds possess the odours indicated below:

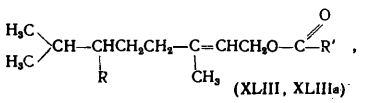


R = R′ = CH_3 (citral) smells like lemons; R = CH_3 and R′ = H unpleasant smell not resembling that of citral; R = CH_3 and R′ = Cl odour similar to that of citral; R = CH_3 and R′ = C_2H_5 odour not reported; R = CH_3 and R′ = iso-C_3H_7, R = CH_3 and R′ = C_4H_9, and R = R′ = iso-C_3H_7 the smell has an unpleasant fatty aroma.

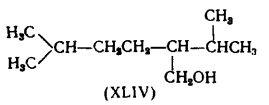
The geranylacetone isomer (XL) (6,8-dimethylundec-5,9-dien-2-one), and also its lower homologue (XLI) (8-methylundec-5,9-dien-2-one) and its analogue (XLII), have been reported as possessing a peculiar, pleasant odour[144]:



Patents issued in 1958 describe the preparation of esters of dihydrogeraniol (XLIII)[145] and of dihydromethylgeraniol (XLIIIa),[146] several of which, for example those in which R′ is not higher than C_8, possess a scent of flowers and are of interest for perfumery:

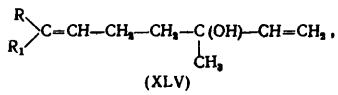


where in (XLIII) R = H and in (XLIIIa) R = CH_3.



The German perfumery journal notes the valuable odour of several esters of tetrahydrolavandulol (XLIV), and the opinion is expressed that they could be usefully employed in perfumery[147,148].

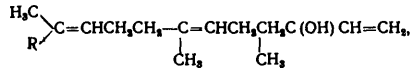
We may note also the homologues and analogues of linalool (XLV) [30] and nerolidol (XLVI) [33] synthesised by Nazarov and his collaborators:



(XLV)

where

R	H	CH_3	CH_3	CH_3	CH_3	CH_3	iso-C_3H_7
R_1	H	H	Cl	C_2H_5	iso-C_3H_7	t-C_4H_9	iso-C_3H_7

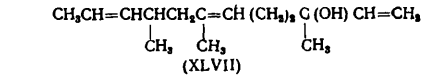


(XLVI)

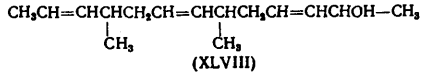
where R = H, Cl, C_2H_5, iso-C_3H_7, t-C_4H_9.

Unfortunately, the odours of these compounds are not reported.

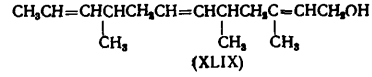
The alcohols (XLVII)–(L), which are isomers of nerolidol and farnesol and were prepared by Shvarts and Petrov [70,93] by the telomerisation of unsaturated chlorides and diene hydrocarbons (for this reaction see above, p.124), as well as the dehydronerolidol isomer (LI), the nerolidol analogue (LII), and the dehydronerolidol analogue (LIII), are described as liquids having a pleasant smell, which when dilute resembles that of nerolidol and farnesol:



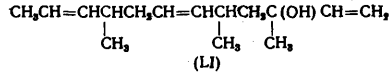
(XLVII)



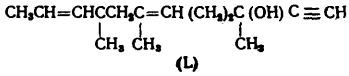
(XLVIII)



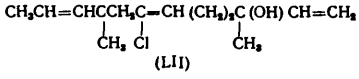
(XLIX)



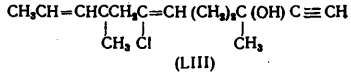
(LI)



(L)



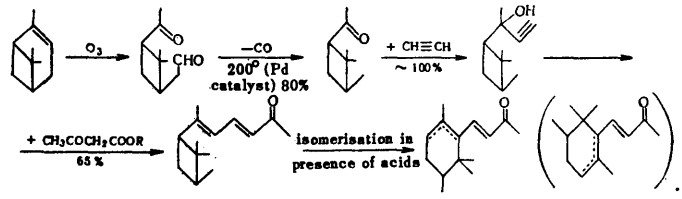
(LII)



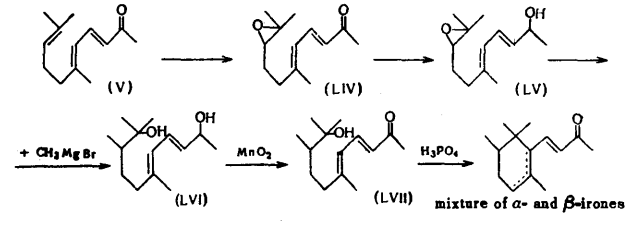
(LIII)

Great progress has been made during recent years in the chemistry of ionone preparations, one of the most interesting groups of odoriferous substances of terpenoid structure. Several new homologues of ionone have been obtained, the most important stage in their synthesis — cyclisation (the transition from pseudoionones to the ionones themselves) — has been studied in detail, new relations have been elucidated between the formation of individual isomers and the reaction conditions, the structure of several isomers has been more accurately determined, etc.

Some of these investigations relate to problems of the synthesis of irone (6-methylionone), the aromatic principle of orris oil. Several routes for obtaining irone which have been proposed recently have been given above in the discussion of general schemes for synthesising isoprenoid compounds. Several other syntheses of this valuable perfume have also been described. The starting material in one of them was α-pinene, which was converted into irone by the following reactions [149]:



According to another scheme, suggested recently by Barton and Mousseron-Canet [150], irone was synthesised from pseudoionone (V), which was converted by perphthalic acid into an epoxide (LIV), the latter yielding on reduction with sodium borohydride in methanol the epoxide of pseudoionol (LV); the Grignard reaction (with methylmagnesium bromide) was then used to introduce a methyl group into position 9 with formation of a diol (LVI), transformed by oxidation into a hydroxy-keton (LVII), from which it was then easy to pass to irone:



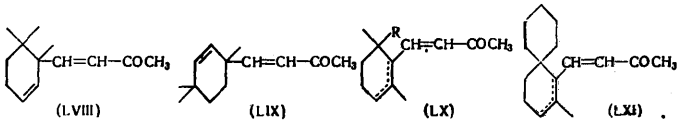
The significance of these two methods of synthesising irone is probably confined to laboratory research. A very tempting possibility mentioned in one of Verley's patents [151] is the *C*-methylation of citral or geraniol with dimethyl sulphate to form a 6-alkyl derivative. If the data in this patent are confirmed, there are good prospects for obtaining irone from citral or geraniol, since the further conversion of the resulting 6-methylcitral or 6-methylgeraniol respectively into irone presents no difficulty.

The possibility of the *C*-alkylation of terpenoid compounds was noted also by the Hungarian chemist Szabó [152] in his work on the mechanism of the cyclisation of pseudoionone in the presence of acid catalysts. According to his results, pseudoionone is converted on treatment with $AlCl_3$ and CH_3Cl into γ-irone; hence in this case cyclisation is accompanied by methylation. He observed the formation of irone also on treating pseudoionone with a solution of HCl in methyl alcohol. In a similar way, the action of isopropyl chloride and $AlCl_3$ on pseudoionone yields 6-isopropylionone, and interaction of pseudoionone with dichloroethylene and $AlCl_3$ results in a 6-hydroxyethyl derivative, which on dehydration gives 6-vinylionone. However, the yields of the alkylation products are not high.

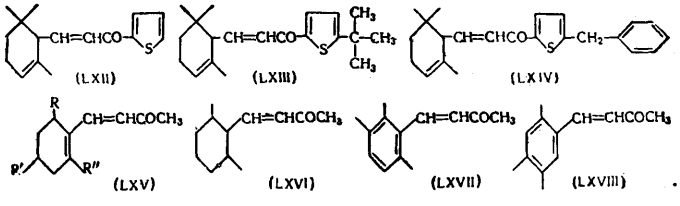
A considerable number of investigations have been devoted also to preparing other homologues and analogues of ionine. An isomer (LVIII) of α-ionone has been described in which the methyl group is in position 2 instead of position 3 in the ring[153]. This ketone possesses an odour of violets differing somewhat from those of α-ionone and α-irone. Another ketone (LIX), isomeric with ionone and having a different arrangement both of methyl groups and of the double bond in the cyclohexene ring, has been described as having a faint smell slightly resembling that of violets[154]. Both the α- and β-forms have been obtained of a homologue of ionone containing both methyl and ethyl groups attached to the second carbon atom in the ring [(LX): R = C_2H_5]. The odour of the α-isomer is stated to resemble that of α-ionone[155], and the β-isomer is described as possessing the aroma of violets with a trace of cedar[156]. Higher homologues of ionone, containing R = iso-C_4H_9 in formula (LX), have a woody smell, which is most distinct with the α-isomer[157].

A series of such homologues and analogues of ionone [(LX) with R = H, Cl, C_2H_5, iso-C_3H_7, t-C_4H_9] have been synthesised by Makin *et al.*[158], but their odours are not described.

Naves and Ardizio[159] prepared structural analogues (LXI) of α- and β-ionones in which the *gem*-dimethyl grouping had been replaced by $[CH_2]_5$; these spiro-compounds were noted to have a faint but persistent odour of cedarwood with a hint of iris:



Interesting work has been carried out on the synthesis of ionone analogues which are derivatives of thiophen[160,161]. It has been found that introduction of a thiophen ring into the molecule of an ionone preparation does not substantially affect its odour: the ketones (LXII), (LXIII), and even (LXIV), which has a considerably higher molecular weight than ionone (molecular weights 350 and 192 respectively), possess a well defined odour of violets, without the smell of sulphur compounds. It is noteworthy that, up to the present time, only comparatively few sulphur-containing organic compounds are known which have a pleasant smell:

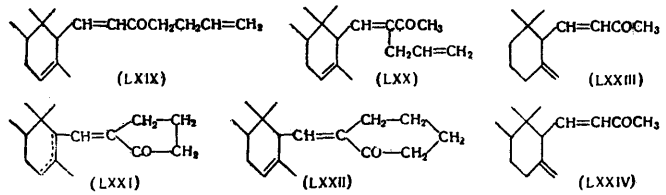


Several analogues of β-ionone of general formula (LXV) were prepared recently by Nazarov, Kugatova, and their collaborators[162,163]; unfortunately, the odour is described only for the cyclohexane ketone (LXVI), which has an agreeable, flowerlike scent[162].

Information on odoriferous properties is also lacking for the aromatic ionone analogues (LXVII) and (LXVIII) obtained fairly recently[164].

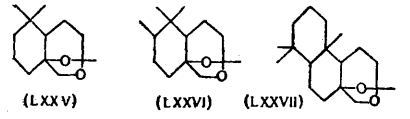
Naves has prepared several new analogues of irone. Thus 2_4-allyl-α-irone (LXIX) and 2_2-allyl-α-irone (LXX) have been synthesised[165], the latter being stated to have a persistent smell resembling that of isovetivone§. In another paper Naves[166] has described α- and β-isomers of 6-methylcyclocitrylidenecyclopentanone (LXXI) and 6-methyl-α--cyclocitrylidenecyclohexanone (LXXII); it is interesting that, in contrast to the corresponding analogues of ionone, which have the odour of violets[167,168], these ketones possess a faint but persistent odour resembling that of oakwood from which the bark has been freshly peeled.

Noteworthy attempts have been made by Schinz and his coworkers to synthesise γ-ionone (LXXIII)[169] and γ-irone (LXXIV)[170] from compounds already containing an *exo*-cyclic methylene group (the conditions necessary for the formation of γ-isomers on cyclisation of the corresponding pseudo--products are not yet known).



The synthesis of γ-irone would be of the greater interest, since it is this structural isomer which constitutes the main component of the mixture of irones present in the oil from iris rhizomes. However, it did not prove possible in the above work to obtain the pure preparations desired: only crystalline derivatives enriched with those of the corresponding γ-isomers were isolated.

Several interesting new products have been obtained from ionones and irones which have been hydrogenated at the double bond in the side-chain. Thus of the bridged polycyclic ketals (LXXV)–(LXXVII), patented by Ruzicka and Jeger[171] and recommended for use in perfumery compositions, the first two can be obtained from dihydro-γ--ionone and dihydro-γ-irone respectively by oxidation to glycols with subsequent dehydration¶:



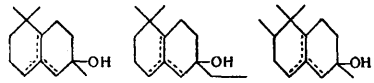
Stoll *et al.*[172,173] have studied the cyclisation of dihydro--γ-ionone in the presence of acid reagents. It has been suggested that three isomeric octahydro-2,5,5-trimethylnaphth-2-ols (LXXVIII), differing in the position of the double bond and termed the α-, β-, and γ-ambrinols, are formed in this process; the α- and γ-isomers were isolated from the reaction mixture and characterised, the structure of γ-ambrinol being confirmed by synthesis.

§ The name "isovetivone" is arbitrarily applied to the mixture of ketones isolated from oil of vetiver and possessing the specific odour of the latter.

¶ The ketal (LXXVII) is obtained in a similar manner from 4-(5,5,9-trimethyl-2-methylenedecalin-1-yl)but-3-en-2-one.

According to the suggested mechanism[172,173], the cyclisation of dihydro-γ-ionone involves the intermediate formation of a carbonium ion. The mixture of ambrinols possesses an odour which is valuable in perfumery, having a similarity to that of ambergris and civet[172,173]; the ethyl ether of ambrinol has a faint smell which is of little interest[173].

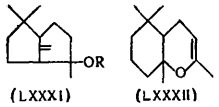
In another paper Stoll[174] has described the octalinols (LXXIX) and (LXXX), obtained by cyclisation of dihydro--2_4-methyl-γ-ionone (dihydro-γ-normethylionone) and *trans*-2,6-dihydro-γ-irone respectively; these homologues of ambrinol proved to have uninteresting odours.



(LXXVIII) (LXXIX) (LXXX)

However, the dihydro-γ-ionones themselves are difficult to obtain. It has already been mentioned above that conditions for the formation of γ-isomers of ionone derivatives on cyclisation of the pseudo-compounds are not yet known. Methods have not yet been described for converting pseudoirone into γ-irone, the latter being found in only very minute quantities in the mixtures remaining after cyclisation; therefore the sole source of γ-irone and dihydro-γ-irone so far is natural orris oil. Only complicated and multistage syntheses have been suggested for the preparation of dihydro-γ-iononeT: for example, Stoll's scheme[177] using dihydro-α-ionone as starting material. According to a 1959 Swiss patent[178], dihydro-γ-ionone is formed from dihydro-α-ionone by the action of phosphoric acid in the presence of pyridine.

Stoll and his collaborators[179-182] have studied also the acid cyclisation of dihydro-α-ionone. They have found that the nature of the reaction products depends to some extent on the solvent which is used. Thus the cyclisation of dihydro-α-ionone under the influence of HCl or BF_3 in solution in a primary alcohol, results in the formation of a bicyclic ether [(LXXXI): R = Alk, corresponding to the radical of the primary alcohol], whereas in solution in a secondary alcohol a bicyclic alcohol is formed [(LXXXI): :R=H]. The action of BF_3 in benzene solution yields an unsaturated oxide (LXXXII). The alcohol and its ethers (for example with R = C_2H_5) possess an odour of ambergris and wood with a suggestion of camphor; this last is attributed to impurities, which may be formed as side-products in the cyclisation of dihydro-α-ionone.



(LXXXI) (LXXXII)

The exceptional significance, for the chemistry and technology of perfumes, of processes involving the cyclisation of terpenoid compounds has been responsible for the great interest of chemists in a comprehensive investigation of these reactions. The detailed reviews published during recent years on the mechanism of the cyclisation of terpene compounds[183,184] make it unnecessary to dwell on this question here, so that we can confine ourselves to those investigations which are directly related to the preparation or study of the individual isomers formed in the course of cyclisation. Several such papers have already been cited above in discussing the synthesis of individual perfumes of terpenoid structure.

Several other workers have studied the effect of various cyclising agents, and of the conditions under which pseudoionone is cyclised, on the composition of the resulting ionone isomers. This question, of very great importance for the perfume industry, is as yet far from being completely elucidated, although its study started at the end of the past century. Krishna and Joshi[185] have specified the conditions necessary for the preferential formation of β-ionone; they emphasise the great value of spectroscopic methods of analysis for determining the content of isomers in the mixture of ionones.

A detailed study of the way in which the composition of the isomeric ionones depends on temperature, duration, and amount of sulphuric acid used as a cyclising agent was made by Kucherov *et al.*[186,187] They established that formation of α-ionone is favoured by the use of low temperatures (of the order of -60° to -40°), small quantities of sulphuric acid, and short times of cyclisation.

The problem of the cyclisation of pseudoionone with the aim of obtaining α-ionone as the main reaction product is dealt with also in a paper by Hung Lu-ming[188]. Kucherov *et al.*[189] had confirmed Schinz's results[190], according to which mixtures containing the same amounts of α- and β-ionones are formed in the cyclisation of the *cis*- and *trans*-isomers of pseudoionone (geometrical isomerism due to the presence of a double bond between carbon atoms 5 and 6). They have suggested a mechanism for this process.

Makin *et al.*[50,158] have studied the cyclisation of a series of homologues and analogues of pseudoionone containing various *gem*-substituents in position 10.

Dulou and Clément[20] compare their results on the cyclisation of pseudoirone by the action of sulphuric acid, phosphoric acid, and boron trifluoride with those published somewhat earlier by Naves‡ (pseudoirone was prepared by the reaction of dehydro-6-methyllinalool with acetoacetic ester; the stereoisomers were determined from the characteristics of crystalline derivatives of the dihydroirones§ and from the ultraviolet and infrared spectra of the latter). The agreement between the results is very good; Naves's statement that the action of boron trifluoride is stereospecific in this reaction is confirmed. The advantage of this cyclising agent in forming the most valuable stereoisomers from the point of view of odour has been reflected in a series of patent claims during recent years[191-194]. However, there are indications that the mixtures of isomers obtained by the cyclisation of pseudoirone in the presence of sulphuric acid[195] or of a sulphuric acid–acetic acid mixture[196] can also be used in perfumery (*cf.* the paper[186] cited above on the cyclisation of pseudoionone).

Fresh data have also been published on the properties and structures of the individual isomers of ionone and its homologues. Lecomte and Naves[197] give the detailed spectroscopic characteristics of several isomers of ionone, methylionone, and irone; new crystalline derivatives of methyliso-α-ionone and of isomeric irones have been described[198].

T Dihydro-γ-ionone is found in minute amounts among the oxidation products of ambrein[175,176].

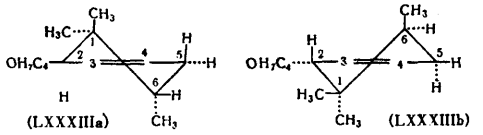
‡ This work of Naves is discussed in our previous review[132].

§ In order to eliminate the stereoisomerism due to the double bond in the side-chain (at the 2_1–2_2 C-atoms).

Beets and van Essen[199] made a thorough investigation of the effect of the conditions under which citral is condensed with ethyl methyl ketone with the aim of elucidating the factors favouring the predominant formation of methylpseudoisoionone (which gives methylisoionone¶ on cyclisation). These workers assume that the condensation of citral with ethyl methyl ketone takes place by two competing reactions, the first being the classical condensation catalysed by anions, and the second a condensation catalysed by anions and cations together, depending more on a hyperconjugation than on a steric effect, and increasing the probability of condensation at the methylene group. They recommend that this condensation should be carried out in the presence of quaternary ammonium bases in lower aliphatic alcohols.

New data obtained by Naves forced him to change his previous view of the structure of the irone isomer whose 4-phenylsemicarbazone melts at 174.5°–175.5°. Previously this isomer had been assigned the structure of iso-α--irone† (*trans*-2,6, *cis*-2_1, 2_2-α-irone).[200] Study of the spectra showed that this isomer has a *trans*-arrangement of the substituents attached to the carbon atoms 2_1 and 2_2, and is thus neoiso-α-irone (*trans*-2,6, *trans*-2_1, 2_2-α--irone).[201-203] By fractional recrystallisation of the mixed semicarbazones of the isomeric irones followed by hydrolysis and fractional distillation in a highly efficient column, however, he was able to isolate an isomer which was iso--α-irone.[201-203] Reduction of iso-α-irone and neoiso-α--irone with lithium aluminium hydride yielded the corresponding alcohols, iso-α-irol and neoiso-α-irol[203].

Somewhat earlier Naves[204] had established an interesting case of stereoisomerism of the incompletely hydrogenated 2_2-methylirones, and had shown that hydrogenation of 2_2-methyl-*trans*-2,6-α-irone yields two dihydro-ketones (LXXXIIIa) and (LXXXIIIb), further hydrogenation of which results in two tetrahydro-2_2-methyl-*trans*-2,6-irones, which are stereoisomeric at the carbon atoms 2 and 3. Naves adopts "half-chair" forms for (LXXXIIIa) and (LXXXIIIb), with carbon atoms 2–5 lying approximately in the same plane, while the positions of carbon atoms 1 and 6 relative to this plane differ. The substituent containing the oxo-group is equatorial in both configurations. Naves remarks that one configuration can be readily converted into the other in the case of 2_2-methyl-*trans*-2,6-α-irone, but the transition is difficult with the dihydro-derivatives.



Some new work has been done on the stereoisomerism of the ionones. Tribolet and Schinz[205,206] established that α-ionone obtained by the cyclisation of pseudoionone possesses a *trans*-configuration at the double bond in the side--chain; they also suggested a *trans*-configuration for α-ionone and its derivatives. Büchi and Yang[207-209] achieved stereoisomeric transformations of the ionones by exposing them to ultraviolet radiation. From *trans*-α-ionone these workers obtained *cis*-α-ionone by this method; the odour of the latter was found to differ from the smell of violets possessed by the *trans*-isomers of ionone, and to resemble that of cedarwood. Irradiation of β-ionone did not yield the *cis*-isomer, since cyclisation took place with the formation of a pyran derivative. From the latter the semicarbazone of *cis*-β-ionone could be obtained, attempts at the hydrolysis of which yielded the pyran compound again.

Great new opportunities for the complete analysis of the complicated mixtures formed in syntheses of ionone preparations are provided by the use of gas–liquid partition chromatography. This research method, which has already been widely used in studying the most diverse organic compounds, has been successfully employed during recent years to separate and determine individual ionone and irone isomers. Naves reports the results of an extensive investigation of the application of gas–liquid chromatography to the analysis of mixtures of citral and some related compounds[210]. He determined the geometrical isomers of citral (geranial, neral) 6-methylcitral, and geraniol (nerol) in various samples of these products, and noted the advantages of gas–liquid chromatography compared with infrared spectroscopy. He confirmed that, of the four possible stereoisomers of pseudoionone (and also of pseudoirone), only two exist, corresponding to the geraniol–nerol isomerism. The content of isomeric pseudoionones was determined in mixtures obtained by the pyrolysis of dehydrolinalool acetoacetate, and the content of isomeric pseudoirones in the mixtures obtained by the pyrolysis of dehydro-6-methyllinalool acetoacetate. It was shown that mixtures of isomeric irones could be reliably analysed by this chromatographic method. Iso-α-irone, neoiso-α-irone, the total content of α-irone and neo-α-irone, and neo-β-irone can be determined in mixtures of α-irones. Furthermore, such a method of analysis can reveal the possible presence of impurities, particularly of oxides, isomeric with the irones, which are formed as side-products during cyclisation, as well as of pseudoirones which have not undergone cyclisation.

In the same work Naves used gas–liquid chromatography to analyse the isomeric constitution of the nerolidols obtained by the action of acetylene on geranylacetone (VII) followed by partial reduction (see Scheme 2, above), compared with samples of nerolidol isolated from natural essential oils. The relative proportions of the isomeric farnesols obtained from specimens of synthetic and of natural nerolidol were determined.

Crisler and Benford[211] used this method of analysis to determine the content of individual isomers of ionone and also of methylionone in mixtures.

There are also interesting new publications on the structure and stereochemistry of other terpenoid perfumes. New experimental results have been obtained on the content in natural products of the isopropylidene (β) and isopropenyl (α) forms of citronellol, geraniol, nerol, linalool, nerolidol, farnesol, citral, citronellal, and other related compounds[212-214].

The absolute configuration has been established of (+)-citronellic acid and of (+)-citronellol[215]. From an examination of the absolute configuration of the optically active linalools, Prelog and Watanabe[216] have explained the long known fact[217] of the formation, by the cyclisation of linalool, of a terpineol whose rotation is opposite in sign to that of the original linalool.

¶ Methylisoionones possess a more pleasant odour than their isomers having a side-chain of normal structure. Methyliso-α--ionone (more precisely a mixture enriched with this isomer) is widely used in perfumery under the trade name "iralia".

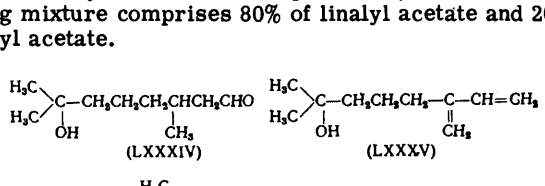
† For the nomenclature adopted for the stereoisomeric irones, see our previous review[132].

We have discussed above new work on the general problems of the synthesis of terpenoid perfumes and also of the separate stages in the synthesis of the most important compounds of this group, ionone preparations, the improvement of methods for their analysis, and several closely connected investigations. In concluding this section we have to consider briefly a small number of papers published during recent years concerned with the preparation and investigation of several other odoriferous compounds of terpenoid structure which are of a somewhat more specialised character.

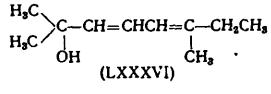
Joffre[218] has patented a method for isomerising citronellol into rhodinol by the action of ultraviolet radiation at ~20°. A new method has been proposed for obtaining citronellol based on the ozonisation of *p*-menth-3-ene, reduction of the ozonide with lithium aluminium hydride, and dehydration of the resulting 3,7-dimethyloctane-1,6-diol by heating it with sulphuric acid[219]. Bag *et al.*[220,221] have worked out a process for converting geraniol into citronellal (dehydrogenation with simultaneous selective addition of hydrogen at one of the double bonds) in the presence of a copper–chromium catalyst containing barium oxide at 220°–230° and a residual pressure of 100 mm. The yield of the aldehyde is 65% (based on the geraniol). Bag *et at.*[222] have discovered the conditions for the selective catalytic hydrogenation of citral which make it possible to obtain mixtures considerably richer in nerol.

Polyakov[223] noted a favourable effect of adding the pinene fraction of turpentine on the yield of citral in the oxidation of pure linalool or of coriander oil containing linalool.

The conversion of hydroxycitronellal (LXXXIV) into 2,6-dimethyloctan-2-ol and the study of the infrared spectrum have confirmed[224] the structure 7-hydroxy-3,7-dimethyloctanal which has long been accepted for this valuable perfume. Myrcene can be hydrated at the isolated double bond, by the action of acetic acid in the presence of a small amount of sulphuric acid followed by saponification of the resulting acetate, with the formation of a tertiary alcohol (LXXXV).[225,226] The alcohol itself, "myrcenol" possesses an agreeable odour resembling that of linalool and α-terpineol, its acetate being reported as having a strong smell with a fruity and bergamot tinge[226]. According to an American patent[227], the isomeric tertiary alcohol (LXXXVI), with an arrangement of double bonds different from that in myrcenol (it is prepared from alloocimene by hydrochlorination followed by hydrolysis), can be employed in perfumery compositions to give the scent of lilies of the valley and of roses. Another patent[228] describes a process for obtaining linalyl acetate by the addition of hydrogen chloride to myrcene with subsequent acetylation: the resulting mixture comprises 80% of linalyl acetate and 20% of geranyl acetate.

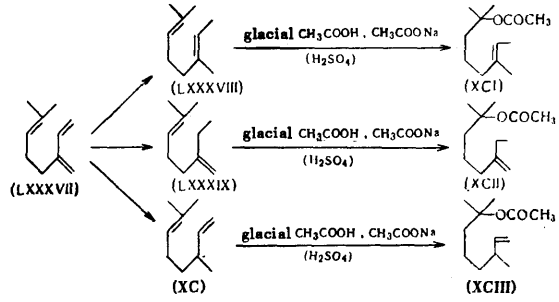


(LXXXIV) (LXXXV)



(LXXXVI)

The patent literature also indicates that several new acetates, prepared from myrcene possess an interesting odour[229]. Depending on the conditions, the incomplete hydrogenation of myrcene (LXXXVII) can yield the diene hydrocarbons (LXXXVIII)–(XC), converted by the addition of acetic acid into (XCI)–(XCIII), the first two of the latter group having a very pleasant odour.



Italian chemists have investigated the isomerisation of linalool to geraniol in the presence of acetic anhydride. Boiling a mixture of linalool with 1.5 moles of acetic anhydride for 10 h leads to the formation of geranyl acetate (34%) and a mixture (40%) of limonene, myrcene, and ocimene. These hydrocarbons were separated by gas chromatography and identified by their ultraviolet and infrared spectra. The kinetics of the isomerisation of linalool have been studied[230].

Several improvements have been suggested for the conversion of α-pinene into terpineol and into terpin hydrate. Thus it has been recommended[231] that the well-known hydration of α-pinene with sulphuric acid should be carried out at a temperature not exceeding 3°; good results are obtained by the addition of small quantities of cetylpyridinium chloride[231], polyethyleneglycol monolauryl ether[231], or gelatin[232] as emulsifiers, which considerably increases the reaction velocity; access of air also has a favourable effect[232].

A study of the influence of the polarity of the medium on the mode and rate of reaction of pinene with acids[233] has established that, in a strongly polar medium (CH_3COOH with water, CH_3COOH with formamide or *N*-methylformamide), α-terpineol containing the acetate as impurity, and limonene with α-terpinene as impurity, are formed respectively; the yield of the terpineol increases with increasing duration of the reaction and decreasing concentration of acid.

In the absence of a catalyst, α-terpineol can be obtained mixed with its acetate by boiling α-pinene with dilute acetic acid[234].

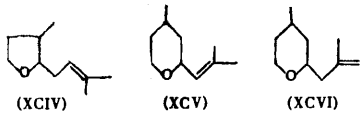
It is recommended[232] that terpin hydrate should be converted into α-terpineol in the presence of 5% sulphuric acid in an organic solvent; when 0.5% of oxalic acid is employed as dehydrating agent, the terpineol obtained is of high quality[232].

The work of Japanese chemists[235] has shown that treatment of terpin hydrate with lead tetraacetate in acetic anhydride at 65° for 8 h yields *d,l*-terpineol together with terpin monoacetate, whereas treatment of terpin hydrate with a mixture of acetic anhydride and acetic acid in the absence of lead tetraacetate gives *d,l*-terpineol, its acetate, and terpin monoacetate, the yield of these products being higher than in the first case. It was concluded from these observations that the transformations of terpin hydrate in the presence of a mixture of lead tetraacetate and acetic anhydride are a result of dehydration and acetylation under the influence of the acetic anhydride.

One patent[236] notes the high yields of terpineol, containing no hydrocarbons, produced by the dehydration of terpin or terpin hydrate in the presence of feebly acid solid catalysts such as silica gel activated with phosphoric acid, titanium hydroxide activated with acetic acid, acid cation-exchange resins, etc.

The conditions for the conversion of α-terpineol, limonene, and some other related compounds into *cis*- and *trans*-terpin under the influence of sulphuric acid have been studied by Lombard and Geiger[237].

Interesting results have been obtained from a careful study of the substance having the composition $C_{10}H_{18}O$, first isolated by Seidel and Stoll[238] from high-boiling fractions of Bulgarian rose oil, and given the name "rose oxide". It has been established that this compound is not a tetrahydrofuran derivative of formula (XCIV), as had at first been supposed, and in conformity with which the first attempts at synthesis had been made[239]; it was in fact a tetrahydropyran derivative having the structure (XCV).[240-243] Stereoisomers of the "rose oxide" were then synthesised in a series of investigations[240,244-246], as well as its structural isomer (XCVI).[246]

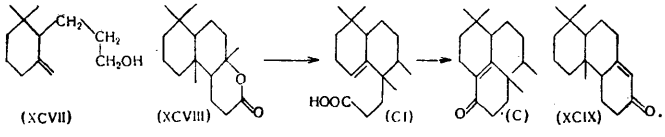


(XCIV) (XCV) (XCVI)

3. PERFUMES OBTAINABLE FROM AMBERGRIS AND FROM SCLAREOL

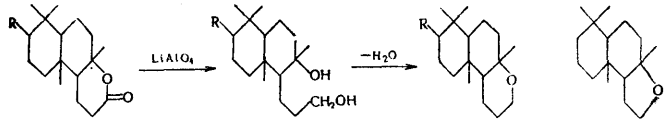
In our review[132] we reported the results obtained mainly by Swiss chemists, which established the nature of the odoriferous substances in ambergris. Since then, some new work has been published which has refined the earlier results and also indicated new routes for the synthesis of compounds having an ambergris odour.

From the non-ketonic portion of ambergris, Seidel and Stoll isolated an alcohol which is a homologue of γ-cyclogeraniol and is a liquid with an ambergris type of smell. The structure of γ-cyclohomogeraniol (XCVII) has been confirmed by synthesis[247]. This alcohol has been synthesised also by other investigators[248], but they do not describe its odour.



(XCVII) (XCVIII) (CI) (C) (XCIX)

Various products have previously been described, obtained by chemical transformations of ambreinolide (XCVIII), a lactone formed together with other products by the oxidation of ambrein, which is contained to the extent of ~25–45% in ambergris. A product of the action of acidic reagents on ambreinolide is an unsaturated tricyclic ketone $C_{17}H_{26}O$, which possesses a strong ambergris–musk smell; this ketone had previously been assigned the structure (XCIX).[249] Recently, a somewhat different structure (C) has been established for this compound; its formation from the lactone (XCVIII) is explained by a Wagner–Meerwein rearrangement yielding an unsaturated bicyclic acid (CI), dehydration of which gives the compound (C).[250] In 1950 the preparation from ambreinolide (XCVIII) of an oxide (CII), having a smell of ambergris, was described[251]. Somewhat later a similar scheme was used to convert 2-methylambreinolide (XCVIIIa) into the corresponding oxide (CIIa), which was described as a compound having a fruity odour[252,253].



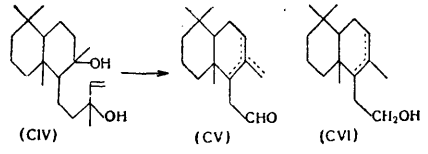
(XCVIII) R = H; (XCVIIIa) R = CH_3 (CII) R = H; (CIIa) R = CH_3 (CIII)

In the development of this work a lactone containing a smaller lactone ring than (XCVIII) and (XCVIIIa), and thus constituting their lower homologue, was converted by reduction followed by dehydration into an oxide (CIII) smelling, like (CII), of ambergris[254].

From the same series of investigations, we may mention papers on the synthesis of (XCVIII) and (XCVIIIa) from dihydro-α-ionone[255] and dihydroiso-α-irone[252,253] respectively. This work again emphasises the close genetic relation between the aromatic principles of ambergris and derivatives of the ionone group; its practical interest consists in the indication of new routes for the synthesis of compounds containing an ambreinolide skeleton and related products.

Another line of work in this field, which in our view is promising, is the preparation of valuable products from sclareol (CIV), a bicyclic triterpene glycol present in the waste remaining from the plant *Salvia sclarea* L. (muscatel sage) after the essential oil has been distilled off. Some years earlier the multistage preparation had been described of bicyclohomofarnesal (CV) and bicyclohomofarnesol (CVI), which have an odour of ambergris, from the products of the oxidative degradation of sclareol (for a description of this work see, for example, our previous review[132]).

A method has now become available for the direct conversion of (CIV) into (CV) by the action of a chromic acid mixture or of chromium trioxide in glacial acetic acid[256-259]:



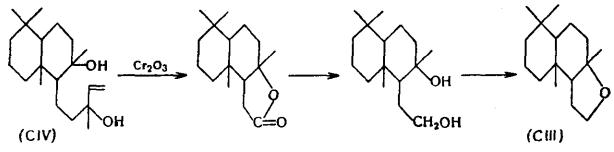
(CIV) (CV) (CVI)

The composition of the products obtained has been studied as a function of the reaction conditions, and a mechanism suggested for their formation[259]; the method for obtaining bicyclohomofarnesal, which is known also as ambrial, has been tested on a large scale in our institute.[258]

The use of bicyclohomofarnesal and bicyclohomofarnesol in perfumery compositions has been described in a recent patent from the Federal Republic of Germany[260].

The work of Soviet chemists[259,261] has repeated and somewhat improved the conversion of sclareol (CIV) through a series of intermediate products into the oxide (CIII) (termed "ambroxide"), which had been accomplished earlier by Ruzicka and his collaborators[262] and later by Stoll and Hinder[263,264]. The lithium aluminium hydride

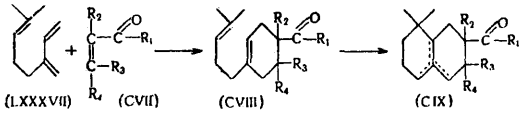
used earlier to reduce the lactone to a glycol was successfully replaced in this work by sodium borohydride[259,265]; however, an attempt to effect the process catalytically was unsucessful[266].



Thus new investigations in this branch of the chemistry of perfumes have led to the discovery of comparatively simple methods for obtaining compounds possessing the odour of ambergris.

4. ALKYLOCTALIN DERIVATIVES

An extremely interesting new class of odoriferous compounds has been described recently in a series of papers by Ohloff[267-272]. He has made a detailed study of the diene synthesis reaction using as the initial compounds myrcene (LXXXVII)‡ and various dienophils (CVII). The cyclisation of the resulting adducts (CVIII) yielded a series of different derivatives of 1,1-dimethyloctalin. The readiness of (CVII) to undergo diene synthesis was found to depend to a considerable extent on the degree of substitution and the positions of the substituents: thus α-substituted (CVII) derivatives are more reactive than the β-substituted compounds.

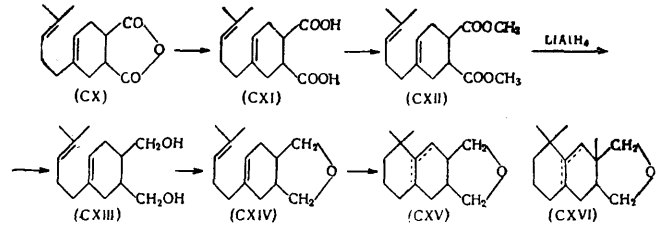


Cyclisation of (CVIII) in the presence of sulphuric or phosphoric acid, or a mixture of formic and sulphuric acids, is made more difficult by increasing the number of substituents in the cyclohexene ring; however, when boron trifluoride is employed as cyclising agent§, the rate of cyclisation is the same independently of the degree of substitution of (CVIII).[270]

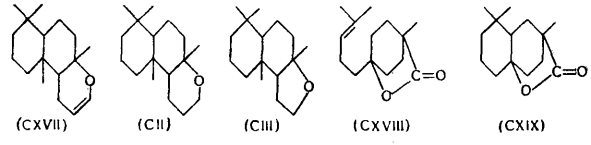
In Ohloff's view[268,271] the formation of isomers [α, β, and γ, differing in the position of the double bond, indicated by dotted lines in formula (CIX)] can be explained by the intermediate formation of a carbonium ion¶, just as in the cyclisation of pseudoionone.

The preparation by the above scheme of a wide variety of derivatives of 1,1-dimethyloctalin has enabled some generalisations to be made concerning the dependence of the odour of these compounds on their structure[268,269,271,272]. Thus (CIX) with $R_1 = CH_3$ or C_2H_5 and $R_2 = R_3 = R_4 = H$ possess an ionone smell, which becomes weaker with increase in the size of R_1 and completely disappears when $R_1 = n\text{-}C_4H_9$ or $C(CH_3)_3$. Special interest attaches to derivatives of unsaturated 1,1,7-trimethyloctalins containing a functional group and a methyl group on the same carbon atom. Thus esters of this group ($R_1 = OR$; $R_2 = CH_3$; $R_3 = R_4 = H$) possess a very persistent odour of animal musk, which becomes especially intense if the COOR group is transesterified with higher iso-alcohols. When $R_1 = H$ or Alk, the 1,1,7-trimethyloctalin derivatives have a woody or ambergris type of smell. For example, (CIX) in which $R_1 = R_3 = R_4 = CH_3$ and $R_2 = H$ is described as a compound having such an odour[275].

A group of French chemists[276] have recently utilised the long known reaction of myrcene with maleic anhydride for the synthesis of new perfumes. The dibasic acid (CXI), which is readily obtainable from the adduct (CX), was converted into the ester (CXII), which on reduction with lithium aluminium hydride gave the corresponding diol (CXIII), dehydration of which yielded the bicyclic oxide (CXIV), which was then isomerised to the unsaturated tricyclic oxide (CXV). The adduct of myrcene with citraconic anhydride was used to synthesise, by an analogous series of reactions, the unsaturated tricyclic oxide (CXVI). These tricyclic oxides possess a very interesting ambergris odour.



It is interesting to note here some analogy in structure between these oxides and those obtained earlier[277] and also possessing an ambergris smell, such as the unsaturated oxide (CXVII), formed by the oxidation of ambrein (a tricyclic triterpene alcohol present in ambergris) and also the saturated oxides (CII) and (CIII) (the so-called ambroxide, obtained from sclareol) mentioned in the present review (see Section 3).



Among other interesting compounds synthesised from myrcene as diene component we may mention the lactones (CXVIII) and (CXIX), the latter possessing a strong odour of animal-faecal type. Experimental details of its preparation have been reported recently by Ohloff in a West German patent[278]. The value of this lactone for perfumery has been confirmed by the work of Soviet chemists[279].

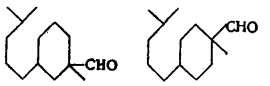
Several adducts of myrcene with unsaturated aldehydes, as well as compounds obtained after their hydrogenation,

‡ In the reactions with some of the dienophils, 3-methylmyrcene[273], its isomer 2-isopropyl-5-methylenehepta-1,6-diene[273], and a homologue of myrcene 2-methyl-6-methylenenona-2,7--diene[274] were also studied as diene components.

§ As in several other cases known previously, this shows the specific character of the catalytic action of boron trifluoride. Another example of this is the stereospecific cyclisation of pseudoirone under the influence of boron trifluoride, which we have examined in detail[132] and which has been mentioned in the present review (Section 2).

¶ The cyclisation of (CVIII) is discussed in greater detail in the review by Smit and Kucherov[183].

also merit attention as perfumes. Thus, for example, the adduct of myrcene with crotonaldehyde [(CVIII): $R_1 = R_2 = R_3 = R_4 = H$] possesses the odour of aubépine (*p*-methoxybenzaldehyde), while the corresponding alcohol is said to have a pleasant delicate scent[280]; the mixture of the isomeric aldehydes (CXX) and (CXXI), obtained by the condensation of myrcene with methacrylaldehyde followed by hydrogenation, has a strong scent of flowers[281].



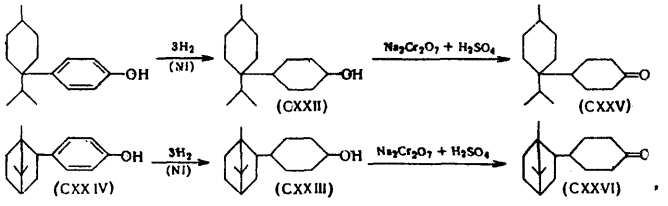
(CXX) (CXXI)

The group of octalin derivatives includes also the ambrinols discussed above [(LXXVIII) in Section 2], as well as bicyclohomofarnesal or ambrial (CV) and bicyclohomofarnesol [(CVI) in Section 3], compounds possessing an extremely valuable scent.

5. PERFUMES BASED ON TERPENYLPHENOLS

On the basis of the little information available, mainly in the patent literature[281-286], Soviet chemists have synthesised a series of new compounds which are oxygen-containing derivatives of cyclohexane with a terpene radical. In view of the great value of some of the products obtained, the synthesis was extended to a wide variety of derivatives, differing from one another in the functional group and the structure of the terpene radical.

Belov and Kheifits[287] have described compounds based on the condensation products of menthyl chloride with phenol, and also of a mixture of bornyl and isobornyl chlorides with phenol†, *m*-cresol, and *o*-cresol respectively. The resulting condensation products were subjected to hydrogenation. It was found that menthylcyclohexanol (CXXII) possesses a weak odour of cedar, whereas alcohols containing a bornyl radical have a stronger smell. Bornylcyclohexanol itself (CXXIII) has a very persistent, but not strong, cedar type of odour.



(CXXII) (CXXV)
(CXXIV) (CXXIII) (CXXVI)

The smell becomes weaker on passing to bornyl-3--methylcyclohexanol, but is intensified with bornyl-2--methylcyclohexanol, which, in the opinion of the authors of the paper, is due to the presence of the tertiary carbon atom, linked to the methyl group, adjacent to the alcoholic hydroxyl. Furthermore, with the 2-methyl isomer the odour acquires a sandalwood nuance. The acetates were almost devoid of smell. Oxidation of the alcohols with a chromic acid mixture yielded previously undescribed ketones. The transition to the ketones results in a considerable intensification of the odour; further, terpenylcyclohexanones containing a bornyl radical possess a pleasant odour, while menthylcyclohexanone (CXXV) has a disagreeable, obtrusive smell.

On passing from bornylcyclohexanone (CXXVI) to its homologues, a similar variation in odour is observed as in the case of the corresponding alcohols: with bornyl-3--methylcyclohexanone the odour does not change in character but becomes weaker, whereas with isobornyl-2-methylcyclohexanone the smell is markedly stronger and has acquired a different character, of musk and balsam.

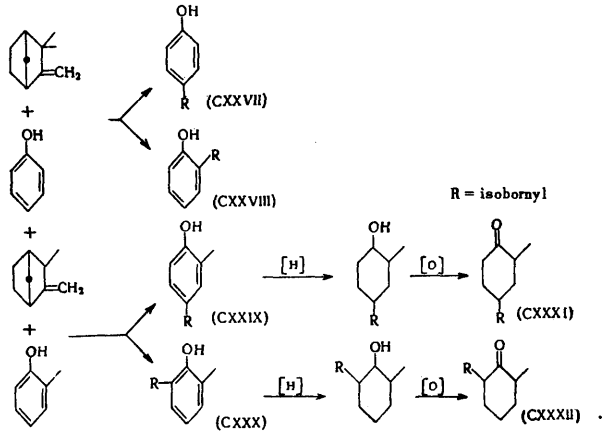
In order to simplify the synthesis of isobornyl-2-methylcyclohexanol and isobornyl-2-methylcyclohexanone, which are valuable compounds for perfumery, the alkylating agent used for the preparation of isobornyl-2-methylphenol, an intermediate in this synthesis, was camphene, a cheap and readily available product which can be made to react with *o*-cresol without preliminary conversion into the chloride[289]. The product formed as a result of the condensation of camphene with *o*-cresol followed by hydrogenation, which is obviously isobornyl-2-methylcyclohexanone, has found application in the perfumery industry under the name "musterone"; some details of its industrial synthesis were published recently[290].

The condensation of camphene with phenols has been studied in detail by Kheifits in the case of the preparation of isobornylphenol: it was found that, on alkylation in the presence of boron trifluoride, the proportions of *ortho*- and *para*-isomers were 3.5 : 1, a simple and convenient method was worked out for separating the isomeric isobornylphenols from their mixtures[291].

Recently Kheifits, Belov, and their collaborators have published a series of papers on the structure and the composition of the condensation products formed by camphene with *o*- and *p*-cresols. It is assumed that, under the conditions of acid catalysis, the camphene undergoes a Wagner–Meerwein rearrangement and enters the aromatic ring as an isobornyl radical. On the basis of the different acidities of the individual isomers, due to the strong screening of the OH group in compounds containing an *o*-isobornyl radical, an elegant method has been worked out for separating the *ortho*- and *para*-isomers, which are thus obtained in a quite pure form, by treatment with an insufficient quantity of aqueous-alcoholic alkali[291,292]. The dissociation constants of the compounds (CXXVII)–(CXXX) in various aqueous organic solvents have been determined[293]; the acidity of the *para*-isomers is considerably the higher. The structure of (CXXVII)–(CXXX) has been rigorously established from the infrared spectra[291,292] and measurements of the dipole moments of their bromo-derivatives[294]. Quantitative analysis by means of the infrared spectra has shown that the ratio of the *ortho*- and *para*-isomers on alkylation with camphene is 3.5 : 1 in the case of phenol[291], whereas with *o*-cresol it is 1.9 : 1 [292] (probably owing to one *ortho*-position being occupied). A method has been developed for identifying the individual isobornylphenols and isobornylcyclohexanones by thin-layer chromatography[295,296]. The compounds (CXXIX) and (CXXX) are converted by hydrogenation and oxidation into the corresponding cyclohexanones (CXXXI) and (CXXXII), when it is found that the former has a strong smell of musk, whereas the latter has a very faint but more pleasant odour of the same type[295]. Musterone contains ~30% of (CXXXI) and ~70% of (CXXXII).[295]

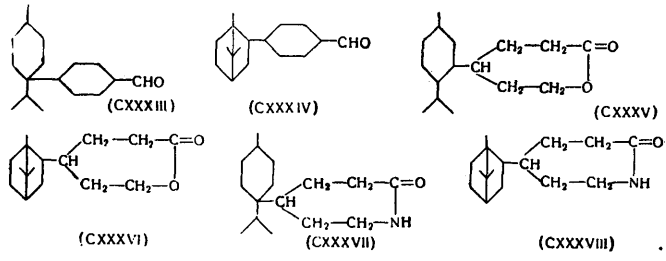
† Later the reaction of bornyl chloride with phenol formed the subject of a special study by Bulgarian chemists[288], who carried it out in the presence of aluminium chloride. They consider that the most probable formula for the resulting bornylphenol is (CXXIV).

2-Isobornyl-4-methylcyclohexanone[296], prepared in a similar manner, has a peculiar faint odour.



Belov and Kheifits[297] have studied the effect on the odour of converting terpenylcyclohexanones into previously undescribed related compounds containing different functional groups. The aldehydes (CXXXIII) and (CXXXIV) obtained from (CXXV) and (CXXVI) respectively were found to have a rancid tinge to their odour and to be of no interest for perfumery. Of the hexan-1,6-olides which have been synthesised, (CXXXV) is completely devoid of smell, and (CXXXVI) possesses an odour similar to but fainter than that of the original (CXXVI). These observations agree with earlier information[298] on the odour of other hexan-1,6-olides; the conversion of substituted cyclohexanones into such lactones is obviously accompanied by the disappearance or weakening of the odour.

The ketones (CXXV) and (CXXVI) have also been converted into the corresponding hexane-1,6-lactams (ε-caprolactams), of which (CXXXVII) is reported to be odourless, while (CXXXVIII) possesses a peculiar smell, somewhat resembling that of the lactone (CXXXVI) but still weaker than that of the ketone.



An extremely interesting product, possessing a sandalwood odour and excellent fixation properties, is formed by the hydrogenation of isobornylguaiacol (isobornyl-2-methoxyphenol). A team of workers at the VNIISNDV (All-Union Synthetic and Natural Perfumes Research Institute) and industrial scientists have worked out and published an industrial method for the synthesis of this most valuable product, which has been provisionally named "santalidol".[299] The preparation of isobornyl-2-methoxyphenol was accomplished by condensing camphene with guaiacol in the presence of boron trifluoride, the benzene ring being subsequently hydrogenated to a cyclohexane ring in the presence of a Raney nickel catalyst. The chemical structure of the product has not been finally elucidated, the authors of the paper regarding it as a mixture of various alcohols of closely similar structure.

A hydrogenation product of isobornyl-2-ethoxyphenol, synthesised from camphene and guaethol, was likewise obtained as a mixture of alcohols, having a very similar odour to that of santalidol[289]. Oxidation on the alcohols with a chromic acid mixture yielded a mixture of ketones having a stronger scent of sandalwood than the original alcohols.

Thus the research done during recent years on terpenylphenols has yielded several products of great value in perfumery, and has provided new data on the effect of the structure of organic compounds on their odour. Even the fact itself of a strong and persistent odour in terpenylcyclohexanols and terpenylcyclohexanones, which have quite large molecules with radicals of high molecular weight, is undoubtedly of interest.

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SECONDARY REACTIONS IN RADICAL POLYMERISATION

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INTRODUCTION

In recent years detailed studies of polymerisation processes of different types have established that the main reactions in these processes are accompanied by a number of supplementary secondary processes or reactions. The distinguishing feature of these secondary reactions is the participation of previously formed polymer chains. It is therefore natural that at low degrees of conversion of monomer, *i.e.* in the range in which polymerisation kinetics, etc. are usually studied, these reactions are almost non-existent and the polymer obtained under these conditions is the product of only the main or primary reactions.

On the other hand, at high degrees of conversion, particularly when the concentration of polymer becomes comparable with the concentration of monomer, the probability of secondary reactions in polymerisation systems is considerable and these reactions have a significant effect on the polymerisation product.

The present review attempts to give a systematic account of the available data on secondary reactions in radical polymerisation.

I. INTRODUCTORY REMARKS

Study of the molecular-weight distribution (MWD) of polymer specimens obtained by bulk polymerisation under the influence of free radicals[1] shows that at low degrees of conversion, in accordance with theory, experiment gives a unimodal function for the molecular-weight distribution. On the other hand, at degrees of conversion close to 100%, experiment often gives complex distribution functions showing several maxima[1]. (In the polymerisation of diene compounds anomalous high-molecular "tails" are often observed in the MWD [2].)

The theory of radical polymerisation in bulk phase, which takes account only of the main reactions of chain initiation, growth, and rupture, never gives these complex multimodal distributions. It has been suggested[1] that MWD with a number of sharp maxima may be produced as a result of doubling, trebling, etc. of the molecular weights of individual groups of molecules as a result of certain secondary reactions accompanying polymerisation[3]. Subsequent more detailed examination of the problem showed that secondary reactions by themselves cannot be responsible for the multimodal character, which arises rather as a result of the microheterogeneity of the system at later stages of the polymerisation. Apart from any relation to the number of maxima, however, the secondary reactions may change significantly the properties of the polymer, so that it is necessary to consider these reactions.

In the work cited[1] and in a number of later papers secondary reactions were not defined sufficiently clearly, and this might lead to terminological confusion. It is shown below that the first stage in any secondary reaction is the transfer of the kinetic chain to the polymer[4]. The relative contribution of this reaction increases with the degree of conversion ψ, however, and its results differ fundamentally at high and low values of ψ. The rate of chain transfer to the polymer is

$$r_{tr,\,p} = k_{tr,\,p}[P^*]\,[P], \qquad (1)$$

where $k_{tr,p}$ is the corresponding rate constant, whose changes with change in ψ are neglected, [P*] the stationary concentration of macroradicals, and [P] is the total concentration of polymer formed in the period under consideration and is proportional to ψ. In bulk polymerisation under conditions where transfer is possible chain transfer to the monomer at first competes with transfer to the polymer, but this competition progressively decreases, since with increase in ψ, [m] (the concentration of the monomer) decreases and [P] increases.

For the same reason, the results of chain transfer are different at high and low values of ψ. At low values of ψ, when chain growth is not diffusion-controlled, activation of any intermediate link leads to growth of a side-chain. Sometimes this reaction is also called a secondary reaction, but this is hardly appropriate, for the growth of the side-chains takes place according to the same laws as the growth of the main chains. At high values of ψ, however, when little monomer remains, the viscosity increases sharply and the growth reaction becomes diffusion-controlled; activation of intermediate links in the chains leads not only to simple growth of the side-chains, as under the conditions where large quantities of monomer are present, but also to a number of other processes. The most probable process is rupture of the chain into two fragments[5,6], one of which will have an active end. These active fragments may subsequently[7-9] (a) be depolymerised by a chain mechanism, (b) transfer their activity to another chain, (c) recombine with another similar fragment or primary "live" chain, (d) disproportionate with another fragment or primary chain, or (e) begin new growth at the expense of monomer. Since [m] is small, process (e) should most probably take place at the expense of process (a).

In reaction of type (b), which is most probably accompanied by new breakdown, *two* fragments are again produced, so that a series of reactions of type (b) should lead to an increase in the total number of macromolecules in the system and to a decrease in the average weight M_n. Secondary reactions which begin with chain transfer and subsequently develop by mechanisms (b) or (d) can therefore be combined in the general class of *degradation reactions*.

Processes of types (a) and (e) (which must be considered together) or (c) involve a rearrangement of monomeric links or whole fragments between different macromolecules. These reactions can be combined under the title of *inter-chain exchange reactions*.

Let us now consider the original chain transfer reaction. Under favourable conditions, a chain activated in its centre can, without breaking down, recombine with another similar chain or with a chain having an active end. It is also possible to picture a process in which two closely adjacent chains with active intermediate links are joined together by a short bridge (two branches begin to grow towards one another and recombine). The probability of such reactions depends on the tendency of the macroradicals to recombine, and should increase sharply in diene polymerisations, the increase being greater, the greater the number of 1,2-links in the chain. Reactions of this type, leading to the formation of branched fractions, microgels, and gels, are most dangerous from the practical viewpoint; they form a third class of secondary reaction, which may conventionally be referred to as *cross-linking reactions* (conventionally, since this includes all recombinations of activated intermediate links with terminal links, leading to ordinary branching).

Reactions of the last class, like ordinary branching reactions, lead to an increase in the polydispersion, revealed as an increase in the high-molecular "tail" in the MWD. As will be shown below, however, there are insufficient grounds for assuming that particular MWD's, corresponding to "fractions" of identical degree of branching, will give separated maxima on the weight distribution curve.

Thus the term "secondary reactions" will be taken to mean the conversion of "dead" chains and macroradicals in the later stages of polymerisation, beginning with the activation of intermediate links as a result of chain transfer to the polymer. These reactions, however, are fundamentally different from ordinary branching reactions, which also result from chain transfer to the polymer. The latter reactions are nevertheless included in the discussion, for in diene polymerisations they may readily change to cross-linking reactions.

Under normal conditions, all secondary reactions should take place simultaneously, and it is impossible to observe them individually. In certain model systems (or combinations of such systems), however, it is possible to "isolate" individual reactions. This is discussed later.

II. INDIVIDUAL FORMS OF SECONDARY REACTION

a. Degradation of Polymer Chains

In recent years it has been shown that the process of radical polymerisation may be accompanied by the direct action of initiator radicals, polymer radicals, etc. on previously formed polymer chains. This usually leads to degradation, *i.e.* to rupture of the C–C bonds of the macromolecules.

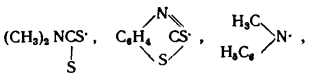
The process of C–C bond rupture is usually accompanied, to some extent, by a depolymerisation process which, as has now been shown[11,12] (Ref. 10, pp. 77–80) is also radical-initiated. Even in model systems — solutions of polymers in the presence of initiators (which are often used to study degradation in the presence of radicals) — however, the depolymerisation process plays an extremely small part[9], and in the case of "polymerisation boilers" this process cannot play a significant part, due to the actual nature of the process taking place.

The majority of the free radical reactions described in the literature relate to those cases of chemical changes in which the radical removes a hydrogen or halogen atom from an inactive molecule (Ref. 4, p. 9), *i.e.* when replacement reactions of the type

$$R_1^{\cdot} + X{-}R_2 \rightarrow R_1{-}X + R_2^{\cdot}.$$

take place.

If the compound $X-R_2$ is a polymer, this reaction produces a macroradical $R_2^{\cdot}$, which, depending on its reactivity and the properties of the surrounding medium, may be stabilised in different ways, including degradation at a weakened C–C bond with the formation of inactive and active macromolecular fragments[5–9]. The degradation of polymer chains under the influence of free radicals has been described by a number of authors. Thus Dolgoplosk *et al.*[13] showed that redox systems (consisting of peroxides and hydroperoxides and different reducing agents), which are sources of free radicals at low temperatures, cause degradation of polyisobutylene and other polymers in hydrocarbon media. In particular, it was shown that at low temperatures (20°–50°) these systems initiate the vulcanisation of rubbers in the absence of oxygen and initiate a degradation process in the presence of oxygen. The rupture of the diallyl bond in complex organic molecules under the influence of free radicals was also established by Klebanskii and Fomina[14]. Dolgoplosk and coworkers[15–18] also studied the degradation of polyisobutylene in solution under the influence of a number of aliphatic radicals† (see Fig. 1), radicals with a reactive centre on nitrogen and sulphur atoms:



and radicals with a reactive centre on an oxygen atom, of the type RO· and $RO_2^{\cdot}$. The experiments were generally carried out in solutions containing 3.5 wt. % of polyisobutylene in ethylbenzene, the quantities of initiators (sources of free radicals) being equivalent to 0.45 wt. % of benzoyl peroxide. The influence of oxygen was eliminated by preparing the solutions in an atmosphere of nitrogen in Shlenk vessels, from which the ampoule-viscometers were filled. The latter were then sealed and placed in a thermostat at 90°–130°, depending on the source of free radicals used. The molecular weights before and after degradation were determined by viscosimetry. Fig. 2 shows the course of the degradation with time for a number of free radical sources.

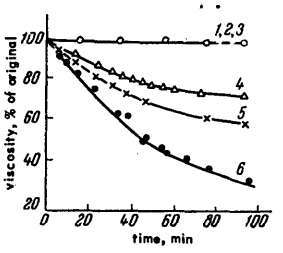


Fig. 1. Degradation of polyisobutylene in ethylbenzene solution in the presence of sources of alkyl free radicals at 110°:[16] 1) without triazene; 2) t-butylphenyltriazene; 3) azobisisobutyronitrile; 4) propylphenyltriazene; 5) ethylphenyltriazene; 6) methylphenyltriazene.

Study of the activity of different types of free radical showed that the most active in degradation are those of the type RO· and $RO_2^{\cdot}$, which are very active hydrogen-atom acceptors[19]. Radicals which are not active hydrogen-atom acceptors, such as $(CH_3)_2\dot{C}CN$, obtained by the thermal decomposition of azobisisobutyronitrile, and $(CH_3)_3\dot{C}$, obtained by the decomposition of t-butylphenyltriazene, do not cause degradation of polyisobutylene (see Fig. 1). Thus the

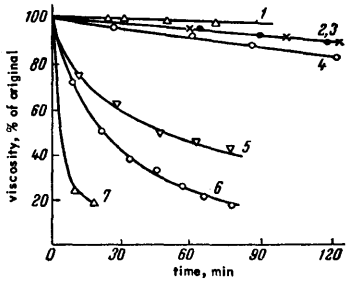
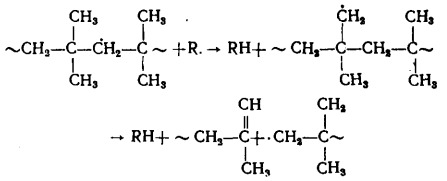


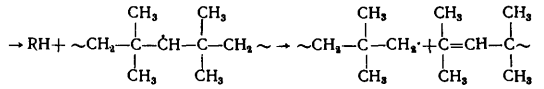
Fig. 2. Degradation of polyisobutylene in ethylbenzene solution in the presence of sources of free heteroradicals[18]: 1) without initiator, 130°; 2) mercaptobenzothiazole disulphide, 130°; 3) dimethyldiphenyltetrazene, 130°; 4) tetramethylthiuram disulphide, 130°; 5) phenylisopropyl hydroperoxide + Fe(III) naphthenate (10 mole % relative to the hydroperoxide), 110°; 6) benzoyl peroxide, 90°; 7) phenylisopropyl hydroperoxide + Co naphthenate (0.5 mole % relative to the hydroperoxide), 110°.

† These radicals were produced by the thermal decomposition of triazenes: $R{-}N{=}N{-}NHC_6H_5 \rightarrow R^{\cdot} + NHC_6H_5$, where R· is an aliphatic radical. The anilino-radical formed simultaneously is inactive.

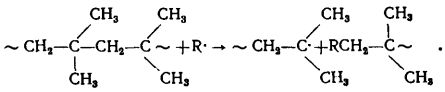
efficiency of a given radical in degradation is determined in all cases by its ability to abstract a hydrogen atom. From this it was concluded that the degradation of polyisobutylene involves the removal of an H atom from the macromolecule with the formation of a macroradical and subsequent stabilisation of the latter by degradation with the rupture of a C–C bond and the formation of a macroradical:



or



A less probable process, in the authors' opinion, is direct attack on the C–C bonds by free radicals:



These degradation steps are possible in principle, since they lead to the formation of more stable free radicals. This reaction mechanism, however, hinders the formation of the intermediate complex and increases considerably the activation energy of the process (Ref. 4, pp. 99–101). The destruction of polyisobutylene in the presence of benzoyl peroxide was also studied by Rado and Simunkova[20]. The experiments were carried out in the condensed phase at 65°–95°. It was established that the decomposition of benzoyl peroxide is a chain reaction with sensitised second-order decomposition, *i.e.* that the phenyl radicals formed by thermal decomposition of the peroxide on the one hand initiate further decomposition of the peroxide and on the other hand abstract H atoms to yield polymer radicals. It was shown that the transfer of the active centre to the polymer takes place by reaction with CH_2 groups and also with CH_3 groups, and that, since the polymer radicals of the type $\sim\dot{C}H_2$ have a high reactivity, they are stabilised by isomerisation before reaction with other radicals takes place. As a result, the reaction indicated above takes place with the formation of a new polymeric fragment radical, and the other fragment is stabilised by the formation of a double bond. It was also shown that stabilisation of the macroradicals takes place mainly by disproportionation, which is the chief means of double-bond formation in the degradation process. Recombination in the case of polyisobutylene macroradicals is complicated by steric hindrance. This mechanism for the degradation is also confirmed by experiments on the sheer degradation of polyisobutylene in the presence of I_2.[21]

It was also established that a direct relationship exists between H atom removal and C–C bond rupture[22,23], in particular in the degradation of polyisobutylene swollen in benzene in the presence of ferric naphthenate at about 100° (see Fig. 3). In this case dehydrogenation of the polymer $Fe^{3+} + RH \rightarrow Fe^{2+} + R^{\cdot} + H^+$ is the primary process, and the rupture of the C–C bond is apparently a secondary stage. The fact that polymer dehydrogenation of this type takes place was established for the case of the ferric naphthenate–isoprene system[23]. It was observed that at

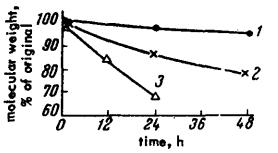


Fig. 3. Degradation of polyisobutylene in the presence of ferric naphthenate[18]: 1) in the absence of Fe(III) naphthenate; 2) 5 mole % of naphthenate relative to the polymer; 3) 20 mole %.

100° ferric naphthenate initiates the homogeneous polymerisation of isoprene. The polymerisation process was accompanied by conversion of ferric naphthenate to ferrous naphthenate. An analogous change accompanied the process of structure-formation in a 2% solution of polyisoprene in benzene at 150°. In spite of all that has been said, however, the degradation of polyisobutylene by free radicals as a result of direct attack on the main chain is also possible. Thus Thomas[24] recently showed experimentally that, in the degradation of polyisobutyelen in the condensed phase at 140° by small quantities (~1.5 wt. %) of dicumyl peroxide, 94% of the cumyloxy-radicals combined with polyisobutylene. For other rubbers under analogous conditions, deactivation of the cumyloxy-radicals takes place by removal of H atoms, and this is accompanied by structure formation. Thomas[24] and the authors[7] observed no significant depolymerisation of polyisobutylene the degradation process.

Bresler *et al.*[6] made a more detailed study of the degradation of polydienes by free radicals in solution over a wide concentration range in an atmosphere of nitrogen. The free radical sources were methylphenyltriazene, azobisisobutyronitrile, and sulphur monochloride S_2Cl_2, whose vulcanising action is apparently of the radical type[23]. The radicals used showed a wide range of activities for the removal of an H atom from organic compounds[16]. The materials studied were natural rubber containing links joined only in the 1,4-position, synthetic polyisoprene polymer containing up to 90% 1,4-links, and polydivinyl rubber containing up to 70% 1,2-links. The experiments were carried out with benzene solutions containing 0.3–10 wt. % of the polymers, the quantity of initiators (sources of free radicals) amounting to 5–50% of the weight of polymer in solution. It was established that in benzene, all the rubber specimens undergo degradation at low concentrations (0.3–1%) and gel formation at higher concentrations (3–10%). (It has recently been shown that a similar dependence on the concentration in solution is observed for the degradation and cross-linking of rubbers under the influence of the residues of complex organometallic catalysts.) The extent of the reactions in both cases, however, depends markedly on the polymer structure and the activity of the free radicals. Radicals of low activity, such as benzyl and allyl radicals, which are incapable of reacting with rupture of a C–H bond[17], were found to be ineffective in the degradation process. The most active radical (methyl) in the case of natural rubber or synthetic polyisoprene caused gel formation at concentrations of 2.7–3% and above, and degradation at lower concentrations. In the case of polybutadiene containing a large number of vinyl groups in the chain gel formation is observed at polymer concentrations of 1–3%. This agrees with the ease with

which lateral vinyl groups add on free radicals[25,26] (particularly compared with internal double bonds). The low tendency of polybutadiene to undergo degradation may be due to the fact that the polymer chain of this rubber contains a very few diallyl links with a weakened C–C bond. The comparatively inactive $(CH_3)_2\dot{C}(CN)$ radical does not cause gel formation in natural rubber and polyisoprene, even at very high concentrations of the polymer (up to 10%), but causes degradation in all cases. This agrees with the low tendency of the internal double bonds of the polymer chain to add on free radicals which are not sufficiently active. In the case of polybutadiene containing a large number of lateral vinyl groups, this radical causes gel formation at polymer concentrations above 3%. The high reactivity of the external double bonds (vinyl groups) towards $(CH_3)_2\dot{C}(CN)$ was established directly in a study of the products of the reaction of this radical with olefines[25,26]. The degradation of natural rubber and synthetic polyisoprene in the presence of $(CH_3)_2\dot{C}(CN)$ is apparently due to to the fact that the cross-linking reaction is bimolecular and requires a comparatively high concentration of polymeric radicals, which the comparatively inactive $(CH_3)_2\dot{C}(CN)$ cannot provide. On the other hand, the degradation reaction is unimolecular with respect to the macroradical concentration and can occur. The behaviour of sulphur monochloride is of particular interest. When solutions of S_2Cl_2 and natural or other rubbers (concentration 1%) are mixed, gel formation takes place in the solution. With subsequent heating, however, the gel disappears and the reduced viscosity of the solution decreases by a factor of 5–10, with a corresponding decrease in the molecular weight. The gel formed at the start of the experiment persists only in the case of comparatively concentrated solutions (2–4%) of synthetic polyisoprene and polybutadiene. Special experiments with rubber which had undergone degradation[6] showed that the relationship $\langle r^2\rangle^{1/2} = KM^a$, where $\langle r^2\rangle^{1/2}$ is the root mean square radius of the molecules, M the molecular weight, and K and a the characteristic parameters of the polymer-homologues in the given solvent, is the same for the degraded and original polymers, indicating that intramolecular cross-linking does not take place during degradation. The reaction of free radicals with polydienes can take place in two ways[27]: (a) by abstraction of a hydrogen atom with the formation of a macroradical and its subsequent decomposition:

$$\sim CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2\sim + R^{\cdot} \rightarrow RH +$$
$$+ \sim CH_2CH{=}C\dot{H}CH_2 \;\vdots\; CH_2CH{=}CH{-}\dot{C}H\sim \rightarrow$$
$$\rightarrow \sim CH_2CH{=}CHCH_2\cdot\cdot + CH_2{=}CH{-}CH{=}CH\sim;$$

(b) by addition to a double bond, which opens to form a macroradical, and subsequent degradation of the latter[24]:

$$\sim CH_2CH{=}CHCH_2{-}CH_2CH{=}CHCH_2\sim + R. \rightarrow$$
$$\rightarrow \sim CH_2CHRCHCH_2 \;\vdots\; CH_2CH{=}CHCH_2\sim \rightarrow$$
$$\sim CH_2CHRCH{=}CH_2 + \cdot CH_2CH{=}CHCH_2\sim.$$

When the concentration of polymer in the solution is sufficiently high, the recombination of macroradicals naturally leads to intermolecular cross-linking, *i.e.* to gel formation. At a sufficiently low concentration of macroradicals this recombination of intermediate activated links is hindered and the degradation process predominates.

Tasset and Smets[9] studied the degradation of poly(methyl methacrylate), polystyrene, poly(vinyl acetate), and poly-(chloroethyl acrylate) in dilute benzene solutions (1%) in the presence of similar quantities of benzoyl peroxide in the absence of oxygen at 65°–100°. The degradation was followed dynamically in sealed Mesrobian–Tobolsky viscometers and statically by determining the MWD before and after degradation, by fractionation and osmotic measurements. Special measurements were also made to determine the quantity of monomer in the product. It was shown that under these conditions, poly(α-chloroethyl acrylate), poly(methyl methacrylate), and polystyrene undergo degradation (at correspondingly decreasing velocities) whereas poly(vinyl chloride) and poly(vinyl acetate) are stable under these conditions. The influence of polymer concentration, degree of polymerisation, initiator concentration, temperature, and chemical structure on the rate of degradation were also studied. If it is assumed that the degradation of the polymer chain takes place randomly and that the number of chain ruptures is proportional to the number of links, *i.e.* to the polymer concentration, the rate of decrease in the number of bonds at time t will be

$$\frac{d(L)_t}{dt} = k_a(L)_t\,, \qquad (2)$$

where L_t is the number of bonds at time t. If we consider only degrees of degradation where $1/P_t \ll 1$, P_t being the degree of polymerisation at time t, we have[9]

$$\frac{1}{P_t} = \frac{1}{P_{t=0}} + k_a t \ddagger \qquad (3)$$

or

$$\frac{1}{M_t} = \frac{1}{M_0} + k_b t, \qquad (4)$$

where k_b, the rate constant for the degradation, is the number of moles of bond broken in 1 g of polymer in 1 min. This constant can thus be found for different polymers by measuring the molecular weights during degradation. The applicability of relationships of types (2) and (3) has been confirmed experimentally.

Fig. 4 shows the course of the degradation of poly(methyl methacrylate) fractions. Experiments at different polymer concentrations showed that the overall rate of degradation is proportional to the concentration, the value of the constant k_b remaining constant within the limits of experimental error. From Eqn. (2) it follows that $k_b = \Delta(1/M)/\Delta t$, *i.e.* after differentiation

$$\frac{dM}{dt} = k_b M^2. \qquad (5)$$

The values of k_b obtained by applying this relationship to the data given in Fig. 4 were also found to be constant within the limits of experimental error, confirming that the dependence of the degradation on molecular weight is in fact given by a relationship of type (5). Study of the dependence of the rate of degradation on the initiator concentration showed that

$$k_b = kC_{\text{init}}, \qquad (6)$$

where C_{init} is the initial concentration of added benzoyl peroxide and k a proportionality coefficient.

Fig. 5 gives the temperature dependence of the rate constants for the degradation of the three polymers studied in benzene solution at polymer concentrations of 0.8% and the

‡ In the general case, as shown by Simha[28],

$$\frac{P_t - 1}{P_t} = \frac{P_0 - 1}{P_0} e^{-k_a t},$$

from which, with the condition $1/P_t \ll 1$, we obtain Eqn. (3) as a first approximation by taking logarithms and expanding in powers of $1/P_t$.

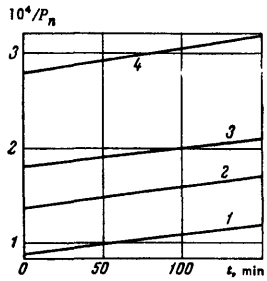


Fig. 4. Degradation of poly(methyl methacrylate) fractions of different degrees of polymerisation under the influence of benzoyl peroxide at 75°. Polymer concentration 5 wt.%, peroxide concentration 1 wt.%:[9] 1) P = 11460; 2) P = 7250; 3) P = 5500; 4) P = 3580.

same peroxide concentration. At 75° the values of k_b found under these conditions were (mole^{-1} sec^{-1}): $2.15 \times \times 10^9$, 1.04×10^9, and 25×10^9 for poly(methyl methacrylate), polystyrene, and poly(α-chloroethyl acrylate) respectively. From the data given in Fig. 5, using the Arrnhenius equation

$$k_b = Ae^{-\Delta U/RT}, \qquad (7)$$

it was found that the values of the activation energy for the degradation process were the same for all three polymers studied and amounted to 31–32 kcal, which corresponds approximately to the activation energy for the decomposition of benzoyl peroxide[29]. The difference in the absolute values of k_b for different polymers is due to differences in the chemical structure of the polymers and in the relative stability of the radicals produced during degradation.

It is suggested that degradation takes place according to the following scheme: (1) initiation of the primary radicals $(C_6H_5COO)_2 \xrightarrow{k_i} 2R^{\cdot}$; (2) transfer of an active centre to the polymer with the formation of a macroradical: $R^{\cdot}$ + + polymer $\xrightarrow{k_t} P_n^{\cdot}$; (3) rupture of a skeletal C–C bond: $P_0 \xrightarrow{k_d} P_x + P_y^{\cdot}$; (4) depolymerisation with subsequent stabilisation of the polymeric "fragment" $P_{y-1}^{\cdot}$ in different ways: $P_y^{\cdot} \xrightarrow{k_p} P_{y-1}^{\cdot}$. It is clear that, although the rate of degradation is determined by all the stages, the viscometric data reflect chiefly the third stage in the scheme, since it is this process that causes the sharp decrease in molecular weight. The effect of the chemical structure of the polymers is shown in (1) the different values of the energy of removal of an H atom from the polymer molecule at the second stage, and (2) the different stabilities of the $P_n^{\cdot}$ radical.

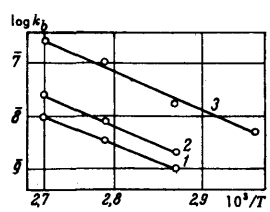
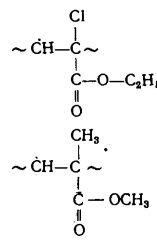


Fig. 5. Temperature dependence of the degradation rate constants[9]: 1) polystyrene; 2) poly(methyl methacrylate); 3) poly(α-chloroethyl acrylate).

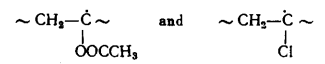
The high rate of degradation of poly(α-chloroethyl acrylate) and poly(methyl methacrylate) is due to the presence of tertiary carbon atoms in their chains, since this facilitates the degradation of the polymer chains by the radicals[21,30]



poly(α-chloroethyl acrylate) macroradical,

poly(methyl methacrylate) macroradical.

The degradation of polystyrene, on the other hand, is hindered by the high stability of the benzyl type radical $\sim CH_2-\dot{C}\sim$ (with C_6H_5), formed in the intermediate stage of the degradation. The absence of appreciable degradation in the case of poly(vinyl acetate) and poly(vinyl chloride) is due to the high activity of the radicals



since this hinders the primary stages of H atom removal. Special experiments showed that the degradation yields mainly large "fragments". As degradation proceeds there is a sharp decrease in the average molecular weight (by a factor of 4–5 after degradation for 12 h) without the presence of significant quantities of monomer in the product. (The average number of monomer molecules liberated by depolymerisation, for one chain rupture, to form a pair of "fragments" was about 30 units, when polymers with a degree of polymerisation of $5 \times 10^3 - 3 \times 10^4$ were used for the experiments.)§

The degradation of polymers under the influence of free radicals has been observed by other workers[31-36]. The displacement of the MWD towards low molecular weights as degradation proceeds, observed by Mesrobian *et al.*[31] in a study of the degradation of polystyrene in toluene under the influence of benzoyl peroxide, is shown in Fig. 6. In this work, as in earlier work by Tobolsky and Mesrobian[32,36] it was found that when the duration of the degradation process is sufficiently great and new quantities of initiator are added to the system at definite intervals to replace the initiator which has decomposed, there is a considerable decrease in the rate of degradation. By taking the monomer under analogous conditions and adding corresponding portions of initiator, however, it was possible to observe polymerisation with subsequent retardation in the same range of degrees of polymerisation as in the case of the

§ In pure depolymerisation (which is possible, for example, during degradation *in vacuo* at high temperatures) the average molecular weights and their ratios should not change at all.

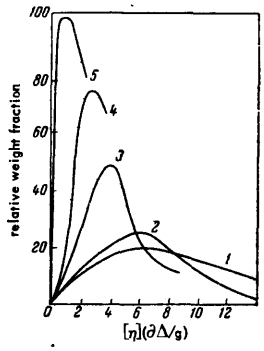


Fig. 6. Differential size distribution for polystyrene at different stages of degradation in toluene at 111°: [31] 1) initially; 2) 21 h; 3) 54 h; 4) 158 h; 5) 518 h.

polymer degradation (see Fig. 7). Analogous behaviour was observed in the case of illumination with ultraviolet light with $\lambda < 3000$ Å.

Mesrobian and Tobolsky suggested that in this case the rates of polymerisation and depolymerisation become equal and that in general thermodynamic equilibrium may be established between a polymer and its monomer. (Tobolsky and Eisenberg recently examined a general theory of equilibrium polymerisation [37].) The results obtained by Mesrobian and Tobolsky show only partial agreement with the results and conclusions of Montgomery and Winkler [33,34], who studied the same system, and with Thompson's data [35].

Mesrobian and Tobolsky obtained polymerisation and depolymerisation curves which approached a common limit. Montgomery and Winkler, and also Thompson, showed equally convincingly that this is only a special case. In general, the polymer undergoes continuous degradation, and in the case where the monomer is the starting material, the initial process is chiefly polymerisation, followed by degradation. In particular, it was shown that the molecular weight of the degradation product may be much lower than the "equilibrium" molecular weight found by Mesrobian and Tobolsky, and depends on the amount of catalyst or ultraviolet illumination. A clearer picture is obtained when we examine the distributions with respect to size of degradation product (see Fig. 6) and polymerisation product (see Fig. 8), observed at the times marked by vertical broken lines in Fig. 7, which presents Mesrobian and coworkers' data [31]. The shape of the curves in Fig. 6. indicates continuous intense breakdown of the polymer. When the monomer is the starting material (see Fig. 8), however, the polymer formed in the initial stage of the polymerisation has a comparatively high average molecular weight; subsequently, as a result of the decrease in the monomer concentration, the molecular weight of the resulting polymer decreases¶. Fig. 7 shows that, after the curves have merged, the viscosity of both solutions decreases slowly. By carrying out more prolonged experiments, Montgomery and Winkler obtained clearer proof of this decrease [33,34].

Mesrobian and coworkers do not attribute great significance to this decrease, but Montgomery and Winkler [33] and Thompson [35] consider it to be direct proof that equilibrium with respect to molecular weight is not established. They suggest that, irrespective of whether the polymer is present at the start of the reaction or appears in the system during polymerisation of the monomer, continuous degradation of the polymer takes place until radicals are formed in the system. They attribute the decrease in the rate of reduction of the viscosity for prolonged processes to the fact that in the case of the polymer with lower molecular weight, a given decrease in the viscosity requires the rupture of a higher number of bonds [34]. Montgomery and Winkler showed by special measurements that the osmotic pressure : viscosity ratio for polymers at different stages

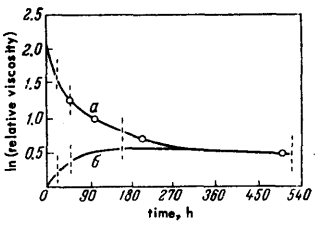


Fig. 7. Polymerisation–depolymerisation equilibrium for polystyrene–styrene in toluene at 111°: [10,31] *a*) concentration of polystyrene solution 16 g ml^{-1}, 0.5 g of benzoyl peroxide per 100 ml added every 8 h; *b*) concentration of styrene solution 16 g per 100 ml, 0.005 g benzoyl peroxide per 100 ml added every 8 h. The original polystyrene specimens consisted of the fractions with $M_n = 72 \times 10^3 - 3.6 \times 10^6$.

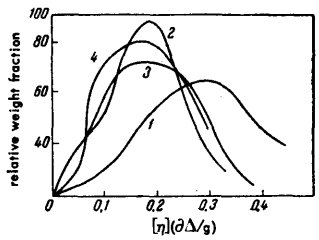


Fig. 8. Differential distribution according to the size of the macromolecules for the polymerisation of styrene in toluene at 111°: [31] 1) 21 h; 2) 54 h; 3) 158 h; 4) 518 h.

¶ In work on the high-temperature degradation of poly(methyl methacrylate) in the presence of monomer at 264° in a closed vessel [38], it was observed that at first almost complete polymerisation of the monomer took place, and this was only later followed by degradation of the newly-formed polymer and polymer added initially. Small [39] measured the equilibrium pressure of the monomer above poly(methyl methacrylate) in the presence of radicals and from the results he calculated the equilibrium concentration of monomer in the polymer, the values found being 0.3% at 100° and 2.87% at 160°.

of the degradation remains constant and that the polymer with low molecular weight (lower than the "equilibrium" molecular weight in Mesrobian and Tobolsky's terminology) cannot aggregate rapidly to polymers with higher molecular weight, although it does not follow from their data that, in the presence of agents causing degradation, its viscosity decreases with time. Grassie (Ref. 10, pp. 77–80) suggests that even in this case an increase in the molecular weight of the polymer is observed, but the increase is very slow, due to the simultaneous intense degradation. Experiment shows that in the equilibrium represented in Fig. 7, irrespective of the direction from which it is approached, approximately 80% of the polymer can be isolated from the solution. The composition of the product remaining in solution has not been established accurately (Ref. 10, pp. 77–80), but Tasset and Smets[9] showed that the quantity of monomer is small. Grassie suggests that the main fraction of the product not extractable by precipitation is a mixture of oligomers[10], and points out that the relatively rapid attainment of a state in which the system contains 80% of the polymer and the retention of this concentration during subsequent reaction indicate the existence of an equilibrium between the reactions of chain growth and of monomer removal from the chain. This equilibrium can be represented by the scheme

$$P_r + M \underset{k_d}{\overset{k_p}{\rightleftarrows}} P_{r+1}, \qquad (8)$$

where k_p and k_d are the rate constants for chain growth and rupture respectively. This also agrees with the data from the work cited above[38], since when at high temperature (264°) the depolymerisation of poly(methyl methacrylate) is accompanied by polymerisation at an appreciable velocity, *in a closed volume* quasiequilibrium should be observed, *i.e.* the attainment of a steady monomer concentration, at which the rate of polymerisation is equal to the rate of removal of monomer from the polymer. This quasiequilibrium in polymerisation–depolymerisation processes involves only the comparatively small "live" fraction of the polymer (the macroradicals or macromolecules with terminal double bonds capable of being activated at the temperature of the experiment). The thermodynamic relationships derived for true equilibria in which the system as a whole takes part cannot in principle be satisfied in the present case of high-temperature degradation and polymerisation in the poly(methyl methacrylate)–methyl methacrylate system[38]. Thus in systems in which polymerisation and degradation are taking place simultaneously, a true steady state with respect to molecular weight is in general not established. As far as Tobolsky and Mesrobian's systems are concerned, the increase in viscosity when the monomer is the starting material is due to polymerisation, but the limiting molecular weight depends on the rate of initiation and temperature. As the polymer accumulates, an ever-increasing part is played by the rupture of macromolecules, and this will not influence the above equilibrium [see Eqn. (8)]. If the pure polymer is the starting material, the removal of monomer from the chain (depolymerisation), combined with chain rupture (degradation) leads to a rapid decrease in the molecular weight of the polymer. When equilibrium of type (8) is established, however, the change in the molecular weight will be determined only by chain rupture. Thus the gradual decrease in the viscosity of a polymerised monomer or depolymerised polymer observed at the end of the reaction is due entirely to rupture (degradation) of the macromolecules, irrespective of the process described by Eqn. (8).

The merging of the polymerisation and degradation processes, observed by Mesrobian and Tobolsky (see Fig. 7) is apparently accidental (Ref. 10, Chapter IV). Mesrobian and Tobolsky's suggestion that an equilibrium molecular weight is shown by the polymer cannot be correct, particularly since the actual process which should lead to the attainment of this "equilibrium" molecular weight is not clear. The actual possibility of approaching the same molecular weight by polymerisation of the monomer or degradation of the polymer indicates merely the attainment of a certain quasisteady state (with respect to molecular weight), determined by the specific experimental conditions. This state was attained, in particular, by ultrasonic irradiation[40], and also in the work of Rossi and Bianchi[41], who irradiated solutions of styrene and polystyrene in chloroform with γ-rays from ^{60}Co. They established that there exists a quasisteady molecular weight, which can be attained either by the polymerisation of styrene in chloroform or by the degradation, also in chloroform, of polystyrene with a molecular weight higher than the quasisteady molecular weight. According to their data, $M_{\text{stationary}}$ amounts to 180×10^3 for an intensity of irradiation of 60 r min^{-1} or 300×10^3 for an intensity of 37 r min^{-1}. Rossi and Bianchi suggest that this quasisteady state of polymerisation and degradation results from an equilibrium between the energy which the macromolecule obtains from the γ-radiation and the energy which it can "remove" or, more accurately, scatter (by transfer of an exciton along the chain or by transfer to the surrounding medium) without chain rupture.

In the above discussion we have not dealt in detail with the problem of the oxidative degradation of polymers[10–12,27,42–47], since this lies outside the scope of the present article.

b. Inter-Chain Exchange

It must first of all be emphasised that inter-chain exchange cannot take place without preliminary degradation of previously formed polymer chains by free radicals, with activation of the end of one of the two resulting smaller chains. This takes place, for example, in degradation according to Tasset and Smets' scheme (see above). The resulting macroradical may begin growth again at the expense of monomer or recombine with another similar (or "normally" growing) macroradical. Thus irrespective of the specific character of the first stage (*i.e.* the reaction of the free radical with the polymer chain, leading to degradation), inter-chain exchange can take place in three ways: (1) macromolecular combination (*i.e.* recombination of the newly-formed radicals derived from different original polymer chains) with one another or with "normally" growing radicals; (2) exchange at the expense of monomer, *i.e.* repeated stages involving degradation and the new growth of activated fragments of the chain; and (3) inter-chain exchange proper, which is observed when degradation takes place as in inter-chain reactions during polycondensation[48,49]. (Such exchange may, for example, take place during the degradation of polyisobutylene by macroradicals with attack "from the side", *i.e.* directly, with rupture of C–C skeletal bonds. It has been reported[50] that in the radiolysis of a mixture of high-molecular-weight and ^{14}C-labelled low-molecular-weight polyisobutylenes, the activity appeared in the high-molecular-weight fraction, indicating inter-chain exchange.) All these three processes lead to rearrangement of the polymer segments

and this in turn, when the polymerisation process is prolonged, should lead to distributions in thermodynamic equilibrium with respect to molecular weight, of the type observed in polycondensation equilibria[48]. There is however a significant difference in the conditions of inter-chain exchange for polymerisation and polycondensation. In polycondensation, the system unavoidably contains some water, acid, amine, etc., *i.e.* materials capable of causing hydrolysis, acidolysis, aminolysis, etc.; moreover, the ends of *all* the chains are active. Thus at any moment in polycondensation, equilibrium between the process of condensation and degradation is ensured. In polymerisation there is usually a comparatively small number of agents causing degradation (free radicals), which are used up, moreover, with the passage of time. As a result, a state of thermodynamic equilibrium is never attained in polymerisation.

Finally, at different stages of the polymerisation, the probability of the above exchange reactions is not the same, and in some systems, individual reactions may not take place at all. For example, in polymerising systems where rupture of the kinetic chain takes place predominantly by disproportionation, macromolecular combination is suppressed to a considerable extent. During polymerisation, as the system becomes more viscous, the mobility of the macroradicals as a whole decreases much more rapidly than that of the microradicals†, so that in the later stages of the polymerisation, when the process becomes diffusion-controlled, exchange at the expense of the monomer becomes most probable. Since, however, the mobility of the individual active links in the macroradicals is much greater than their mobility as a whole, macromolecular recombination and inter-chain exchange proper (if the latter is possible for molecules of a given chemical structure) under these conditions cannot be completely excluded. The possibility of macromolecular recombination up to high degrees of conversion was established by a number of workers in a study of the mechanism of rupture of the kinetic chain for polystyrene and other polymers, by radioactive tracer methods. In general, however, at very high concentrations of polymer and free radicals (in particular, these may be radicals formed by decomposition of the initiator), deactivation of the latter by removal of an H atom from an intermediate link in an inactive molecule, with subsequent "cross-linking" by recombination of the macromolecules activated in this way becomes possible (this process is examined in detail below).

The process of inter-chain exchange has been studied, albeit implicitly, by a number of workers. Thus it has been established that recombination of the macroradicals of a number of polymers, in particular polystyrene, takes place during radical polymerisation[51,52]. Since polystyrene is capable of undergoing degradation by free radicals (this has been studied by Tobolsky, Mesrobian and coworkers, Tasset and Smets, Montgomery and Winkler, etc.[53]), it is clear that two aspects of the same process of inter-chain exchange were studied. It is true that Tobolsky, Mesrobian, and other authors of papers on the study of the simultaneous degradation and polymerisation of polystyrene deal only with exchange at the expense of monomer (using our terminology). These papers have been examined in detail above in the consideration of degradation. Degradation during the polymerisation of methyl methacrylate was noted by Kern *et al.*[54] It should, however, be added that there are certain indirect indications that, when the "steady state" has been established, we have to deal not only with inter-chain exchange at the expense of monomer, but also with exchange by macromolecular combination (it is possible, at least in the degradation of polystyrene, that exchange by macromolecular combination plays the chief part). Indirect proof of this, taken from papers on the study of the "steady state", is provided by the following considerations.

1. If the polystyrene + solvent + initiator systems studied by these workers showed only depolymerisation of the same type as that which takes place *in vacuo*, *i.e.* taking place, for a given macromolecule, entirely after its activation‡, appreciable quantities of monomer would be observed in these systems immediately after the start of degradation (since the viscosity decreases sharply in the first moments!), and the molecular weight would not change with time. In actual fact neither of these results is observed. Even at high degrees of degradation, the quantity of monomer remains negligible and the molecular weight decreases considerably, the MWD being displaced towards low molecular weights (see Fig. 8).

These facts indicate that depolymerisation (at any rate up to considerable degrees of degradation of polystyrene) plays almost no part, the only processes being the individual ruptures of skeletal bonds in the macromolecules with the formation of active and inactive fragments. The active fragments (macroradicals) of polystyrene are extremely stable and may recombine with one another, normally growing radicals, initiator radicals, etc.

2. Montgomery and Winkler[34] studied the efficiency of benzoyl peroxide (the number of ruptures of the polymer chain per molecule of added peroxide) in the degradation of polystyrene in different solvents by means of this radical source. The values found were 0.003, 0.001, 0.03, and 0.45 for methyl ethyl ketone, toluene, ethyl acetate, and carbon tetrachloride respectively. Carbon tetrachloride is an extremely efficient kinetic-chain carrier (one of the Cl atoms is readily given up to the macroradicals). In this solvent, therefore, the recombination of macroradicals has a much higher probability, and this is apparently revealed by the increase in the efficiency of the peroxide by a factor of 450, compared with its efficiency in toluene, which is extremely stable towards active-centre transfer.

Finally, Bresler *et al.*[7] made a special study to obtain direct proof that inter-chain reactions take place in radical polymerisation and degradation. Experiments were carried out to study the time dependence of the degradation of polystyrene under the influence of initiators (sources of primary free radicals) in solution at moderate temperatures (~100°). Since reactions of the macromolecular recombination type may be suppressed to a considerable extent at high initiator concentrations, the experiments

† At first sight it appears that the reactions between macroradicals in the presence of microradicals (formed, for example, by decomposition of the initiator) have an extremely low probability, due to the low mobility of the macroradicals. Allowance must be made, however, for the fact that (as noted in the examination of inter-chain exchange in polycondensation) individual links of the macromolecules, in particular active links (terminal groups or links with unpaired electrons), have a mobility close to that of monomer molecules.

‡ The removal of monomer from the polymer radical has an activation energy of 18–25 kcal mole^{-1}, *i.e.* this reaction may take place at a fairly high velocity even at 100°. In actual fact, thermal depolymerisation requires a temperature of ~200°, due to the high activation energy of the initiation stage.

were carried out in moderately concentrated solutions (2–4 wt. %) of polystyrene at initiator concentrations of ≤ 1% of the weight of polymer in the solution. This corresponded to a ratio of 1 molecule of initiator to 1 molecule of polymer. The experiments were carried out under strictly oxygen-free conditions§ in inert solvents (benzene and toluene). The course of the degradation was followed viscometrically. Fig. 9 shows the time dependence of the degradation of polystyrene in the presence of methylphenyltriazene. The first stage is evidently rapid decomposition of the initiator with the formation of free radicals:

$$CH_3—NH—N=NC_6H_5 \rightarrow CH_3\cdot + \cdot NHC_6H_5 + N_2.$$

Fig. 9 shows that the sharp initial decrease in viscosity mirrors the decomposition of the initiator. After about 1 h, the greater part of the initiator has decomposed and the degradation of the chains stops, after which the viscosity actually increases, apparently due to the recombination of macroradicals. It is of course possible that some part in this change in viscosity with time is played by a depolymerisation process. Control experiments show, however, that the concentration of polymer in solution before and after degradation does not change, within the limits of error (this agrees with the data of Tasset and Smets[9] and Thompson[35]). Study of the MWD of polystyrene specimens before and after degradation shows that in both cases the MWD is of the recombination type, and calculation of the number of recombinations from the values of the number-average molecular weights before and after degradation shows that ~50% of the macromolecules which have undergone degradation recombine. This provides further proof that macromolecular recombination takes place. Experiments were also carried out in the absence of oxygen and with mixed solutions of polystyrene and polyisobutylene and of polystyrene and poly(methyl methacrylate) in toluene and benzene, in which thermal decomposition of the initiators took place. The initiators used were benzoyl peroxide and methyl- and ethyl-phenyltriazene, at concentrations of 2–10% of the weight of the polymer in the solution. These systems showed the formation of

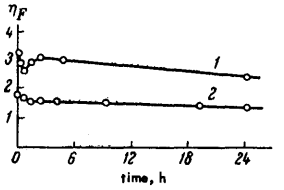


Fig. 9. Degradation of polystyrene under the influence of $CH_3^{\cdot}$ radicals[7]. Concentration of solution during degradation: 1) 4 g per 100 ml, 140°; 2) 2 g per 100 ml, 120°.

"hybrid" (*i.e.* of the block or graft type) polymers, which are evidently formed by macromolecular recombination of different macroradical fragments.

c. Kinetic-Chain Transfer to the Polymer with Subsequent Growth of a Side Chain

In bulk polymerisation, and also in solvents at high monomer concentrations, an increase in the rate of the process at high degrees of conversion is observed. An increase in the molecular weight of the product also occurs.

These phenomena are due to the increase in the viscosity of the medium, leading to a decrease in the rate constant of the rupture reaction due to recombination and disproportionation, since this depends on the rate of diffusion of the polymeric radicals to one another. Miyama[55] showed that the life-time of the polymer radicals increases in the same sense (see Fig. 10). Bresler *et al.*[56] showed by electron paramagnetic resonance in the photopolymerisation of vinyl acetate and methyl acrylate for degrees of conversion above 50–60%, that the concentration of macroradicals increases rapidly and at the end of the polymerisation process reaches 2×10^{-3} M for vinyl acetate and 0.5×10^{-3} M for methyl acrylate.

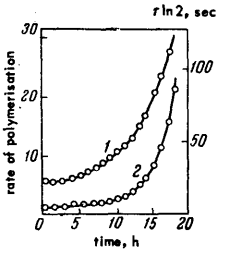


Fig. 10. Dependence of the rate of polymerisation (1) and the life-time of the polymer radicals (2) on the duration (extent) of polymerisation[55].

§ The part played by oxygen in degradation reactions depends to a considerable extent on its ability to form hydroperoxides at vulnerable points on the polymer molecule, *i.e.* tertiary carbon atoms in vinyl polymers and α-methylene groups in polydienes. Grassie considers that the hydroperoxides decompose with the formation of initiating radicals according to one of the following schemes:

$$\sim CH_2—CHX—CH_2—CHX \sim + O_2 \sim \rightarrow \sim CH_2—\underset{\displaystyle OOH}{\underset{|}{C}}X—CH_2—CHX \sim \rightarrow$$
$$\rightarrow \sim CH_2—\dot{C}X—CH_2—CHX \sim + \cdot OOH$$

or

$$\sim CH_2—\underset{\displaystyle O\cdot}{\overset{/}{C}}X—CH_2—CHX + \cdot OH.$$

Oxygen may also affect the course of a reaction by its ability to react with radicals:

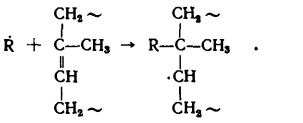
$$\sim CH_2—\dot{C}X—CH_2—CHX \sim + O_2 \rightarrow$$
$$\rightarrow \sim CH_2—\underset{\displaystyle O—O\cdot}{\underset{|}{C}}X—CH_2—CHX \sim$$

These oxygen-containing radicals have a much greater tendency to decompose than the radicals from which they were formed. An example is provided by the reactions in rubber initiated by light: in the absence of oxygen these lead to the formation of cross-linkages and in the presence of oxygen to degradation. The part played by oxygen has been discussed in detail by Grassie (Ref. 10, Chapter IV).

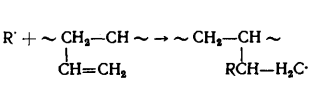
As free radicals accumulate in the polymerisation system and the concentration of the polymer increases at high degrees of polymerisation, the process of active-centre transfer to the polymer molecules with the subsequent growth of a side-chain plays an ever-increasing part. This reaction, which was described by Flory as early as 1937, is now widely used for the preparation of graft polymers. Two forms of cross-linkage formation are possible: (1) in vinyl polymerisation this reaction passes through a stage involving the abstraction of a hydrogen or halogen atom by free radicals:

$$R^{\cdot} + \sim CH_2{-}CHX \sim \rightarrow RH + \sim \dot{C}H{-}CHX \sim ,$$

where R· is a micro- or macro-radical; (2) in the case of the polymerisation of dienes, the reaction involves the abstraction of a hydrogen atom¶ or the addition of radicals to double bonds:



Kinetic-chain transfer to the polymer takes place particularly readily in the case of polymers of the 1,2-polybutadiene type with "outer" double bonds:



There are, however, data which indicate that the first type of chain transfer to the polymer also takes place for polydienes. The removal of an H atom is most probable for 1,4-polydienes. In all these cases, molecules with anomalously high molecular weights are formed.

If it is assumed that in a real polymerisation system the free radicals formed by decomposition of the initiator do not take a direct part in the reaction of active-centre transfer to the polymer, the rate of transfer to the polymer molecules $r_{tr,p}$, which is equal to the rate of formation of the side-chains in the polymeric molecules, is determined by Eqn. (1) (see above).

The experimental constant $k_{tr,p}$ is not always the constant for a definite reaction, since the polymer molecule may contain groups with different structures, reacting with the polymer radicals at different velocities. The constant is an "effective" constant. In general the primary radicals of the initiator do not act merely as initiators of the polymer chains. Their part in chain transfer to the polymer is shown by work on graft polymerisation (see below).

The absolute values of the constants for chain transfer *via* groups in the polymer molecules are usually much lower than those for transfer *via* the corresponding low-molecular-weight compounds. This is due to the fact that the inactive molecule → radical changes are associated with a change in the configuration (for example CH_4 is a tetrahedron and $CH_3^{\cdot}$ has a planar structure) and in the case of polymers this causes displacement of sections of the macromolecules. This also apparently explains the reduced reactivity of the inner double bonds of polydienes compared with that of the outer double bonds. This does not mean, however, that the transfer reaction to the polymer has a very low probability.

¶ Particularly that in the α-position with respect to a double bond.

Schulz and coworkers[57-59], in a study of the polymerisation of methyl methacrylate in the presence of low-molecular-weight poly(methyl methacrylate) prepared by a radical mechanism, found that the value of $k_{tr,p}$ decreases with increase in the molecular weight of the polymer added to the system. The authors attributed this to a difference in the rate of reaction of radicals with terminal groups (containing double bonds as a result of disproportionation) and with intermediate groups in the chain. The data obtained were used to calculate the constants for chain transfer *via* the terminal groups:

$$\left(\frac{k_{tr,p}}{k_p}\right)_{\text{terminal}} = 0.10 ,$$

where k_p is the rate constant for chain growth, and for chain transfer *via* the inner groups:

$$\left(\frac{k_{tr,p}}{k_p}\right)_{\text{inner}} = 2.2 \times 10^{-5}.$$

The fact that the terminal groups taking part in chain transfer are groups containing double bonds is confirmed by the marked decrease in the value of the ratio $k_{tr;p}/k_p$ for polymers obtained in the presence of chain carriers (butyl thioglycollate), *i.e.* containing no terminal groups with double bonds, and also by the fact that this ratio is independent of the nature of the initiator. If the added polymer contains no terminal double bond (for example, one obtained by polymerisation on metallic sodium or potassium), the value of $k_{tr,p}/k_p$ is independent of the molecular weight of the added polymer and has the value 2.2×10^{-5}. Recently, Henrici-Olive and Olive[60] used azobisisobutyronitrile labelled with ^{14}C for the polymerisation of styrene and determined the degree of conversion of the monomer and the average number of terminal groups (from the radioactivity of the polymer); they found that the resulting polystyrene is branched. They determined the ratio of the rate constants for the transfer reactions $R^{\cdot} + P \xrightarrow{k_{tr,p}} RH + P^{\cdot}$ and for initiation $R^{\cdot} + M \xrightarrow{k_{st}} RM^{\cdot}$, *i.e.* $K = k_{tr,p}/k_{st}$. For 50°, $K = 0.3 \pm 0.1$, which is fairly high. The authors derived an equation relating the constant K to the experimental values of Z (the number of terminal groups) and ψ (the percentage conversion). In the absence of the "gel effect", the equation has the form

$$\frac{1}{K-1}\ln(1 + K\psi - \psi) = -\frac{Z\ln(1-\psi)}{2Z-2} , \qquad (9)$$

from which it follows that K can be determined (1) by preparing a polymer with labelled initiator, and (2) measuring ψ and Z.

The average degree of grafting (ADG), *i.e.* the number of grafts per polymer molecule, is found from the equation

$$ADG = Z - 2 = \frac{-\frac{2}{K-1}\ln(1 + K\psi - \psi) - 2\ln(1-\psi)}{\frac{2}{K-1}\ln(1 + K\psi - \psi) + \ln(1-\psi)} , \qquad (10)$$

which follows from the previous equation.

The fact that the reaction of active-centre transfer to the polymer has a high probability is also indicated by its successful application for the preparation of graft polymers.

Smets[61,62] gives the following complete scheme for the reactions accompanying the ordinary mechanism of grafting.

On the one hand, normal polymerisation takes place:

$$\text{initiator} \xrightarrow{k_d} 2R^{\cdot}, \qquad \text{(I)}$$

$$R^{\cdot} + CH_2{=}CHB \xrightarrow{k_a} R{-}CH_2{-}\dot{C}HB, \qquad \text{(II)}$$

$$R{-}CH_2{-}\dot{C}HB + n\,CH_2{=}CHB \xrightarrow{k_p} R{-}(CH_2{-}CHB)_n{-}CH_2{-}\dot{C}HB. \qquad \text{(III)}$$

These processes are accompanied by active-centre transfer to the polymer dissolved in the monomer:

$$\left.\begin{array}{l}\dot{R} + \sim CH_2{-}CHA{-}CH_2{-}CHA \sim \rightarrow \\ RH + \sim CH_2{-}\dot{C}A{-}CH_2{-}CHA \sim \rightarrow\end{array}\right\}, \qquad \text{(IVa)}$$

$$\left.\begin{array}{l}R{-}(CH_2{-}CHB)_n{-}CH_2{-}\dot{C}HB + \sim CH_2{-}CHA \sim \rightarrow \\ R{-}(CH_2{-}CHB)_n{-}CH_2{-}CH_2B + \sim CH_2{-}\dot{C}A \sim \rightarrow\end{array}\right., \qquad \text{(IVb)}$$

and the formation of side-chains on the molecules both as a result of "growth";

$$\left.\begin{array}{l}\sim CH_2{-}CHA{-}CH_2{-}\dot{C}A{-}CH_2{-}CHA \sim + n\,CH_2{-}CHB \rightarrow \\ \rightarrow \sim CH_2{-}\underset{\underset{A}{|}}{C}\begin{array}{l}\diagup\, CH_2{-}CHB{-}CH_2{-}CHB \sim \\ \diagdown\, CH_2{-}CHA{-}CH_2{-}CHA \sim\end{array}\end{array}\right\}, \qquad \text{(Va)}$$

and as a result of recombination with normally growing radicals:

$$\left\{\begin{array}{l}\sim CH_2{-}\dot{C}A{-}CH_2{-}CHA \sim + \dot{C}HB{-}CH_2{-}(CHB{-}CH_2)_n \sim \rightarrow \\ \rightarrow \sim CH_2{-}\underset{\underset{A}{|}}{C}\begin{array}{l}\diagup\, CHB{-}CH_2{-}(CHB{-}CH_2)_n \sim \\ \diagdown\, CH_2{-}CHA{-}CH_2{-}CHA \sim .\end{array}\end{array}\right. \qquad \text{(VIa)}$$

If active-centre transfer takes place at the terminal group of the dissolved polymer, block-copolymers are formed according to the two analogous schemes

$$\left.\begin{array}{l}\sim CH_2{-}CHA{-}CH_2{-}\dot{C}HA + n\,CH_2{=}CHB \rightarrow \\ \rightarrow \sim CH_2{-}CHA{-}CH_2{-}CHA{-}CH_2{-}CHB \sim\end{array}\right\}, \qquad \text{(Vb)}$$

$$\left.\begin{array}{l}\sim CH_2{-}CHA{-}CH_2{-}\dot{C}HA + \dot{C}HB{-}CH_2 \sim \rightarrow \\ \rightarrow \sim CH_2{-}CHA{-}CH_2{-}CHA{-}CHB{-}CH_2{-}CHB{-}CH_2 \sim\end{array}\right\}. \qquad \text{(VIb)}$$

As Smets points out, it was previously assumed that only reaction (IVb) can lead to the formation of macroradicals, since primary radicals should react more readily with vinyl monomers than with the polymer molecule (IVa). This hypothesis was confirmed by the higher value of the activation energy for the chain transfer reaction, compared with the reaction of attachment to the monomer. It has now been proved, however, that reaction (IVa) takes place. In analogous fashion, Allen *et al.*[63] arrived, after detailed study, at an extremely complex reaction scheme for grafting (on rubber). Smets established that, in the polymerisation of methyl methacrylate in the presence of polystyrene, a large quantity of graft polymer is formed if the initiation is brought about by benzoyl peroxide (BP) and that, on the other hand, almost no graft polymer is formed if azobisisobutyronitrile (AIN) or t-butyl peroxide are used as initiator. An analogous result was observed by a number of workers for grafting, where in the presence of benzoyl peroxide the number of graft branches was about 100 times greater than that predicted by the theory of chain transfer to the polymer, but when AIN was used as initiator, no grafting was observed.

Thus the process of chain transfer to the polymer is usually accompanied by a whole series of secondary reactions, including the direct action of initiator radicals on the macromolecules. [It is for this reason that we consider (see the Introduction) that it is inappropriate to include the chain transfer reaction to the polymer among secondary reactions without describing its consequences more precisely.] An alternative suggestion is that the activity of the macroradicals formed from the same monomer may differ considerably, depending on the initiator radical, but this is unlikely. In particular, Allen *et al.*[63] have shown that in the preparation of graft polymers by this method, the initiator used in the polymerisation has a significant influence on the side-chains.

Finally, it should be noted that intramolecular active-centre transfer is possible when a terminal radical attacks a methylene group in the same molecule:

$$\sim CH_2{-}CH_2{-}CH_2 \rightarrow \sim \dot{C}H{-}CH_2{-}CH_2 \quad (CH_3{-}CH_2)$$

This process leads to the appearance of a large number of short side-chains in the case of high-pressure polyethylene.

d. Cross-Linking of Macromolecules in Linear Polymerisation

In polymerisation with "insufficient" monomer (high degrees of conversion) or with a relatively large quantity of macroradicals (in diene polymerisation), where a further source of the latter is provided by the "opening" of double bonds under the influence of temperature and initiators, and also in the ω-polymerisation considered below, etc., the macroradicals active "in the centre" will recombine in two ways (see Fig. 11), *i.e.* the appearance of ordinary branched molecules will be accompanied by "cross-linking" of the molecules by means of intermediate links. This type of reaction has been examined theoretically by Flory[64], Taylor and Tobolsky[65], Case[66], and others. Cross-linking of linear polymers has been observed experimentally by a number of workers. Thus Bardwell and Winkler[67] observed cross-linking of molecules of the butadiene–styrene copolymer latex when potassium persulphate was added; the rate of cross-linking was proportional to the persulphate concentration. Baker[68] cross-linked pure polyundecanoates, containing no unsaturated bonds, and monomers with more than two functional groups, containing methylene hydrogen atoms labile towards removal by radicals; these hydrogen atoms can be removed fairly readily. Bryant *et al.*[69] showed that commercial polyethylene prepared by free-radical polymerisation often contains a small quantity (~1.5 vol.%) of microgel particles with an effective molecular weight of 10^{14}, and also a considerable quantity of highly branched macromolecules. Moore and Peck[70] made an electron microscope study of high-pressure polyethylene and observed a considerable number of molecules with $M \sim 40 \times 10^6$, which had a marked influence on the MWD. Flory[71] and Fox and Gratch[72] showed that these particles can be formed only by the recombination or cross-linking of macromolecules but not as a result of ordinary chain branching. The formation of microgel particles with a diameter of ~0.1 μ was also established by Baker. Some polymers, for example, poly(vinyl acetate), form only highly branched molecules

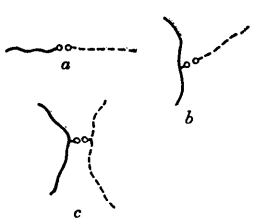


Fig. 11. The three types of macroradical recombination.

in radical polymerisation at 100°. In radical polymerisation of dienes, cross-linking of macromolecules is often observed at room temperature and above. A reaction of the type involving cross-linking of "formed" macromolecules, apparently accompanied by inter-chain exchange, was also studied by Bresler *et al.*[7] Mixed solutions of the polymers (polystyrene and polyisobutylene) with concentrations of 1–2% were kept in the presence of initiators at 80°–100°, depending on the initiator. The action of the free radicals of the initiator (methylphenyltriazene, benzoyl peroxide, etc.) led to the formation of macroradicals, which reacted partially with one another. The reaction of macroradicals of different chemical character gave "hybrid" polymers (*i.e.* of the block and graft type), which were then detected by specific sensitive methods (u.v. absorption spectra, etc.). It was found that the formation of "hybrid" polymers did in fact take place, although their yield did not exceed several per cent of the total quantity of macromolecules in the solution. It was possible to estimate the intensity of reactions of types (V) and (VI) (see above) in systems where styrene was polymerised in the presence of polyisobutylene. In these systems also, however, the yield of "hybrid" polymer for the polyisobutylene–polystyrene pair did not exceed 5%, indicating that these reactions are not rapid, apparently due to steric hindrance in the reactions between the macroradicals of polyisobutylene and polystyrene on the one hand, and the low activity of the polyisobutylene macroradicals in styrene polymerisation on the other†.

The polymerisation of styrene was also carried out in the presence of polybutadiene (5%) with ~ 20% of 1,2-linkages. The polymerisation was carried out under the influence of azobisisobutyronitrile (0.1 g per 100 ml), which has a low activity in the removal of an H atom but reacts readily with "outer" double bonds. It was established that as a result of inter-chain reaction, ~ 25% of the rubber dissolved in the monomer reacted with polystyrene at 80° and ~ 50% reacted at 120°. In both cases more than half of the resulting hybrid polymer had a gel structure, indicating high intensity of cross-linking at the double bonds of the 1,2-linked groups. The grafting of styrene on polybutadiene by secondary reactions was also carried out by Uemura *et al.*[73] with azobisisobutyronitrile and benzoyl peroxide. In the presence of the former, the styrene polymerised more rapidly but the efficiency of grafting was lower.

Recently, Miller[74] made a kinetic analysis of the cross-linking of saturated polymers by a radical mechanism in the condensed phase and verified the resulting relationships experimentally. Miller suggests that the following reactions take place:

(I) $I \xrightarrow{k_1} R^{\cdot}+R^{\cdot}$ — decomposition of initiator,

(II) $R^{\cdot}+PH \xrightarrow{k_2} RH+P^{\cdot}$ — formation of polymer radicals by H atom abstraction by the initiator radical,

(III) $R^{\cdot}+P^{\cdot} \xrightarrow{k_3} RP$

(IV) $R^{\cdot}+R^{\cdot} \xrightarrow{k_4} RR$

(V) $P^{\cdot}+P^{\cdot} \xrightarrow{k_5} PP$

— recombination of radicals of different type with one another.

Assuming further that the polymer radicals are not removed by disproportionation and do not undergo degradation, that $k_3 = \sqrt{k_4 k_5}$, and that the whole system of reactions reaches a steady state, Miller obtained the following expression for the cross-linking coefficient C (the number of cross-linkages per molecule of initiator decomposed):

$$C = \{(k_4 k_1 [I])^{1/2}/k_2[PH] + 1\}^{-2}. \quad (11)$$

At constant temperature and [PH] = const, this equation reduces to the simpler form

$$C = (K[I]^{1/2} + 1)^{-2}, \text{ where } K = \{(k_4 k_1)/k_2[PH]\} = \text{const}$$

for a given polymer–initiator system. Obviously, $C \to C_{max}$ as $K[I]^{1/2} \to 0$. This is attained (a) at low values of k_1, (b) at low values of (I), and (c) at high values of k_2. (For polyethylene, for example, $C \sim 1$, due to the high value of k_2.)

The concentration of cross-linkages for any degree of decomposition of the initiator is found by integrating (11). These kinetic expressions were verified by Miller by experiments on the cross-linking of polydimethylsiloxane with benzoyl peroxide at 125° and with dicumyl peroxide at 170°.

On the basis of his experimental and theoretical studies, Miller established that ionising irradiation is much more effective in cross-linking [since of reactions (III), (IV), and (V) above, only (V) leads to cross-linking; (III) and (IV) only decrease the number of free radicals formed].

The formation of cross-linkages in polyethylene by the action of peroxides and irradiation was studied by Rado and Lazar[75–77], who calculated the number of cross-linkages from the change in the solubility of the polyethylene in boiling CCl_4, using the relationships between solubility and degree of cross-linking for polyethylene[78]. The experiments were carried out in the range 70°–90°, the quantity of peroxide added to the polymer being 0.01–0.5 mole kg^{-1}. The specimens were heated for 10^4–10^5 sec. A kinetic scheme of radical reactions was established, and, in particular, it was shown that the decomposition of the peroxide in polyethylene is a chain process, initiated by benzoate radicals produced by thermal decomposition of the peroxide. The kinetic scheme proposed by the authors for the formation of cross-linkages is identical with that given above. Increase in temperature decreased the yield of cross-linkages, since the considerable difference in the energies of activation, initiation, and transfer at higher temperatures causes the reaction of polymer radicals with primary radicals to predominate. Despite the fact that the peroxide decomposes by a chain mechanism, Rado and Lazar's experimental data correspond fairly accurately with the kinetic equation derived by Miller for the dependence of the number of cross-linkages on the peroxide concentration, if it is assumed that monomolecular decomposition of the peroxide takes place:

$$\left(\frac{[BP]}{[P-P]}\right)^{0.5} = K[BP]^{0.5} + 1,$$

where [BP] and [P–P] are the concentrations of benzoyl peroxide and cross-linkages respectively, and K is a constant (at T = const).

Finally, the so-called ω-polymerisation in fact results from an intense structure-formation process which is preceded and accompanied by processes of chain transfer to the polymer and chain rupture at points corresponding to fluctuations in the concentration of polymer molecules and free radicals[79–83]. Thus Pravednikov and Medvedev[80,81] showed by labelling the "nucleus" with a radioactive tracer that, for example, the ω-polymerisation of chloroprene is accompanied by continuous rupture of the macromolecules

† The styrene was polymerised in the presence of methylphenyltriazene and benzoyl peroxide, which cause intense degradation of polyisobutylene.

of the network (due to osmotic overstrain at points of high polymer concentration) and their cross-linking by a radical mechanism, *i.e.* in our terminology, intense inter-chain exchange takes place in ω-polymerisation.

III. METHODS OF RECORDING AND STUDYING SECONDARY REACTIONS

a. Influence of Secondary Reactions on Molecular Weight Distributions

Let us examine the influence of each of the above secondary reactions on the molecular weight distributions.

Degradation. By definition, this reaction involves the rupture of single skeletal bonds of the macromolecules and obviously leads to a decrease in molecular weight. Montroll[84] and Tuckett[85] showed that with highly disordered chain rupture, irrespective of the original distribution, an equilibrium length distribution of the Kuhn–Schulz–Flory type,

$$W_x = xP^{x-1}(1-P)^2, \qquad (12)$$

is established after some time. This expression reduces to the form

$$W_x = \beta^2 x e^{-\beta x}; \qquad (13)$$

where W_x is the weight fraction of chains consisting of x links, P the probability that a given bond between two structural units remains unaffected, and $\beta = 1/\sqrt{x_n}$. Expression (12) is illustrated by Fig. 12. Thus if the initial average molecular weights and MWD are known and if the latter differed from an MWD of type (12), the decrease in average molecular weight with time and the attainment of an MWD of the Kuhn–Schulz–Flory type are a direct consequence of the disordered degradation.

Inter-chain exchange. Inter-chain exchange in radical systems, *i.e.* the recombination of macroradical "fragments", their "growth" at the expense of monomer, etc. in addition to chain degradation under the influence of radicals leads to a reduction in the rate at which the average molecular weights decrease with time, compared with that for "pure" degradation. Moreover, a quasi-steady state may be established, as has been observed by Mesrobian and Tobolsky, Rossi, and others. The influence of inter-chain exchange on the molecular weight of the polymer can be illustrated by the following example. In one of our experiments on the degradation of polystyrene in benzene solutions in the presence of methylphenyltriazene, we found the MWD of the specimen before and after degradation (both were of the recombination type[1]) and from the MWD we calculated the average molecular weights, the values being 5.06×10^5 and 3.6×10^5 respectively. Let us assume that originally there were N macromolecules with a number-average molecular weight M. Of these, n molecules underwent degradation, with the production of $2n$ chains (of which n were active) with an average molecular weight of $M/2$. If all n active chains recombine with one another, the average molecular weight after degradation $\overline{M}'_n$ will be given by

$$\overline{M}'_n = \frac{(N-n)M + nM/2 + n/2\,M}{(N-n) + n + n/2} = \frac{NM}{N + n/2}. \qquad (14)$$

If, however, all the macroradical fragments disproportionate, combine with initiator radicals, etc., *i.e.* if they are deactivated in any way other than by recombination with one another, we have

$$\overline{M}''_n = \frac{(N-n)M + 2n \times M/2}{(N-n) + 2n} = \frac{NM}{N+n}. \qquad (15)$$

The original number-average molecular weight of polystyrene in this experiment was $M_n = M = 5.06 \times 10^5$ and that after degradation was $\overline{M}_n = 3.6 \times 10^5$, *i.e.* $M_{n\,\text{init}}/\overline{M}_n = 1.4$. In case (1), $M_{\text{init}}/M' = 1 + n/2N$ and in case (2), $M_{\text{init}}/M'' = 1 + n/N$. The phenomenon is thus intermediate between cases (1) and (2), *i.e.* $1 + n/2N < 1.4 < 1 + n/N$, from which $0.8\,N > n > 0.4\,N$, *i.e.* n was about $0.6\,N$.

Assuming that $n = 0.6\,N$, it is possible to estimate the number of macroradical "fragment" recombinations which have taken place. If no recombination of radicals with one another took place, we should have, in accordance with (15),

$$\overline{M}'_{nd} = \frac{NM_{\text{init}}}{N + 0.6N} = \frac{5.06 \times 10^5}{1.6N} = 3.13 \times 10^5.$$

Experimentally, however, $\overline{M}_{nd} = 3.6 \times 10^5 > M'_{nd}$, *i.e.* recombination has taken place. Assuming that the number of recombinations was xN, we can write

$$\frac{0.4NM + 0.6N \times M/2 + (0.6-x)NM/2 + xNM}{0.4N + 0.6N + (0.6-x)N + xN} = 3.6 \times 10^5.$$

Cancelling N and substituting $M = M_{n\,\text{init}} = 5.06 \times 10^5$, we have

$$\frac{1 + 0.5\,x}{1.6} = \frac{3.6 \times 10^5}{5.06 \times 10^5} = 0.71,$$

from which

$$x = \frac{(1.6 \times 0.71) - 1}{0.5} = \frac{1.14 - 1}{0.5} = 0.28,$$

i.e. the number of recombinations was ~0.3 N. Thus the probability of inter-chain reaction was about $x/n = 0.3/0.6 = 50\%$.

It should be noted, however, that in this experiment we studied the degradation of polystyrene, whose macroradicals have a particularly strong tendency to undergo recombination. Moreover, the calculation is only approximate, since we do not make direct allowance for the cross-linking of "centres" with "ends" and of "centres" with "centres", assuming that these processes, being bimolecular, are less probable than simple degradation. In addition, if

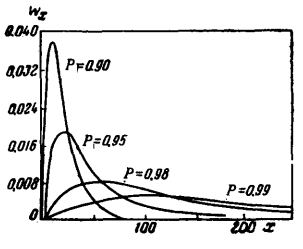


Fig. 12. Form of the Kuhn–Schulz–Flory equilibrium distribution (see text for symbols).

some "growth" of the fragments took place at the expense of monomer formed during degradation, *i.e.* exchange at the expense of monomer, this is mathematically equivalent to the above mechanism, which assumes simple recombination of macroradical "fragments".

Kinetic-chain transfer to the polymer. This process produces branched molecules, which, as Beasley[2] has shown, cause broadening of the MWD of the product and the appearance of high-molecular-weight "tails" on the distribution curve. The MWD remains unimodal, but since the longer the chain, the greater the probability that it will branch again, the MWD shows marked asymmetry (the ratio $\overline{M}_w:\overline{M}_n \to \infty$ with decrease in the most probable molecular weight $\overline{M}_{max}$). The degree of branching can be expressed in terms of the parameter $\beta = k_{transfer}[P]/ak_g[M]$, where $k_{transfer}$ is the constant for transfer to the polymer, [P] the polymer concentration, $1/a$ the average number of monomeric units in the growing chain (main or lateral), k_g the rate constant for chain growth, and $[M]$ the concentration of monomer. The weight fraction of polymer with X monomeric units in the chain (including all degrees of branching) is given by the expression

$$W(X)dX = \frac{(1-\beta)(aX)\,d(aX)}{[1+\beta aX]^{(1+1/\beta)}}. \qquad (16)$$

The form of this distribution function for different values of β is shown in Fig. 13.

Cross-linking of macromolecules. When the MWD is already established (for example at high degrees of conversion) in polymerisation, this process leads to characteristic changes in the MWD, which reduce to the form[6]

$$q_n(M) = \sum_{k=0}^{\infty} p_k \frac{\alpha^{k+1}}{\Gamma(k+1)} M^k e^{-\alpha M}, \qquad (17)$$

where $\alpha = 1/\overline{M}_n$, p_k represents "weighting" coefficients, and k is the number of side-chains per macromolecule. When $p_k = 1$, this distribution is equivalent to (13)‡. The coefficients p_k take account of the distribution of doublets, triplets, etc., *i.e.* the increase in the width of the MWD due to cross-linking of existing macromolecules. Under certain conditions this distribution may prove to be equivalent to Beasley's distribution[2]. In the case of polydienes, where branching during polymerisation takes place as a result of chain transfer to the polymer, account is already taken of this process in the differential form of the MWD [Eqn. (16)]. In the polynomial of type (17) for this case ($p_k = 1$) the numerical fractions of doublets, triplets, etc. (more accurately, species with $1, 2, \ldots k$ side-chains) decrease successively [thanks to the factor $\alpha^{k+1}/\Gamma(k+1)$] and although the number-average molecular weights of the fractions are in simple ratios of the type $1:2:\ldots:k$, the distribution as a whole remains unimodal (see Fig. 14). When secondary reactions of the type under consideration take place (*i.e.* cross-linking of formed molecules with an established MWD), the number of fractions of doublets, triplets, etc. may be of the same order of magnitude (allowance is made for this by the coefficients p_k) as the number of linear (not cross-linked) macromolecules, the major fraction of which was formed at lower degrees of conversion. In this case the distribution maximum may be displaced towards higher values of M, but the *separation* of the maxima, of the type represented in Fig. 15, may be obtained only if each "k-th" fraction (17) corresponds to *its own* value of $\alpha = \alpha_k$. When α is constant, the polynomial (17) may have only one maximum, as can be seen by taking $e^{-\alpha M}$ outside the summation sign. The sum is now a monotonically increasing function of M, and multiplication of the latter by the monotonically decreasing $e^{-\alpha M}$ should give a bell-shaped curve so long as all the p_k are real and ≥ 0 ("Dodge's rule" of higher algebra).

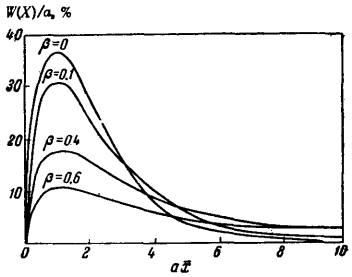


Fig. 13. Form of the Beasley weight distribution function for different degrees of branching produced as a result of chain transfer to the polymer[2].

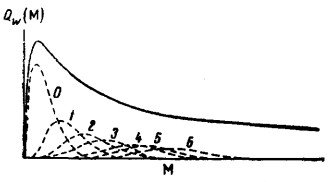


Fig. 14. Weight distribution function for a branched polymer[86]. The broken lines represent the partial distributions for fractions with different numbers of side chains per macromolecule (indicated by the numerals).

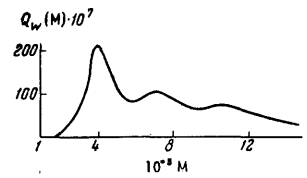


Fig. 15. Weight distribution function for poly(butyl phenyl methacrylate) obtained with stepwise increase in temperature[3].

‡ With allowance for the fact that (16) describes a numerical distribution function with respect to molecular weights and (13) a weight distribution function with respect to degrees of polymerisation[86].

The situation is different if the values of α_k differ; in this case even simple linear combinations of Schulz functions *of the same order of magnitude* may be given a multimodal curve. A large number of values of α may result from the succession or coexistence of *several* polymerisation mechanisms.

Under the conditions of a microheterogeneous medium at high values of ψ, polymerisation at different rates in different phases should initiate a multimodal distribution. In the case under discussion the cause of the multimodal character was most probably the two sudden increases in temperature.

Unlike the distributions $q_n(M)$, the corresponding distributions of $[\eta]$§ or of sedimentation coefficients *may* be resolved into separate maxima even when α = const. This can be seen from the following fundamental theorem of statistics:

$$q_n(M)\,dM = q_n(X)\,dX, \qquad (18)$$

where X is any single-single-valued function of M.

Assuming that $[\eta] = KM^{\beta}$ and substituting this in $q_n([\eta])$, corresponding to the distribution (17), we see that now the sum contains *variable* exponents of the form $\alpha + \beta_k$, since β depends on the degree of branching.

Thus, for example, analysis in the ultracentrifuge is more reliable than direct determination of $q_n(M)$, for in the first case we obtain the distribution of the sedimentation coefficients with respect to weight, which are sensitive to branching. It should again be emphasised that simply multimodal MWD may be produced in a number of cases without any secondary cross-linking reaction. This is the case with the superposition of several independent polymerisation mechanisms, each characterised by its own set of rate constants. Usually the presence of several maxima is due to a large number of polymerisation loci, *i.e.* the multimodal character should result from the heterogeneity of the polymerisation process.

b. Study of Secondary Reactions in Model Systems

The advantage of the MWD method is its general character and the fact that it can be used directly to study the products obtained in polymerisation. The fact that we are studying secondary reactions, which in ordinary polymerisation processes are "masked" by the main processes, however, means that this method is not always convenient. A more convenient method for studying secondary reactions is that involving model systems, in which these reactions take place in a more or less pure form.

The degradation of polymer chains in solutions at moderate temperatures (~ 100°) under the influence of small quantities of initiators causing degradation has been examined above. Particularly valuable results are obtained when the study of degradation gives not only one of the average molecular weights (or viscosity) before and after the reaction, but also the MWD (see above).

Inter-chain exchange may be detected directly by heating a solution of two fractions (differing considerably in molecular weight) of the same polymer in the presence of an agent causing degradation (or without it, if we are dealing with polycondensation products with active ends), with determination of the MWD before and after the reaction.

§ $[\eta]$ is the intrinsic viscosity.

Particularly interesting results may be obtained if one of the fractions is labelled with radioactive atoms. As a result of inter-chain exchange, a fraction of macromolecules with intermediate molecular weight should appear in the mixture, with a corresponding decrease in the proportions of macromolecules with extreme molecular weight values. A modification of this method involves analogous manipulations with a mixed solution of two different polymers. In this case inter-chain exchange and recombination by the centres (cross-linkages) give "hybrid" polymers of the block and graft type, the yield of which in these systems characterises the probability of inter-chain reactions. Although in principle this method may be quantitative data, detailed study of the reation product is difficult, since it contains both homopolymers (usually in the polydisperse state after the reaction, even if fractions were taken initially) and the hybrid polymer, which is polydisperse with respect to both composition and molecular weight.

For a quantitative study of inter-chain exchange, the most convenient method is by polymerisation of inactive monomer in the presence of "monodisperse" radioactive polymer of the same type, to a 100% degree of conversion, followed by fractionation and analysis of the distribution of radioactivity in the fractions. (The radioactive tracer technique can also be used in the experiment with two fractions, of the type considered above.)

Kinetic-chain transfer to an intermediate link of the polymer may be studied either by preparing graft polymers by polymerisation in the presence of an existing polymer of a different type or by establishing the deviation from the normal values (for linear polymers of this type) of the constants in the Mark–Kuhn–Hauwink relationship[87].

Henrici's method is particularly convenient for this purpose (see above).

The MWD method is the most reliable for establishing cross-linking of molecules. For this purpose, however, it is also possible to use the method of "hybrid polymer" preparation, used in the study of inter-chain exchange. It is also possible to use fractionation of the reaction product from a model system (or polymerisation boiler) with subsequent determination of the deviations from the relationship of type (13) for the corresponding linear polymer.

In the study of secondary reations during diene polymerisation, in addition to the MWD method and the methods used to study "branched" vinyl polymerisation, it is possible to use infrared analysis (to record the disappearance of double bonds) and also sol–gel analysis.

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CHEMISTRY OF SOME INORGANIC NITROGEN FLUORIDES

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I. INTRODUCTION

In recent years there has been an increasing number of studies outside the Soviet Union of a new class of compounds characterised by the presence of the NF or NF_2 group. In the USA interest in compounds containing the NF_2 group is due to their use in rocket fuels[1]. The published studies relate mainly to the simplest gaseous nitrogen fluorides, most of which are reagents for the preparation of compounds containing the NF_2 group. These fluorides include tetrafluorohydrazine, the two difluorodiazine isomers, difluoramine, chlorodifluoramine, and fluorine azide.

This review is concerned with the chemistry of these nitrogen fluorides. The chapter on the structure of the nitrogen trifluoride molecule does not embrace all the literature data, but is given solely to provide a more correct understanding of the properties of the nitrogen fluorides.

II. STRUCTURE OF THE NITROGEN TRIFLUORIDE MOLECULE

The geometry of the nitrogen trifluoride molecule has been studied by electron diffraction[2,3] and by microwave spectroscopy[4]; the molecular dimensions have also been obtained from infrared spectroscopy and dipole moment measurements.

The nitrogen trifluoride molecule is an equilateral triangular pyramid in which the apex angle is 102°, N–F distance 1.37 Å, and F...F distance 2.14 Å.

The experimental N–F distance is in good agreement with the interatomic distance calculated from the Schomaker–Stevenson formula[5]:

$$r_{A-B} = r_A + r_B - 0.09(X_A - X_B),$$

where r_A and r_B are the covalent radii of atoms A and B, and X_A and X_B are the corresponding electronegativities. Here $r_F = 0.72$ Å, $r_N = 0.74$ Å, and $X_F - X_N = 0.95$,[6] and hence $r_{A-B} = 1.38$ Å. The above formula takes the ionic nature of the bond into account, and the agreement between the experimental and calculated distances demonstrates that the N–F bond is partially ionic.

The mean energy of the N–F bond, calculated from the heat of formation of NF_3 ($\Delta H = -29.7 \pm 1.8$ kcal mole^{-1} [7]), is 66.3 kcal mole^{-1}. The dissociation energy of the first bond D_{N-F} is determined[8–10] from the thermochemical equation

$$\Delta H_{NF_3} = \Delta H_{NF_2} + \Delta H_F - D_{N-F},$$

where $\Delta H_{NF_2} = 9.8 \pm 2.1$ kcal mole^{-1} (see Section III) and $\Delta H_F = 18.9 \pm 0.5$ kcal mole^{-1};[11] hence $D_{N-F} = 58.4 \pm 4.4$ kcal mole^{-1}. Assuming that the dissociation energies of the other two N–F bonds are the same, these will be 70.5 ± 1.6 kcal mole^{-1}.

Thus, unlike ammonia and many other inorganic substances[12], the energy of dissociation of the first bond in the NF_3 molecule is less than that of succeeding bonds.

Reese and Dibeler[13] recorded the mass spectrum of nitrogen trifluoride, determined the appearance potential of the ions NF_2^+ and NF^+, and calculated the ionisation potentials of the radicals NF_2 and NF. The appearance potential $A \geqslant I + D_{bond}$, where I is the ionisation potential and D_{bond} is the bond energy. The ionisation potentials, calculated from Reese and Dibeler's data using the above values for the N–F bond energies in nitrogen trifluoride and the experimental results of Herron and Dibeler[10], are $I_{NF_2} = 11.9 \pm 0.2$ eV and $I_{NF} = 12.4 \pm 0.3$ eV.

Ramaswamy determined the dielectric constant of NF_3 at -80°, -33°, 25°, and 95°, and calculated the dipole moment to be $\mu = 0.21$ D.[14,15] This low value is surprising (*cf.* the dipole moment of ammonia, which is 1.46 D). Almost all those who have studied the structure of the nitrogen trifluoride molecule have attempted some explanation of this low value, but despite the attempts made[16,17], there is no satisfactory quantitative explanation. The qualitative explanation[2,4,18–20] is that the moment due to the N–F bonds is counteracted by a moment, which must be of opposite sign, produced by the free electrons of N and F because of *sp* hybridisation.

The infrared spectrum of nitrogen trifluoride[21–23] contains four main frequencies: 907 cm^{-1}, $\nu_3(E)$, the doubly degenerate stretching frequency; 1031 cm^{-1}, $\nu_1(A_1)$, the fully symmetrical stretching frequency; 642 cm^{-1}, $\nu_2(A_1)$, the fully symmetrical deformation frequency; and 497 cm^{-1}, $\nu_4(E)$, the doubly degenerate deformation frequency.

The light absorption of nitrogen trifluoride commences at a wavelength < 1800 Å.[24] There are no absorption lines

or bands in the ultraviolet; the whole electronic spectrum appears continuous. An attempt was made[24] to find the absorption coefficient α as a function of the wavelength λ, with the expectation of detecting a discrete spectrum from the nature of the $\alpha-\lambda$ curve but α increases smoothly with decreasing λ. There is intense absorption at 960 Å, which is thought[24] to correspond with the energy of ionisation of NF_3 (934 Å).

III. TETRAFLUOROHYDRAZINE

Tetrafluorohydrazine N_2F_4 was first obtained in 1958 by Colburn and Kennedy[25] from nitrogen trifluoride, and caused great interest among chemists; within two years of its first preparation five different methods for its production had been described.

In Septemper 1960 the Stauffer Chemical Co. (USA) reported its industrial production by conversion of nitrogen trifluoride over carbon[26]. Most of the methods are variations of Colburn's original preparation.

1. Methods for the Preparation of Tetrafluorohydrazine

Colburn and Kennedy[25] obtained tetrafluorohydrazine by thermal conversion of nitrogen trifluoride over stainless steel, copper, arsenic, antimony, or bismuth:

$$NF_3 + M \rightarrow N_2F_4 + MF_n .$$

The reaction was carried out in a flow reactor over copper turnings at 375° with a contact time of 13 min; the degree of conversion of the NF_3 was 42–62%, and the yield of tetrafluorohydrazine was 62–71% based on reacted NF_3. During the reaction a film of copper fluoride is formed, and this hinders the establishment of a steady-state process[27]. The preparative conditions depend on the metal used, *e.g.* a temperature of 250°–300° is used when arsenic is employed[28].

Modifications of Colburn's method are the preparation of tetrafluorohydrazine by thermal conversion of NF_3 over liquid mercury[27] or over carbon[26].

Dresdner *et al.*[27] found that nitrogen trifluoride reacts readily with mercury at optimum temperatures of 320°–330° to form tetrafluorohydrazine, using a flow rate of NF_3 of 40 ml min^{-1}, with the gas bubbling through the liquid mercury for 30–60 sec; the degree of conversion of NF_3 is 72%, and the yield of tetrafluorohydrazine based on reacted NF_3 is 60%†. Water and oxygen-containing substances must be absent.

The method which has attained industrial use is the conversion of NF_3 over carbon[26]. The NF_3 is contacted with a fluidised layer of carbon at 400° ± 10° at a rate of flow of 14.9 ml sec^{-1}, with a time of contact of several seconds. The tetrafluorohydrazine is obtained in 75% yield with 75% conversion of the NF_3. Hexafluoroethane (b.p. -76°), nitrogen trifluoride, and carbon tetrafluoride are also obtained.

Johnson's method for the isolation of tetrafluorohydrazine[29] is based on the differing solubilities of the reaction products in various solvents (chloroform, chlorobenzene, benzene, cyclohexane, or methanol).

† The reported formation in the reaction of small quantities of the active isomer of difluorodiazine is apparently incorrect.

Frazer[30] obtained tetrafluorohydrazine together with difluorodiazine by subjecting nitrogen trifluoride to an electrical discharge in the presence of mercury vapour, using a discharge potential of 2900–3100 V and 1–4 mm Hg pressure. The maximum degree of conversion of nitrogen trifluoride was 16%. The reaction products are tetrafluorohydrazine (50–60% yield based on reacted NF_3), difluorodiazine (12–16% yield), mercury fluoride, and nitrogen.

A process for the preparation of tetrafluorohydrazine based on the reaction

$$2NF_3 + NO = N_2F_4 + 2FNO ,$$

has been proposed[31]. The reaction is carried out at 150°–800°, with contact times between 0.01 sec and 15 min and NF_3 : NO molar ratios of 0.5–2.

The above are the only methods for the production of tetrafluorohydrazine based on the conversion of nitrogen trifluoride.

The presence of nitrogen in the reaction products indicates that the reaction involves the combination of one or more fluorine atoms of the nitrogen trifluoride molecule with the heterogeneous reagent used. In the presence of a heterogeneous reagent the conversion of nitrogen trifluoride comprises three parallel reactions:

$$NF_3 + M \rightarrow N_2F_4 + MF_n,$$
$$NF_3 + M \rightarrow N_2F_2 + MF_n,$$
$$NF_3 + M \rightarrow N_2 + MF_n .$$

The difluorodiazine formed is decomposed by heat or reacts with M, so that under the conditions of the thermal reaction difluorodiazine is effectively absent from the reaction products. When preparing tetrafluorohydrazine by the discharge method, however, the residence time of the gas in the reaction zone is small, conditions are less favourable for the decomposition of difluorodiazine, and its yield is consequently increased.

Tetrafluorohydrazine can be obtained in low yield by the fluorination of ammonia. The homogeneous gas-phase reaction between fluorine and ammonia was studied by Ruff[32]. The main reaction is

$$3F_2 + 2NH_3 = N_2 + 6HF ,$$

but the side-reaction

$$3F_2 + 4NH_3 = NF_3 + 3NH_4F ,$$

was also observed. The yield of nitrogen trifluoride did not exceed 6% based on reacted fluorine. Ruff showed the presence of other nitrogen fluorides, but these were not isolated.

Unlike Ruff, Morrow[33-35] used a copper packing in the reactor, enabling the reaction to be effected under milder conditions (18°). The yield of products depended primarily on the relative amounts of fluorine, ammonia, and nitrogen used, and also on the method of packing the reactor and the quality of the packing. With molar ratios $NH_3 : F_2 : N_2$ = = 1.5–2 : 1.5, the maximum yields were tetrafluorohydrazine 11% and nitrogen trifluoride 24% (based on reacted fluorine).

Cleaver has proposed[36] an electrochemical method for the production of nitrogen fluorides, including tetrafluorohydrazine, which is similar to the usual reactions for preparing nitrogen trifluoride by electrolysis, but with various fluorides (BF_3, PF_5, HF) added to the ammonium hydrogen fluoride electrolyte. The gaseous electrolysis products,

TABLE 1. Physical constants of nitrogen fluorides.

Substance	Mol. wt.	$B.p.$, °C	$M.p.$, °C	Vapour pressure, mm Hg	Heat of vaporisation, kcal mole^{-1}	Trouton's constant	Critical conditions: t, °C	Critical conditions: P, atm	Density, g cm^{-3}	Standard enthalpy of formation, kcal mole^{-1}
Nitrogen trifluoride NF_3	71	−129	−208.5	$\log P = 4.27264 - \frac{613.330}{T}$	2.769	19.94	−40.90	44.72	$d = 2.103 - 3.294 \cdot 10^{-3} T - 4.675 \cdot 10^{-6} T^2$	−29.7±1.8
Tetrafluorohydrazine N_2F_4	104	−73 −74	about −162°	$\log P = -\frac{862.9}{T} + 7.2163$[41a]	3.170	—	36 37.5	77^{25} 54^{37}	1.5 at −100°	−2±2.5
Difluoramine NF_2H	53	−23	-131^{28} -116^{61}	$\log P = -\frac{1298}{T} + 8.072$	5.940	23.7	130	93	$d = 1.424 - 0.00202t$ $d_{-23} = 1.378$	
Chlorodifluoroamine NF_2Cl	87	−62	between −183 and −196	$\log P = -\frac{950}{T} + 7.478$	4.350	— 21.0		—	—	—
Fluorine azide FN_3	61	approx. −82	approx. −154	—	—	—	—	—	—	—
trans-Difluorodiazine N_2F_2	66	−111.4	−172	$\log P = -\frac{742.3}{T} + 7.470$	3.400		−13	55	—	—
Active difluorodiazine N_2F_2	66	−105.7	below −195	$\log P = -\frac{803.0}{T} + 7.675$	3.670		−1	70	—	+25.3±2.0

* There are also data represented by the equations: $\log P = -\frac{692}{T} + 6.33$ [25] and $\log P = 6.9643 - \frac{811}{T}$. [37]

freed from hydrogen fluoride, contain nitrogen trifluoride (90 mole %), tetrafluorohydrazine (> 4%) and difluorodiazine (> 5%).

Tetrafluorohydrazine has been considered in the USA as an oxidant for rocket fuels[37,38]. It is produced in the USA in two grades by the reaction of nitrogen trifluoride with carbon, a technical grade containing 96% N_2F_4, and 99% N_2F_4. Tetrafluorohydrazine in 1.4 kg amounts is transported in steel cylinders under 7 atm pressure[39].

In 1961 the price of tetrafluorohydrazine in the USA was $200 per kilogramme, but it was considered possible that this could be reduced to the level of prices for fluorine[37].

2. Physical Properties of Tetrafluorohydrazine

Tetrafluorohydrazine is a colourless substance with a characteristic odour resembling that of fluorine‡; its physical properties are given in Table 1. Its heat of formation was determined by Armstrong[40] by the reaction $3N_2F_4 + 4NH_3 = 12HF + 5N_2$. Its infrared frequencies are given in Table 2.[41]

The mass-spectrum of tetrafluorohydrazine[42] consists mainly of the ions NF_2^+ and NF^+. Its nuclear magnetic resonance spectrum has been determined[25].

The structure of the tetrafluorohydrazine molecule has not been fully elucidated. Assuming that the N–F interatomic distances are the same as in nitrogen trifluoride and the N–N distance is the same as in hydrazine, Lide and Mann[43] found that the F–N–F angle is 108°, the N–N–F angle 104°, and the angle of rotation of the NF_2 groups 65°; it was assumed that tetrafluorohydrazine, like hydrazine, has the *cis*-structure.

The dissociation energy of the N–N bond in tetrafluorohydrazine is equal to the heat of the reversible process

TABLE 2. Infrared frequencies of the nitrogen fluorides.

Compound	Lines in the spectrum
Nitrogen trifluoride NF_3	very strong line at 907 cm^{-1} strong line at 1031 cm^{-1} lines of medium intensity at 1809 and 1929 cm^{-1} weak lines at 497, 642, 985, 1135, and 1525 cm^{-1}
Tetrafluorohydrazine N_2F_4	strong lines at 968, 10140, and 700 cm^{-1} lines of medium intensity at 459 and 1937 cm^{-1} weak lines at 469 and 513 cm^{-1}
Nitrogen difluoride NF_2	gas: 1074.3 cm^{-1} matrix: 1069.6, 573.4, and 930.7 cm^{-1}
Difluoramine NF_2H	strong doublet lines at 1430, 1282, and 980 cm^{-1} triplet at 893 cm^{-1}
Chlorodifluoramine $ClNF_2$	strong lines: triplet at 927 cm^{-1} doublet at 855 cm^{-1} triplet at 695 cm^{-1} lines of medium intensity at 747 cm^{-1} weak lines at 1851, 1756, 1696, and 1370 cm^{-1}
trans-Difluorodiazine N_2F_2	strong line at 989 cm^{-1} lines of medium intensity at 1996, 1581, 1434, 1366, 421, and 360 cm^{-1}
Active isomer of difluorodiazine N_2F_2	strong lines at 737, 896, 952, and 1524 cm^{-1} lines of medium intensity at 1774 cm^{-1}

‡ The different colours (pink, blue, green) often observed in liquid tetrafluorohydrazine, which vary with the temperature, are due to the presence of nitric oxide as impurity.

$N_2F_4 \rightleftharpoons 2NF_2$; this was determined experimentally (see below) to be 21.5 ± 1.6 kcal mole^{-1} [10] (*cf.* the dissociation energy of the N–N bond in hydrazine, which is 60 kcal × × mole^{-1} [46]). The values obtained by Herron and Dibeler[44] and Loughran and Mader[45] are high because the reaction $N_2F_4 = 2NF_2$ was not allowed for.

The mean energy of the N–F bond in the NF_2 radical, determined from the heat of formation of the radical (ΔH = 9.8 ± 2.1 kcal mole^{-1}), is 71.0 kcal mole^{-1}; this is the accepted value for the mean energy of the N–F bond in tetrafluorohydrazine.

A most important characteristic of the tetrafluorohydrazine molecule is its reversible dissociation into NF_2 radicals:

$$N_2F_4 \rightleftarrows 2\,NF_2,$$

as found by Colburn and Johnson[8,42]§. This reaction can be considered as definitely established.

The ultraviolet spectrum of tetrafluorohydrazine exhibits absorption bands with a maximum at 2600 Å. The absorption becomes more intense as the temperature is increased and the pressure decreased. This band is considered[8] to be due to absorption by the NF_2 radical.

The infrared spectrum of tetrafluorohydrazine recorded at 1–10 mm Hg and 25°–175° exhibits new lines (at 1074 cm^{-1}) not present in the spectrum of the tetrafluorohydrazine molecule[48]. These lines are fully reversible under changing conditions, and may also be assigned to the NF_2 radical.

The electron paramagnetic resonance spectrum of tetrafluorohydrazine recorded at 20–40 mm Hg and 67°–162° [49] contains a broad band which can be reasonably assigned to the formation of the NF_2 radical, which has one unpaired electron.

The equilibrium $N_2F_4 \rightleftharpoons 2NF_2$ has been studied by several physicochemical methods. Johnson and Colburn[8] used measurements of pressure and of the absorption of monochromatic light (λ = 2600 Å), in each case at 25°–150° and 0.1–0.6 atm. In the first method K_p was found from the pressure increase at various temperatures, and the coefficients A and B of the equation $\log K_p = -A/T + B$ were determined, from which the changes of enthalpy ΔH and entropy ΔS were calculated. In the second method the variation of the intensity of light absorption by the NF_2 radical with the temperature was determined, and the change of enthalpy ΔH calculated.

The dependence of K_p on T is given by the equation

$$\log K_p = -\frac{4.239 \times 10^3}{T} + 8.519,$$

whence ΔH = 19.85 kcal mole^{-1} and ΔS = 39.90 cal mole^{-1} × × deg^{-1}. The light absorption method gives ΔH = = 21.7 kcal mole^{-1}.

From Johnson and Colburn's data[8], the degree of dissociation of tetrafluorohydrazine can be calculated as a function of temperature and pressure (Table 3).

TABLE 3. Degree of dissociation of tetrafluorohydrazine (α)*.

t, °C \ P, atm	1		10^{-1}		10^{-2}		10^{-3}	
	K_p	α	K_p	α	K_p	α	K_p	α
150	$3.67 \cdot 10^{-2}$	0.9	$3.02 \cdot 10^{-2}$	0.26	$2.96 \cdot 10^{-2}$	0.65	$2.95 \cdot 10^{-2}$	0.94
100	$1.94 \cdot 10^{-2}$	0.02	$1.30 \cdot 10^{-2}$	0.05	$1.24 \cdot 10^{-2}$	0.18	$1.23 \cdot 10^{-2}$	0.50
25	$6.3 \cdot 10^{-5}$	0.004	$6.3 \cdot 10^{-5}$	0.01	$6.3 \cdot 10^{-5}$	0.04	$6.3 \cdot 10^{-5}$	0.12
−100	10^{-16}	10^{-8}	10^{-16}	$1.14 \cdot 10^{-8}$	10^{-16}	$4 \cdot 10^{-8}$	10^{-16}	10^{-6}

* The calculation is strictly correct only for the range 100°–150°, for which the conversion factor from K_f to K_p is given. With the other temperature ranges the calculation assumes that the coefficients B_1 and B_2 of the equation $\log K_p = -B_1/T + B_2$ are independent of pressure (concentration).

The equilibrium $N_2F_4 \rightleftharpoons 2NF_2$ has also been studied by electron paramagnetic resonance[49]; ΔH for the reaction was found by measuring the variation of the resonance peak of the radical with the temperature of the gas. The value 19.3 kcal mole^{-1} was found for ΔH (Kennedy and Colburn[50] use the value 19.8 ± 0.8 kcal mole^{-1}).

The mass-spectroscopic method[9] gives ΔH as 21.5 ± ± 1.6 kcal mole^{-1}. Four independent methods thus give values for ΔH for the reaction which agree satisfactorily.

The thermochemical equation

$$\Delta H_{N_2F_4} = 2\Delta H_{NF_2} - D_{N-N},$$

has been used to determine the heat of formation of gaseous NF_2: ΔH = 9.8 ± 2.1 kcal mole^{-1} at 25°.

Harmony and coworkers have studied the infrared spectrum of the NF_2 radical in the gaseous state[48] and in the solid form in a nitrogen matrix at −253° [51] (Table 2). The frequency 1074 cm^{-1} is assigned to symmetrical stretching vibrations. Assuming the N–F distances in NF_2 and NF_3 to be the same, the infrared data were used to calculate the F–N–F angle: this is 104°.

The thermodynamic functions of NF_2 have been calculated[51].

3. Chemical Properties of Tetrafluorohydrazine

Tetrafluorohydrazine can react chemically in two ways:

$$N_2F_4 + M \rightarrow M(NF_2)_n, \quad \text{(I)}$$
$$N_2F_4 + M \rightarrow MF_n + N_2. \quad \text{(II)}$$

Type (I) (radical) reactions arise because of the ready dissociation of tetrafluorohydrazine at the N–N bond, which makes tetrafluorohydrazine a good reagent for the introduction of the NF_2 group. These reactions can arise in two ways. In the first the N–N bond is dissociated by the action on the tetrafluorohydrazine of any free radical produced by the photochemical dissociation of a substance which can react with N_2F_4, and in the second, the NF_2 radicals are produced by the reaction $N_2F_4 \rightleftharpoons 2NF_2$.

According to Frazer[52], a mixture of methyl or ethyl iodide and tetrafluorohydrazine, in which there is no reaction at room temperature in the dark, reacts rapidly on

§ The compound NF_2 was first reported in 1931 by Ruff[47], who obtained a new substance by the reaction between fluorine and ammonia; he determined its boiling point (−125°) and identified it from its molecular weight as NF_2. However, Ruff himself indicated that this conclusion was not necessarily correct, and his results must now be considered as being in error.

irradiation with ultraviolet light of wavelength $\lambda \geq 2600$ Å¶:

$$AlkI + N_2F_4 \xrightarrow{h\nu} AlkNF_2.$$

The reaction products also contain elemental iodine, HCN, and NF_2H. The reaction of CH_3I with N_2F_4 apparently consists of three stages:

$$CH_3I + h\nu = CH_3^{\cdot} + I,$$

$$CH_3^{\cdot} + NF_2 - NF_2 = CH_3NF_2 + NF_2^{\cdot},$$

$$NF_2^{\cdot} + CH_3I = CH_3NF_2 + I.$$

The reaction of AlkI with tetrafluorohydrazine in the presence of nitric oxide gives[53] *N*-fluoro-*N'*-trifluoromethyldiazine-*N'*-oxide $CF_3-N(=O)=N-F$, the first known compound containing the $-N(=O)-N-F$ group. The mechanism of formation of the $=N-F$ group from tetrafluorohydrazine is not clear.

Petry and Freeman[54] have carried out the following photochemical reactions (i)–(v).

$$N_2F_4 + Cl_2 \xrightarrow{h\nu} 2\,NF_2Cl. \qquad (i)$$

The reaction was carried out in a Pyrex vessel at 80° using an excess of chlorine and irradiation with ultraviolet light; it is said to be reversible.

$$N_2F_4 + R{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}R \xrightarrow{h\nu} RCONF_2, \qquad (ii)$$

where R=H, CH_3, or C_6H_5.

A mixture containing 0.06 mole of biacetyl and 0.06 mole of tetrafluorohydrazine irradiated for 16 h with polychromatic light from a mercury lamp gave 0.077 mole of CH_3CONF_2 in 80% yield (calculated on converted tetrafluorohydrazine).

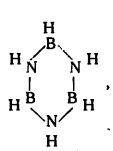
$$N_2F_4 + (CH_3)_2\underset{\underset{CN}{|}}{C}{-}N{=}N{-}\underset{\underset{CN}{|}}{C}{=}(CH_3)_2 \xrightarrow{h\nu} (CH_3)_2\underset{\underset{CN}{|}}{C}{-}NF_2, \qquad (iii)$$

$$N_2F_4 + (CH_3)_3C{\equiv}N{=}N{-}C{\equiv}(CH_3)_3 \xrightarrow{h\nu} (CH_3)_3CNF_2, \qquad (iv)$$

$$N_2F_4 + (C_6H_5)_3C{-}C(C_6H_5)_3 \xrightarrow{h\nu} (C_6H_5)_3CNF_2. \qquad (v)$$

In reactions (i)–(v) organic radicals or chlorine atoms are apparently first produced photochemically, and then react with the tetrafluorohydrazine.

The second form of the type (I) reaction of tetrafluorohydrazine is found in its reaction with acetaldehyde at 150° [54] and with diborane at 140°–160° and a partial pressure of tetrafluorohydrazine of less than 50 mm Hg.[55] In the latter reaction Pearson and Frazer obtained a mixture of fluoroborazines of general formula $B_3N_3H_nF_{6-n}$, and also BF_3, B_5H_9, H_2, N_2, and $BF_3.NH_3$. Separation of the fluoroborazines gave fractions consisting of mixtures of the isomers $B_3N_3H_5F$, $B_3N_3H_4F_2$, and $B_3N_3H_3F_3$; these are fluoro-derivatives of borazole:



containing the fluorine and hydrogen atoms in different relative positions. Infrared data indicated that the mixture also contained NF_2 derivatives of borazole.

¶ Frazer quotes $\lambda \geq 2750$ Å (Ed. of Translation).

The formation of difluoramine from tetrafluorohydrazine and thiophenol at 50° [56] (see Section IV) is also a reaction of this type.

These two cases of dissociation of the N–N bond are not the only possible type (I) reactions of tetrafluorohydrazine, which would be expected to undergo dissociation at the N–N bond by the direct action of substances having an odd number of outer electrons, such as nitrogen dioxide, nitric oxide, and oxygen.

The ability of tetrafluorohydrazine to undergo type (II) reactions $N_2F_4 + M \rightarrow MF_n + N_2$ is shown by its reaction with aqueous potassium iodide solution[57]. Pankratov and coworkers have shown that two parallel reactions take place:

$$N_2F_4 + 10KI + 8H_2O = 5I_2 + 4KF + 2NH_4OH + 6KOH, \qquad (1)$$

$$N_2F_4 + 4KI = 2I_2 + 4KF + N_2. \qquad (2)$$

Reaction (1) is a type (I) reaction, the tetrafluorohydrazine behaving like an NF_2 radical, which reacts with the potassium iodide solution similarly to difluoramine (see Section IV). Reaction (2) is a type (II) reaction, the tetrafluorohydrazine behaving as a normal fluorinating agent, like nitrogen trifluoride and difluorodiazine.

The relative proportions of reactions (1) and (2) depend on the pH of the medium; tetrafluorohydrazine reacts by reaction (2) to the extent of 65% of the overall process in acid medium and 90% in a neutral medium.

Colburn and Kennedy[56] were probably dealing with a type (II) reaction when reacting tetrafluorohydrazine with thiophenol, arsine, and n-butanethiol (see Section IV), but they did not describe the reaction.

The relative proportions of the two types of tetrafluorohydrazine conversion depend on the actual experimental conditions, but primarily on the other reactant. If this has an odd number of outer electrons (such as the O_2 and NO_2 radicals), the tetrafluorohydrazine undergoes a type (I) radical reaction; if it does not have an odd number of outer electrons, and particularly if it is a reducing agent, it will react with the electronegative fluorine atoms to give a type (II) reaction.

The thermal stability of tetrafluorohydrazine has not been studied. It would appear[29] that under certain conditions tetrafluorohydrazine can explode, producing nitrogen trifluoride and nitrogen.

IV. DIFLUORAMINE AND CHLORODIFLUORAMINE

1. Difluoramine

Three fluorine derivatives of ammonia are possible: the known nitrogen trifluoride NF_3, difluoramine NF_2H, and fluoramine NFH_2.

Ruff[47,58] was the first to refer to fluoramines. In the electrolysis of ammonium hydrogen fluoride to obtain nitrogen trifluoride as the main product, he prepared some new compounds in very small quantities. Separation of the by-products gave fractions of molecular weight corresponding by the formulae NF_2H, NFH_2, and NF_2. Difluoramine was identified by reaction of the gas with molten sodium. For difluoramine, Ruff found b.p. -65° and m.p. -125°.

Ruff identified fluoramine NFH_2 only by its molecular weight; its b.p. was estimated to be -77°. However, later work has not confirmed Ruff's results (method of production, physical constants), nor has the preparation of fluoramine been confirmed.

The data of Ruff and Staub on fluoramines (and especially on nitrogen difluoride), and also the results obtained by Kreft[59] and Ch'ih Chang-li[60] are dubious; Kennedy and Colburn[28] must be considered the first to obtain difluoramine. Nothing has yet been published on fluoramine NFH_2.

Three methods are known for the preparation of difluoramine: (*i*) Kennedy and Colburn's method, by the conversion of nitrogen trifluoride over arsenic in the presence of water vapour[28]; (*ii*) the reaction of tetrafluorohydrazine with mercaptans and arsine[56]; and (*iii*) Lawton and Weber's method, by the fluorination of urea[61]. Attempts to prepare fluoramine by electrolysis of ammonium hydrogen fluoride[28], as in Ruff's method[47], have been unsuccessful.

Kennedy and Colburn[28,56] obtained difluoramine from nitrogen trifluoride over arsenic at 250°–300° in the presence of water vapour; it was obtained as a by-product in low yield, with tetrafluorohydrazine as the main product. The difluoramine is apparently obtained by a secondary reaction of the tetrafluorohydrazine with arsine.

Difluoramine can be obtained by reaction of tetrafluorohydrazine with thiophenol, n-butanethiol, or arsine[56], in each case at 50°. Thiophenol gives the greatest yields:

$$N_2F_4 + 2\,C_6H_5SH = 2\,NF_2H + C_6H_5SSC_6H_5.$$

The reaction is carried out under static conditions in glass apparatus for 4 h with a fivefold excess of thiophenol. The yield of difluoramine was 74%. In metal apparatus there is more formation of nitrogen. This reaction was not identified, but is probably a type (II) conversion:

$$N_2F_4 + M \rightarrow MF_n + N_2.$$

The reaction with n-butanethiol was also carried out under static conditions at 50°–60° for 2 h with a fivefold excess of mercaptan. In this case nitrogen formation was the main reaction, with only a 9% yield of difluoramine. Unlike the reduction with thiophenol, difluoramine is only produced in stainless steel apparatus, and not in glass.

The reaction $N_2F_4 + AsH_3 \rightarrow NF_2H + As$ was carried out under static conditions for 1 h at 50° in a stainless steel cylinder at atmospheric pressure with a 1 : 1 molar ratio of the reactants; difluoramine was produced in 52% yield. The gaseous reaction products contained difluoramine, nitrous oxide (34 mole %), and unreacted arsine (8.5 mole %) and tetrafluorohydrazine (4.3 mole %).

Difluoramine can be obtained analogously in all reactions of tetrafluorohydrazine with organic compounds containing labile hydrogen, the hydrogen being replaced by the NF_2 group[54].

In the method of Lawton and Weber[61] the fluorination of urea produces a yellow liquid containing 16% of active fluorine and 45–55% of total fluorine; difluoramine, CO_2, SiF_4, COF_2, and HNCO have been found in the reaction products. The yield of difluoramine is 15%, based on the fluorine introduced. Apparently all the active fluorine in the urea fluorination products is present as difluoramine. After distillation of the volatile fractions, the residue contains difluoraminourea[62].

The fluorination of ammonia[34] also produced difluoramine, which was not separated, but absorbed in water together with the ammonia. The presence of difluoramine was in fact only deduced from the explosions which occurred during the reaction. Difluoramine is apparently also formed as a by-product in the fluorination of sodamide[63]. It is thus seen that of all the methods for the preparation of difluoramine, only the reduction of tetrafluorohydrazine produces it in good yield.

The physical constants of difluoramine[28,61] are given in Table 1. Attention is directed to the different values reported for the melting point: -131°,[28] and -116°.[61] The infrared frequencies of difluoramine[28] are given in Table 2. There have been no other structural studies on difluoramine.

Difluoramine is an unstable substance which is liable to explode. Solid difluoramine at low temperatures apparently has a greater sensitivity towards explosion. There are indications[34] that liquid and solid difluoramine explodes on contact with air.

An important property of difluoramine is its ability to lose hydrogen and produce tetrafluorohydrazine on contact with various solids[61]; thus with lithium hydride the yield of tetrafluorohydrazine is 70%.

The lability of the hydrogen atom is demonstrated by the reaction of difluoramine with boron trichloride to form the new product chlorodifluoramine[64] (see below).

The reaction of difluoramine with hydriodic acid has been described:

$$NF_2H + 4HI = 2I_2 + NH_4F + HF.$$

The I : F atomic ratio is 2, *i.e.* the reaction can be formally represented as follows:

$$NF_2H + 2HI = I_2 + 2HF + \cdot\ddot{N}H,$$

$$\cdot\ddot{N}H + 2HI = I_2 + NH_3,$$

$$\overline{NF_2H + 4HI = 2I_2 + NH_4F + HF}.$$

Difluoramine reacts with water[34], probably according to the equation

$$NF_2H + 2H_2O = NH_4F + HF + O_2.$$

Difluoramine therefore has (*i*) a strong oxidising action, (*ii*) a labile hydrogen atom, making difluoramine a good reagent for the introduction of NF_2 groups, and (*iii*) it is unstable and liable to explode.

2. Chlorodifluoramine

Chlorodifluoramine NF_2Cl was first obtained by Petry[64] in 1960 by the reaction between difluoramine and boron trichloride. The reactants were condensed into an evacuated flask at -130°, and formed a white solid stable up to -80°. The product decomposed on heating to room temperature to volatile compounds and an involatile solid whose composition was not determined. The volatile products were hydrogen chloride, chlorine, and chlorodifluoramine; the yield of chlorodifluoramine was 50%.

Chlorodifluoramine was also prepared by Petry and Freeman[54] by the photochemical reaction between tetrafluorohydrazine and chlorine; the reaction conditions and yield of chlorodifluoramine were not reported.

Table 1 gives the physical constants of chlorodifluoramine, and Table 2 the frequencies of its infrared

spectrum[64]. Its mass spectrum and nuclear magnetic resonance spectrum have been determined[64].

Chlorodifluoramine is a colourless gas which does not react with atmospheric oxygen. Unlike difluoramine, it is relatively stable: according to Petry, it is not decomposed at room temperature in Pyrex vessels for a long time.

Like difluoramine with its labile hydrogen atom, chlorodifluoramine has a labile chlorine atom. It reacts with mercury at room temperature:

$$2NF_2Cl + 2Hg = N_2F_4 + Hg_2Cl_2.$$

It loses its chlorine when reacted with ammonia at 150°, producing ammonium chloride, and reacts with a solution of sodium in liquid ammonia at -50° to form sodium chloride and fluoride.

Chlorodifluoramine may prove to be of considerable interest as a reagent for the introduction of NF_2 groups.

V. FLUORINE AZIDE AND THE DIFLUORODIAZINE ISOMERS

1. Fluorine Azide

Fluorine azide FN_3 is a very unstable explosive substance which was obtained in 1942 by Haller[65] by the reaction between gaseous hydrogen azide, diluted with nitrogen, and elemental fluorine at 25° in a tubular copper reactor 1 m in length and 0.6 cm in diameter. The optimum temperature is 25°; at 0° the yield of fluorine azide is low, while at 50° the fluorine azide already undergoes decomposition. The yield of fluorine azide was not determined, and the amounts of fluorine, nitrogen, and hydrogen azide used were not measured. The reaction products contain ammonium fluoride but no hydrogen fluoride, and Haller therefore assumes the reaction to proceed according to the equation

$$4HN_3 + 2F_2 = NH_4F + N_2 + 3FN_3.$$

The ammonium fluoride is thought to form by the reaction

$$3HN_3 + HF = NH_4F + 4N_2.$$

The extremely explosive nature of fluorine azide has hindered the study of its properties, and it has only been identified by its molecular weight. Its preparation from hydrogen azide, its explosive nature, and its molecular weight all indicate that the substance obtained by Haller is in fact fluorine azide.

Fluorine azide is a greenish yellow gas resembling chlorine, with an odour like that of ClO_2. It condenses to an oily greenish yellow liquid at -82° and solidifies to greenish yellow crystals at -154°; these temperatures were not accurately determined, and may not be correct. Fluorine azide explodes on evaporation. According to Haller, solid fluorine azide does not usually explode. The liquid explodes when subjected to slight shock or vibration, or to the action of a 100 W lamp at a distance of 30 cm. While the liquid explodes the gas does not detonate at pressures up to 200 mm Hg.

Gaseous fluorine azide is decomposed by heat: at 25° the colour of the gas is completely lost after 1 h, and at 100° the colour disappears within a few minutes. Fluorine azide decomposes to form difluorodiazine:

$$2FN_3 = N_2F_2 + 2N_2.$$

Fluorine azide also decomposes when evaporated. By analogy with the decomposition of HN_3, which according to Audrieth[66] proceeds by way of the biradical $\cdot\dot{N}H$, Haller assumes that the decomposition of FN_3 proceeds by way of the biradical $\cdot\dot{N}F$.

Fluorine azide reacts with elemental fluorine. Reaction is slow at room temperature, but at 80° in excess fluorine all the fluorine azide is converted to nitrogen trifluoride.

With alkali FN_3 reacts to form HF [fluoride? (Ed. of Translation)]; an alkaline solution treated with FN_3 has oxidising properties. Haller considers that nitrous acid is formed during the reaction between FN_3 and KOH, by analogy with its formation in the reaction of HN_3 with alkali.

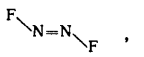
Fluorine azide reacts with water; it reacts explosively at room temperature with gaseous ammonia and with hydrogen. It displaces iodine from aqueous potassium iodide solution.

Dry fluorine azide does not react with glass within 40 h; the moist gas immediately produces a film on the glass.

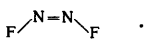
Gaseous fluorine azide dissolves at low temperatures in anhydrous liquid HF, NH_3, HN_3, pentane, acetone, and Freons. Haller estimated the solubility of fluorine azide qualitatively by the solvent's taking on the greenish yellow colour of the FN_3.

2. The Difluorodiazines

Two difluorodiazines are known, the chemically inactive isomer which is *trans*-difluorodiazine:



and the chemically active isomer which is apparently *cis*-difluorodiazine:



The first report on difluorodiazine was by Haller[65], who obtained it by the thermal decomposition of fluorine azide; it was identified only by its molecular weight.

Difluorodiazine is obtained by the electrolysis of ammonium hydrogen fluoride[36,67,68] as a by-product accompanying nitrogen trifluoride.

According to Colburn[67], difluorodiazine is obtained in 5–10% yield (based on the gases condensed in liquid nitrogen) by the electrolysis of fused (120°–130°) ammonium hydrogen fluoride. The current density may be 0.03–0.04 A cm^{-2}.[68] A solution of ammonium fluoride in liquid hydrogen fluoride can also be used as electrolyte. Difluorodiazine is also obtained as a by-product in all preparations of tetrafluorohydrazine[23,25,30,33].

The difluorodiazine isomers have been separated by chromatography[67], which gave 99.7% pure *trans*-isomer. Low-temperature distillation of the isomers gave the active isomer containing not more than 2.1% of *trans*-isomer.

Both isomers are colourless gases with a characteristic odour resembling that of fluorine. The physical constants of difluorodiazine[67] are given in Table 1, and its infrared frequencies[69] in Table 2.

The enthalpy of formation of the active isomer of difluorodiazine, determined by Pankratov *et al.* from its

reaction with acid potassium iodide solution[70], is 25.3 ± ± 2.0 kcal mole^{-1} at 25° and 20.5 ± 2.0 kcal mole^{-1} at -105.7° (for the liquid isomer). Herron and Dibeler[10] refer to a private communication from Armstrong and Marantz, and quote the values 16.4 kcal mole^{-1} and 19.4 kcal mole^{-1} for the enthalpy of formation of the *cis*- and *trans*-isomer respectively, but without giving any experimental data.

The nuclear magnetic resonance spectra of both isomers have been determined[67,71].

The structure of the difluorodiazine isomers was first studied by electron diffraction by Bauer[72], who assumed that the gas is an equimolar mixture of *cis*- and *trans*--difluorodiazine and that both isomers have the same structural parameters. The values obtained by Bauer (r_{N-F} = 1.44 ± 0.04 Å, $r_{N=N}$ = 1.25 ± 0.04 Å, ∠ NNF = = 115° ± 5°) require confirmation. Analysis of the nuclear magnetic resonance spectra of the difluorodiazine isomers has suggested[71] that the valence angles are different in the two isomers.

The question of the structure of the difluorodiazine isomers has not yet been definitely solved. Colburn *et al.*[67] have shown that the isomers have different chemical properties. The chemically inactive isomer was allotted the *trans*-structure, and the chemically active isomer the *cis*-structure, since the inactive isomer has the lower boiling point and higher melting point, as would be expected for the compound with the smaller dipole moment, *i.e.* the *trans*-isomer. It was also reported that there is some evidence for a third very unstable isomer, in all probability of the structure:



The *trans*-structure of the chemically inactive isomer is definitely established, but the question of the structure of the active isomer is still under discussion.

Sanborn[69,73] has suggested that the active isomer has the 1,1-structure:



mainly on the basis of his analysis of the infrared spectrum of the active isomer and because of the similar frequencies of deformation vibrations in this difluorodiazine isomer and in carbonyl fluoride COF_2, which is isoelectronic with 1,1-difluorodiazine. However, mass-spectroscopic studies[10,74] and nuclear magnetic resonance (NMR) data favour the *cis*-structure.

The mass spectra of the active isomer have no peak of mass 52, corresponding to the ion NF_2^+, the expected disintegration product of the 1,1-isomer.

The assignment of the NMR spectra[71] is also in agreement with the *cis*-structure: both nitrogen atoms in the NMR spectrum of the active isomer have the same chemical shift. According to Herron[10], the appearance potentials of the ions NF^+ and N_2F^+ are equal for the active and inactive isomers. He refers to a private communication from Armstrong regarding the enthalpy of formation of the isomers (16.4 kcal mole^{-1} for the active isomer and 19.4 kcal mole^{-1} for the *trans*-isomer); the closeness of these energy values also indicates that the active isomer has the *cis*-structure. The active difluorodiazine isomer is thus apparently the *cis*-isomer.

The bond energies in the molecule of the active difluorodiazine isomer can be calculated from the known enthalpies of formation of the isomer[70] and the NF group. The latter is found from the enthalpy of formation of the NF_2 radical and the average energy of the N–F bond in the NF_2 radical, assuming that the average bond energy is equal to the dissociation energy of the first N–F bond[10]. The energy of the N=N bond is calculated from the thermochemical equation

$$E_{N=N} = 2\Delta H_{NF} - \Delta H_{N_2F_2}.$$

Since ΔH_{NF} = 61.4 ± 4.2 kcal mole^{-1} and $\Delta H_{N_2F_2}$ = 25.3 ± ± 2.0 kcal mole^{-1}, $E_{N=N}$ = 97.5 ± 6.4 kcal mole^{-1}.

Putner[75] has calculated the thermodynamic functions of *trans*-difluorodiazine from the infrared frequencies and Bauer's structural parameters. The functions are given for the range 100°–6000°K.

The difluorodiazines are fluorinating agents, reacting by dissociation of the N–F bond to form fluorides and nitrogen; for example, they react with mercury and potassium iodide to form the corresponding fluorides and nitrogen. Difluorodiazine is a polymerisation initiator for hydrocarbons, such monomers as methyl methacrylate, styrene, and cyclopentadiene polymerising in contact with gaseous difluorodiazine at a pressure of the latter of 300 mm Hg. At room temperature the polymerisation took 12 h or less. Difluorodiazine catalyses the polymerisation of tetrafluoroethylene at 125° and of ethylene and propene at 140°. The polymerisation of ethylene and propene produces polymers containing fluorine[67].

The active isomer reacts considerably more rapidly in all chemical reactions than the *trans*-isomer; thus the former reacts with glass and is completely converted to SiF_4 and nitrogen within two weeks, while with the *trans*--isomer there is no reaction with glass in a month.

The isomers also show different rates of reaction with potassium iodide solution[70] and mercury. This substantial difference in the chemical properties of isomers having close energy characteristics is surprising.

The difluorodiazines do not react with oxygen or water at room temperature.

Both difluorodiazine isomers are relatively stable to heat[67]. On heating, the *trans*-isomer is first converted into the active isomer, but without decomposition into its elements, which does not occur until about 300°. Heating the isomers to 285° produces an equilibrium mixture containing 13% of the *trans*-isomer and 87% of the active isomer.

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RUSSIAN CHEMICAL REVIEWS
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ADVANCES IN THE PREPARATION, INVESTIGATION, AND USE OF QUINOLINIUM COMPOUNDS

G.T. Pilyugin and B.M. Gutsulyak

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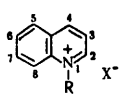
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I. INTRODUCTION

Quinolinium compounds are quaternary salts of quinoline in which the radical R can vary from methyl to complex aliphatic and aromatic radicals:



Positions 2–8 may also have any substituents; X is an acid residue. Quinolinium compounds are intermediates in the production of dyestuffs for sensitising photographic emulsions, for dyeing natural and synthetic fibres, and for biological preparations. They have a number of interesting biological properties, of which their cancerostatic, photodynamic, mutagenic, and plant growth regulating properties are only just beginning to be studied. Quinolinium compounds are widely studied for antiseptic, chemotherapeutic, hypotensive, and ganglion-blocking properties, and a number of very valuable substances have been found.

Because of the electrophilic nitrogen atom in the ring and the consequent reduction of electron density on the carbon atoms, quinolinium salts are good models for studying nucleophilic reactions, which they undergo fairly readily. Quinaldinium and lepidinium salts, which have a labile methyl-group, are extremely reactive, and readily condense with organic carbonyl-compounds, ortho-esters, diazonium salts, nitroso-compounds, etc., to form various types of dyestuff.

Cyanine dyes are good models for studying the relationship between structure and colour, and possess interesting photoelectric properties[1].

Quinolinium compounds are also used as surface-active substances and analytical reagents.

This review will consider in some detail work of the last 25–30 years, which have seen the most interesting studies in the field of quinolinium compounds. We shall not touch upon matters covered sufficiently in other reviews (*e.g.* the relationship between colour and structure, structure and photographic properties, etc.).

II. PREPARATION OF QUINOLINIUM SALTS

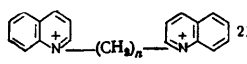
1. Production of Quaternary Salts by Alkylation

The simplest quinolinium salt, *N*-methylquinolinium iodide, was first prepared by Williams[2] by heating quinoline with methyl iodide; *N*-methylquinaldinium and *N*-methyllepidinium halides were obtained similarly[3,4]. The rate of reaction depends on the alkylating agent and the substituents in the quinoline nucleus. Some quinoline derivatives, *e.g.* 8-nitroquinoline, do not react with alkyl halides:

Decker[5] used dimethyl sulphate to obtain the 8-nitroquinolinium salt. Aralkyl halides also react with quinolines to form the quaternary salts.

A considerable number of substituted quaternary salts derived from quinoline, its homologues, and derivatives are known.

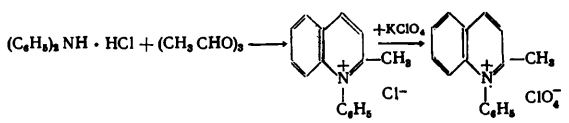
This reaction can be carried out in various ways, in the presence of a solvent (ether, alcohols, benzene, nitrobenzene, etc.) or in its absence. Alkyl and aralkyl halides are used as alkylating agents there as well as alkyl esters of sulphuric or various aromatic sulphonic acids. If dihalogenoalkanes are used bis-quarternary salts are obtained[6-8]:



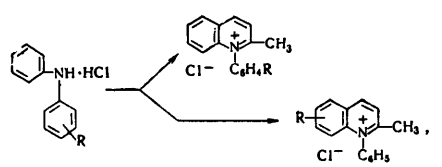
The kinetics of the alkylation of quinoline with alkyl halides were first investigated by Menschutkin[9]. Winkler and Hinshelwood[10] used Menschutkin's method to study the rate of reaction between quinoline and methyl iodide in benzene. The influence of the alkyl radical, the halogen, and the heterocyclic base on the rate of formation of the quaternary salts has also been studied[11], using equimolar amounts of quinoline and alkyl halide in methanol. The rate of reaction, measured conductimetrically, decreases with increasing number of carbon atoms in the alkyl radical, but increases in the series I > Br > Cl.

2. Preparation of Quinolinium Salts by Cyclisation of Secondary Arylamines

The principal new method for the preparation of quinolinium salts is the cyclisation of secondary aromatic amines with organic carbonyl compounds. This is a general method, and can be used to prepare quaternary salts with aliphatic, aliphatic-aromatic or aromatic radicals on the nitrogen. These last have not yet been prepared by other methods, since the direct arylation of quinoline does not produce *N*-arylquinolinium salts[12]; aryl halides and aryl esters of aromatic sulphonic acids do not form quaternary salts on heating with quinoline or its derivatives, because of their low reactivity. This was one of the reasons why until recently no such quarternary salts, or derivatives with aryl radicals on the nitrogen, were known. Pilyugin and Krainer[13,14] applied the Doebner–Miller reaction to diarylamines, and developed a general method for the preparation of *N*-arylquinaldinium salts:



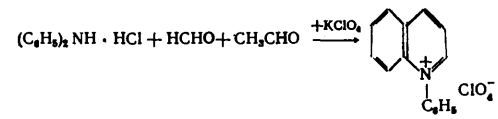
Symmetrical secondary aromatic amines can condense with paraldehyde to form only one compound; an asymmetrical amine can form two isomers with equal probability[15]:



but in the overwhelming majority of cases only one of the two possible isomers has been isolated.

It was later shown[16] that in acid medium secondary arylamines react with vinyl ethers to form *N*-arylquinaldinium salts. The use of butyl vinyl ether instead of paraldehyde considerably reduces the period of reaction and increases the yield of quinaldinium salts. Acetal, which is converted into acetaldehyde by hydrolysis, can also be used in this reaction[17]. Higher saturated aldehydes can also be used as the carbonyl component; *e.g.* propionaldehyde and butyraldehyde give respectively 2-ethyl-3-methyl- and 2-propyl-3-ethyl-*N*-arylquinolinium salts[18]. *N*-Phenylquinaldinium salts can also be prepared by heating diphenylamine in solution in isobutyl alcohol with sodium isobutoxide, the reaction mixture then being heated in acid solution[17]. Ferric chloride and zinc chloride have been suggested as condensing agents for the preparation of quinaldinium salts by cyclising secondary arylamines with acetaldehyde, paraldehyde, aldol, or crotonaldehyde in anhydrous alcohol[19].

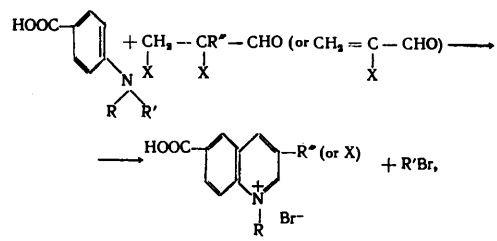
Aliphatic aromatic amines, *e.g.* ethylaniline, react with paraldehyde to form *N*-alkylquinaldinium salts. Applying Beyer's reaction[20] to secondary amines, Pilyugin and Gutsulyak prepared a number of *N*-aryllepidinium salts[21-25]. The preparation of certain aryllepidinium salts has been described in the patent literature[26,27]. Ardashev and Tertov[28] prepared 1-phenyl-3-methyllepidinium perchlorate by using ethyl methyl ketone in place of acetone. The use of acetaldehyde instead of acetone produces an *N*-arylquinolinium salt[29]:



N-Phenylquinolinium salts are also obtained by the reaction of β-hydroxypropionaldehyde with diphenylamine in the presence of nitrobenzene and sulphuric acid: the perchlorate has been isolated[30].

Unsaturated carbonyl compounds react with diarylamines to form *N*-aryl quaternary salts of quinoline and its homologues[26,27,31]. Heterocyclic secondary amines also produce quinolinium derivatives[26,32]. Replacing the aldehydes by methyl vinyl ketone gives the corresponding lepidinium salts.

Weygand and coworkers[33,34] have developed an interesting method for the preparation of quaternary salts of 3-substituted quinoline-carboxylic acids, by boiling halogenoaldehydes with *N*-substituted aminobenzoic acids in dioxan:

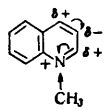


where R = $C_6H_5CH_2$, R′ = H, CH_3, or $C_6H_5CH_2$, R″ = H, Br, CH_3, or C_2H_5, and X = Br.

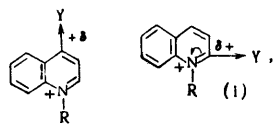
Other material on the preparation of *N*-arylquinolinium salts has also been published[35-41].

III. CHEMICAL PROPERTIES OF QUINOLINIUM SALTS

Because of the electron-accepting quaternary nitrogen atom in quinolinium salts, the electron density on the carbon atoms of the pyridine ring is less than in the base, particularly in positions 2 and 4:



Quinolinium compounds are therefore particularly prone to nucleophilic addition and substitution reactions at positions 2 and 4, and electrophilic reactions proceed with difficulty at position 3. If the quinolinium ring is 2- or 4-substituted by one of the electron-withdrawing groups I, SR, OAr, or CN, nucleophilic substitution becomes easier, these groups being split off; this is explained by the increased positive charge on the 2- or 4-carbon atom:

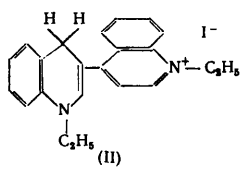


(I)

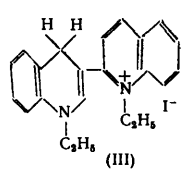
where Y = I, SR, OAr, or CN.

Nucleophilic reactions proceed more readily at the 4-position than at the 2-position, although some, *e.g.* addition of the OH-group and reactions with organometallic compounds, take place exclusively at the 2-position.

The electron distribution given above for the quinolinium ring (I) is supported by the experimental fact that heating a concentrated alcoholic solution of an *N*-alkylquinolinium iodide with alkali produces two isomeric red and yellow dyes which have been named erythroapocyanine (II) and xanthoapocyanine (III):[45-47]



(II)



(III)

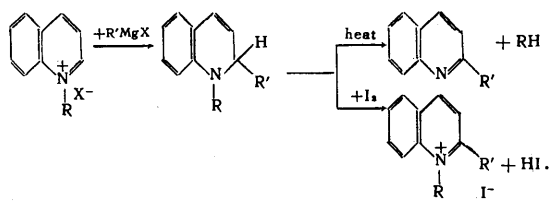
1. Addition Reactions

(a) Addition of hydrogen. Addition of 1 mole of hydrogen to a quinolinium salt can produce an *N*-substituted 1,2- or 1,4-dihydroquinoline derivative. Ishii[48] found that in some cases the reduction of 1-ethylquinolinium, quinaldinium, and lepidinium iodides with $Na_2S_2O_4$ in 5% $NaHCO_3$ could lead to the isolation of the dihydro-derivatives. The lithium tetrahydroaluminate reduction of *N*-alkylquinolinium salts can produce the unstable 1,2-dihydro-derivatives[49], which are isolated only with difficulty when $Na_2S_2O_4$ is used as reducing agent.

De Mayo and Rigby[50] obtained 1-methylquinolinium, identified as the chloroplatinate, by the $LiAlH_4$ reduction of 1-methylquinolone in ether; however, it was later shown[51] that the $LiAlH_4$ reduction of 1-methylquinolinium iodide and 1-methylquinol-2-one produces 1-methyl-1,2-dihydroquinoline in each case. The reduction of 1-(2,6-dichlorobenzyl)-3-carbamoylquinolinium bromide with $Na_2S_2O_4$ and with $NaBH_4$ produces the same product, a 1-(2,6-dichlorobenzyl)-1,*x*-dihydroquinoline carboxylic acid amide[52]; its chemical properties (stability to acids) and ultraviolet spectrum indicate it to be the 1,4-dihydro-derivative.

With more vigorous reduction of quinolinium compounds, 2 moles of hydrogen are added, forming 1,2,3,4-tetrahydroquinolines. These show all the properties of tertiary amines: they distil with steam, form salts with acids, produce quaternary salts on alkylation, and couple with aromatic diazo-compounds to produce valuable dyes. Nitrous acid produces the nitroso-compounds. Tetrahydroquinolines are also intermediates in the production of valuable pharmaceuticals, and their preparation has accordingly received much attention[53-57].

(b) Other addition reactions. Addition in the 2-position. Freund[58,59] studied the action of CH_3MgBr and C_6H_5MgBr on *N*-methylquinolinium iodide; in each case he obtained the corresponding 1-alkyl-2-alkyl-(or -aryl-)1,2-dihydro-quinoline or -quinaldine, which were readily reduced to the 1-alkyl-1,2,3,4-tetrahydroquinolines. Oxidation produced acylanthranilic acids. In 1954 Bradley and Jeffrey[60] studied the reaction between organometallic compounds and quinolinium salts in more detail, and found that methyl-, ethyl-, propyl-, and butyl-magnesium iodides and bromides, irrespective of structure, react with quinolinium salts to form 2-substituted 1-alkyl-1,2-dihydroquinolines, which on heating give the 2-substituted quinolines. Oxidation of the dihydro-compounds with iodine in alcoholic solution produces the 1,2-disubstituted quinolinium iodides:

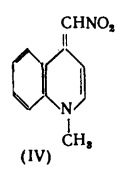


Bradley and Jeffrey were the first to study the reaction between quinolinium salts and dialkylcadmiums.

Boiling an aqueous solution of a quinolinium salt with piperidine produces the 2-addition product[61].

(c) Addition in the 3-position. ω-Chloroacetophenone reacts with the quaternary salts in alcoholic alkali solution to form the 3-phenacyl-derivatives[62].

(d) Addition in the 4-position. The reaction of quinolinium salts with nitromethane was studied by Leonard and coworkers[63], who found that the reaction product, despite Kaufmann's statement[64], has the structure (IV):

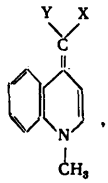


(IV)

This was shown by reducing (IV) over Raney nickel to the amine, the benzoyl derivative of which was found to be

identical with the benzoyl derivative of 1-methyl-4-amino-methyltetrahydroquinoline prepared from 1-methyl-4--cyanodihydroquinoline. Nitromethane also adds to *N*-methylquinaldinium iodide, but *N*-methyllepidinium iodide does not give a crystalline product.

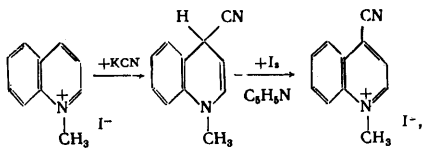
Malononitrile and cyanoacetic ester add in the 4-position of quinolinium compounds in the same way as nitromethane (V):[65]



(V)

where X = Y = CN, or X = $COOC_2H_5$, and Y = CN. Thus the condensation of *N*-(2,4-dichlorobenzyl)quinolinium bromide with malononitrile produced *N*-(2,4-dichlorobenzyl)-4--dicyanomethylene-1,4-dihydroquinoline in 90% yield[62]; under the same conditions ethyl cyanoacetate produces *N*-(2,4-dichlorobenzyl)-4-ethoxycarbonylcyanomethylene--1,4-dihydroquinoline. Leonard and Foster[66] showed that the reaction between *N*-methylquinolinium iodide and phenylacetonitrile produces 1-methyl-4-(α-cyanobenzyl)-1,4-dihydroquinoline, and not *o*-$CH_3NHC_6H_5CH{=}CHCH_2C_6H_4CN$ or 1-methyl-2-(α-cyanobenzyl)-1,2-dihydroquinoline, which Kaufmann[64] had earlier considered to be the product of condensation of *N*-methylquinaldinium sulphate with phenylacetonitrile.

With potassium cyanide, quinolinium salts give the 1,4-addition products:



which are converted into the quaternary salts by the action of iodine in the presence of pyridine[67].

(e) Addition to form adducts. Quinolinium salts tend to form coloured adducts with aromatic diamines and phenols[68-70]. Izmail'skii and Solodkov[71] showed that quinolinium compounds react with secondary and tertiary monoamines to form intensely coloured complexes which are decomposed by water; by choosing a suitable solvent, however, they can sometimes be isolated in the crystalline form. By reaction with hydroquinone or 1- or 2-naphthol, quinolinium salts give products of various shades of yellow. Mikhailenko and Minaf'ev[72] reported the formation of red products by the reaction of *N*-benzylquinolinium chloride with aniline, *p*-toluidine, diphenylamine, *p*-nitraniline, and piperidine, but incorrectly ascribed to them the structure of polymethine dyestuffs. Vompe[73] studied the reaction of *N*-benzylquinolinium chloride with primary amines of the formula:



where R = CH_3, Cl, Br, I, NO_2, OCH_3, or OC_2H_5; he obtained products of the formula:

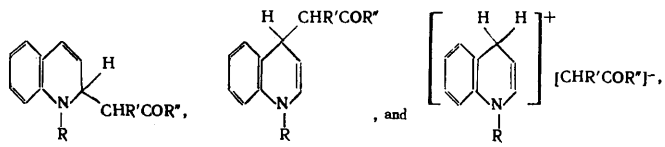
$$C_9H_7\overset{+}{N}CH_2C_6H_5 \cdot H_2NC_6H_4R\text{-}n \quad Cl^-,$$

which were shown to be of complex structure, but crystalline adducts could not be isolated. The reaction of the same quinolinium salt with benzidine gave a crystalline product of formula:

$$(C_9H_7\overset{+}{N}CH_2C_6H_5, Cl^-)_2 \cdot (H_2NC_6H_4C_6H_4NH_2)_3.$$

The structure of the complexes remains an open question. Vompe considers that the bonding and the state of colour are due to intermolecular interaction of the type discussed by Izmail'skii[74,75]. Later the optical properties of the complexes of 2-*p*-dimethylaminostyrylquinoline with ethyl-2-styrylquinolinium iodide, etc. were studied[76], and it was suggested that there is here a special type of π bond, the *exo-bond*, differing from a normal π bond in that there is no accompanying σ bond.

Kröhnke and Vogt[61] have shown that quinolinium salts form adducts with methyl- or methylene-ketones. Of the three possible structures for the adducts:



the last is the most probable. Oxidation of the adducts with $AgNO_3$, benzoquinone, or *p*-nitrosodimethylaniline produces 4-acetonylidene- or 4-benzal-1,4-dihydroquinolines; oxidation with $KMnO_4$ gives 2-acetonylidene- or 2-benzal-1,2-dihydroquinolines[77]. Under mild conditions bromine reacts with the adducts to form the 3-bromoquinolinium salts.

2. Substitution Reactions

The direct nitration, sulphonation, and halogenation of quinolinium salts have hardly been studied, since the desired groups (NO_2, SO_3H, halogen, etc.) can be introduced into the tertiary base (quinoline) before its quaternisation, or, even earlier, into the aromatic amine (or amine precursor) before its conversion into the quinoline. In the former case the substituting group can enter either the pyridine or the benzene ring of the quinoline nucleus, and in the latter case only the benzene ring.

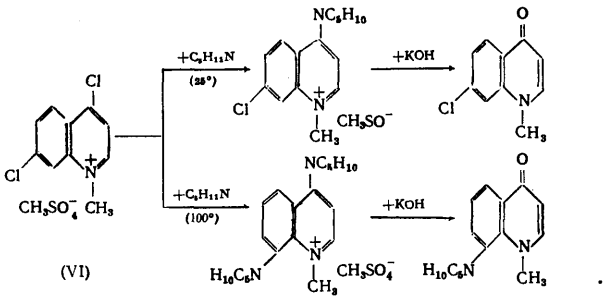
There is, however, an indication that nitration of *N*-ethylquinolinium nitrate produces the 5-nitro-derivative[78].

Halogen atoms present in the 2- or 4-position in quinolinium salts are labile and are easily replaced by other atoms or groups. This can be used to obtain cyanine dyes, which are valuable photographic emulsion sensitisers, or to obtain intermediates from which cyanine dyes can be produced. This type of reaction has been most studied.

An iodine atom in the 2-position of quinolinium salts is readily replaced by various thioether groups in the presence of triethylamine[79].

4-Halogenoquinolinium compounds are used to determine the structure of isocyanines[80], and 2-iodo- and 2-alkylthioquinolinium salts are used in the production of pseudocyanines. The hydrolysis of 4,7-dichloro-1-methylquinolinium methyl sulphate with aqueous alkali produces a mixture of 4,7-dichloro-1-methylquinol-2-one and 7-chloro-1-methylquinol-4-one[81]. The corresponding

iodide does not give quinolones on oxidation[82]. With aliphatic and aromatic amines and their hydrochlorides[81] the **4-chloro**-atom is replaced by the amino-group even at **room** temperature, and the 7-chloro-atom is similarly replaced at elevated temperature:

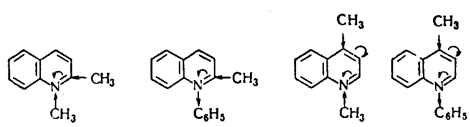


(VI)

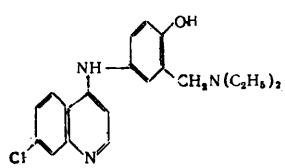
The reaction of (VI) with 4-amino-2-diethylaminomethylphenol dihydrochloride produces the quaternary salt (VII) of the antimalarial drug "Amodiaquin".†

When boiled with alcohol in the presence of triethylamine, 4-alkoxyquinolinium salts can exchange the alkoxy--radical for the alcohol residue[83].

Substitution reactions at 2- and 4-methyl groups. The hydrogen atoms of methyl groups in the 2- and 4-positions of quinolinium salts are highly labile, and can be replaced by various groups; with longer alkyl chains the hydrogen atoms on the α-carbon atom are labile. Replacement of an electron-donating group, *e.g.* methyl, on the ring nitrogen atom by an electron-withdrawing group, *e.g.* the phenyl radical, increases the lability of the hydrogen atoms, and hence the activity of these compounds

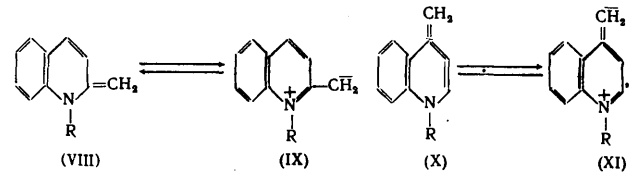


† Equation omitted from Russian text. Amodiaquin (VII) is:



(Ed. of Translation).

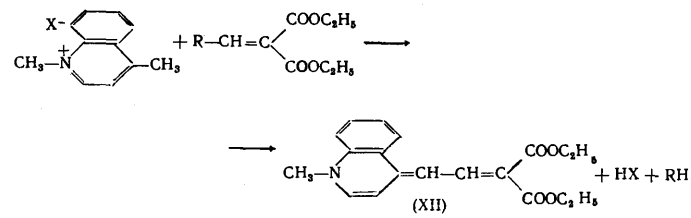
Under the action of bases, quinaldinium and lepidinium salts lose hydrogen to form the so-called methylene bases (VIII) and (X):



(VIII) (IX) (X) (XI)

which were isolated at low temperatures[84]. Compounds (VIII) and (X) can be presented as the bipolar ions (IX) and (XI), *i.e.* as betaines, which are typical nucleophilic reagents, and because of this Kharkharov[85] put forward an expanded form of the Porai–Koshits rule[86] for the activity of the methyl group.

Quinaldinium and lepidinium salts react with alkylidenemalonic esters to give the corresponding 4-methylene-1,4--dihydroquinoline derivatives (XII):[87,88]

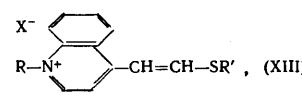


(XII)

where R = OH, OAlk, or NHAr.

Quinaldinium and lepidinium toluenesulphonates react with the acetal of β-ethylthioacrolein to form 1-methyl--4(2)-ω-ethylthiobutadienylquinolinium salts[89]. Ketomethylene compounds containing a thioether group react with lepidinium and quinaldinium salts to give cyanine dye intermediates[90]

Lepidinium salts react with trithioorthoformic ester to produce compounds of type (XIII):[91]

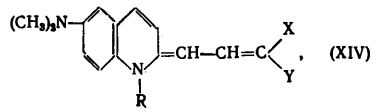


(XIII)

and as a consequence it was shown that trithioacetals react with the quaternary salts to form intermediates and symmetrical trimethinecyanines[92,93]. Halogenation of quinaldinium and lepidinium salts replaces all three hydrogen atoms of the active methyl group by halogen[94,95].

Nitroalkenes add on to the active methyl group of *N*-methylquinaldinium iodide[96,97]. Reduction of the resulting condensation products gives the corresponding amines, and hydrolysis with hydrochloric acid gives the carboxylic acids. The quaternary salts condense with mono-, di-, and tri-bromoacetaldehyde, chloral, and compounds containing

an active methylene group; thus 1-alkyl-6-dimethylaminoquinaldinium salts react with unsaturated esters and ketones to form compounds (XIV):[98,99]



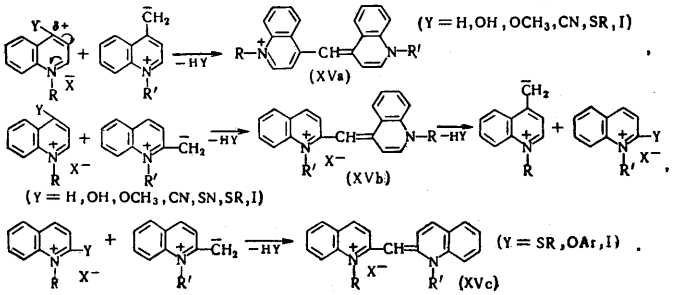
(XIV)

where R = CH_3, X = OCH_3, and Y = $COOC_2H_5$; R = C_2H_5, X = $COCH_3$, and Y = $COOC_2H_5$; and R = CH_3, X = Y = = $COCH_3$.

3. Reactions Forming Quinolinium Dyes

Quinocyanine dyes. Reactions of quinolinium salts, which lead to the formation of cyanine dyes, have been the most widely studied, because the cyanine dyes are used as sensitisers for photographic emulsions. Many reviews on the chemistry of all types of cyanines have been published[100-105].

(a) Monomethinecyanine dyes. As stated above, quinolinium compounds containing a methyl group in the 2- or 4-position readily lose a proton in the presence of bases, forming the bipolar ions (IX) and (XI), which readily react with quinolinium compounds in the 2- or 4-position. Unsubstituted quinolinium salts add the nucleophilic reagent (IX) or (XI), always in the 4-position. If the quinoline ring is substituted in the 2-position by I, OAr, SR, or CN, the addition takes place at this position; with such groups in the 4-position, reaction proceeds more readily than with the unsubstituted compounds. The reactions can be shown thus:



(Y = H, OH, OCH_3, CN, SR, I)

(XVa)

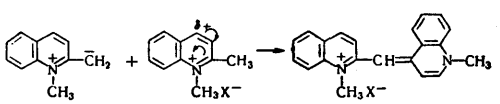
(XVb)

(Y = H, OH, OCH_3, CN, SN, SR, I)

(Y = SR, OAr, I)

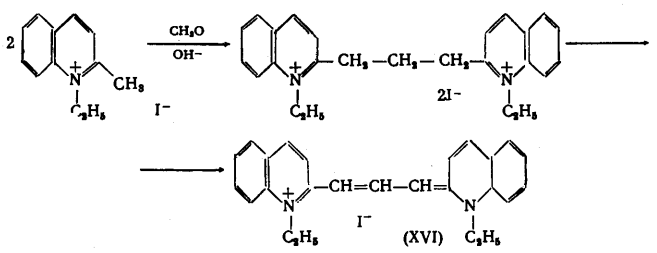
(XVc)

Quinaldinium compounds react as follows[4,106,107]:



The first dye of type (XVa) was obtained by Williams[108], and named cyanine because of its blue colour. The dyes of type (XVb), named isocyanines, were discovered simultaneously by Spalteholz[109] and Hoogewerff and van Dorp[4,106]. The pseudocyanines (XVc) were first prepared by Kaufmann and Wonderwahl[107], and their structure proved by Scheibe and Rossner[110]. All these compounds contain a single methine group and are called monomethinecyanines. They are prepared by heating alcoholic solutions of the reactants with bases such as KOH, K_2CO_3, CH_3COONa, diethylamine, triethylamine, and piperidine. This method can also be used to obtain asymmetric quinocyanines in which the second heterocyclic ring is not a quinoline ring; thus a series of thiaquinomonomethinecyanines has been prepared by reacting *N*-methylthiobenzothiazolium salts with quinaldinium or lepidinium salts in the presence of sodium acetate[111]. Monomethinequinocyanines have been prepared containing benzothiazole[112], diazole, pyrimidine[113], and other rings[114-139].

(b) Trimethinequinocyanines (carbocyanines). Quinolinium dyes containing two quinoline nuclei joined at the 2- or 4-position by a bridge of three methine groups are known as trimethinecyanine or carbocyanine dyes. The first dye of this type (XVI) was prepared by condensing *N*-ethylquinaldinium iodide with formaldehyde in alkaline medium[140]. The formation of (XVI) (which is known as pinacyanol or sensitol red) is shown by the equation:



(XVI)

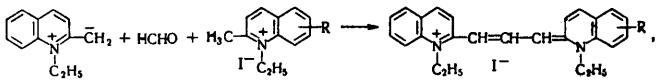
Of other methods for obtaining carbocyanines, Hamer's method[141] has found practical application. Dyes derived from lepidinium salts, where the bridge is at the 4-position, are known as cryptocyanines[142]. The trimethinecyanine dye containing one quinaldinium and one lepidinium ring can be obtained from the corresponding salts and di-*o*-(formylmethylamino)diphenyl disulphide in pyridine[143]. The reaction of 2- or 4-methylquinolinium salts with chloroform and Na_2S produces a dicyanine, pinacyanol, and cryptocyanine[144-146].

The preparation of trimethinecyanines by condensing the quaternary salts with thioformanilide, thioformamide, or formamidoxime has been suggested[147], using as condensing agents organic bases (triethylamine or pyridine), sodium acetate, acetic anhydride, or alkali metal hydroxides or carbonates[148]. Zenno[149,150] used 2-aminothiazole, formanilide, diphenylmethane, phenylacetonitrile, 2-amino-4-methylthiazole, acetamide, acetanilide, etc., as condensing agents for the production of trimethinecyanines from quinaldinium salts and orthoformate; best results were obtained with acetamide and acetanilide[150]. Brooker and Heseltine[151] prepared a number of trimethinequinocyanines with *N*-carbamoylmethyl groups; these are of use for sensitising silver halide emulsions.

Al'perovich and Ushenko[152] prepared a series of symmetrical quinocyanines containing unsaturated substituents at the 5- and 6-positions.

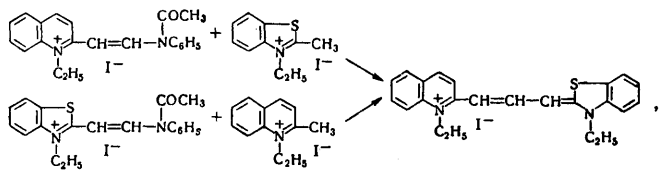
Symmetrical carbocyanines derived from lepidine having hydroxy-groups in the 6- and 7-positions have been prepared[153]. The reaction of hydroxyquinaldinium salts with diphenylformamidine in the presence of carboxylic acid anhydrides produces intermediates suitable for the production of asymmetrical dyes, the hydroxy-groups being acylated[154]. Takahashi and Satake[155] have prepared dimethylamino-substituted quinocarbocyanines, and also other analogous dyes[156,157]. Pailer and Kuhn[158] obtained trimethinecyanines from 7-acetamido-1-ethyl-2,4-dimethylquinaldinium iodide and ortho-esters of monocarboxylic

acids; a mixture of the 2,2'-, 2,4'-, and 4,4'-trimethinecyanine dyes would be expected, but chromatography showed that the product was mainly the 2,2'-derivative, with two dyes absorbing at longer wavelengths (the 2,4'- and 4,4'--derivatives). Asymmetrical quinocarbocyanines were first prepared by Mills and Raper[159]:

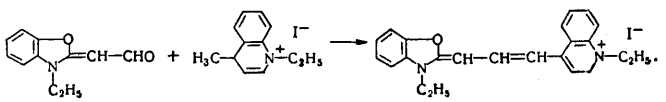


where R = 6-CH_3 or 5,6-benzo.

The most widely used method for obtaining asymmetrical carbocyanines is that of Piggott and Rodd[160], in which aminovinyl derivatives of quaternary salts are heated with other heterocyclic *N*-containing quaternary salts containing an active methyl group:

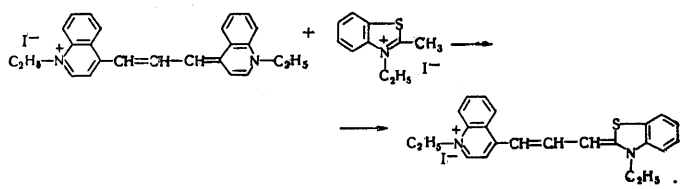


Somewhat later it was suggested that asymmetrical carbocyanines could be prepared from lepidinium or quinaldinium salts and formylmethylene compounds[161].

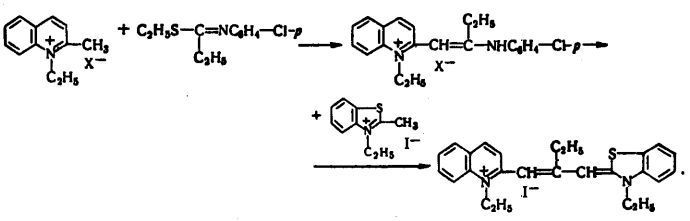


Other work which should be mentioned is that of Kiprianov and Stetsenko[162,163] on the preparation of carbocyanines with the quinone nucleus, and the preparation of quinobenzimidazolecarbocyanines[164] and quinothiadiazolecarbocyanines[165,166].

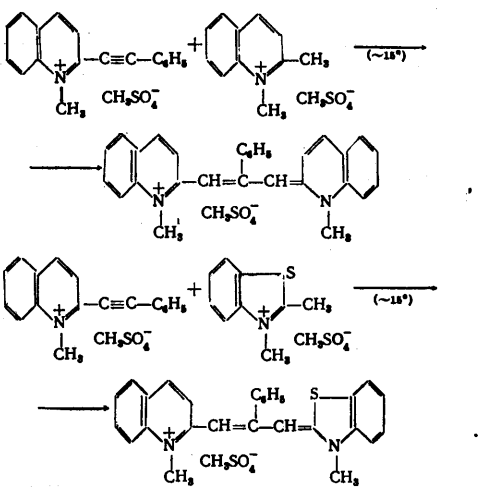
A new method for the production of asymmetrical carbocyanines, proposed by Ogata and Noguchi[167], is illustrated by the reaction:



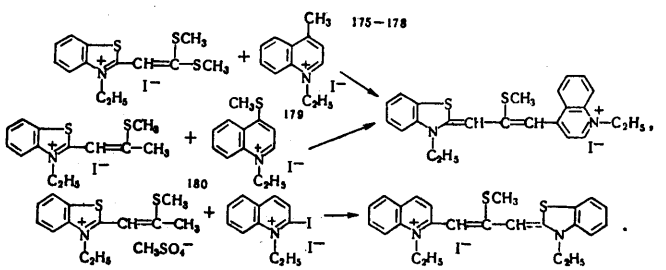
Symmetrical carbocyanines with an alkyl group on the trimethine chain can be obtained by using homologues of orthoformic ester, *e.g.* orthoacetic and orthopropionic esters, in place of the orthoformic ester. Symmetrical and asymmetrical trimethinecyanines with an alkyl radical in the *meso*-position can be prepared from acylmethylene compounds[168,169]; other asymmetrical quinocarbocyanines, derivatives of benzothiazole and benzoselenazole with *meso*-substituents, are prepared similarly[170]. Nawiasky and Speer[171] developed another method for the production of such dyes, which may be illustrated as follows:



When quinaldinium and lepidinium salts react with methyl dithioacetate, symmetrical 10-methyl trimethinecyanines are obtained as by-products. A method for the simultaneous production of *meso*-alkyl carbocyanines and thioketones has been found[172]. Kiprianov and Dyadyusha[173] have proposed an interesting method for obtaining *meso*--phenylquinocarbocyanine dyes of symmetrical or asymmetrical structure:

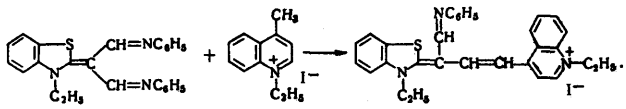


Schultz[174] prepared 1,1'-diethyl-6,6'-dimethylquinoline--*meso*-(ethylthio)trimethinecyanine iodide by condensing ethyliminodithiocarboxylic acid diethyl ester with 1-ethyl--2,6-dimethylquinolinium iodide. Other methods for the production of *meso*-(alkylthio)carbocyanines are illustrated by the following:



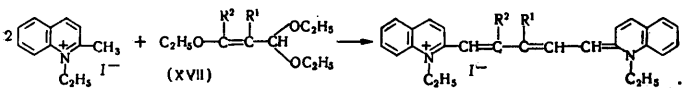
When these dyes are boiled with ammonia or primary or secondary amines, the SCH_3 group is replaced by the amino--group; OR and SeR groups on the polymethine chain are similarly replaced by the amino-group[177].

These dyes are useful for sensitising photographic emulsions, as filter dyes, etc. They differ from the dyes with an SR group on the polymethine chain in that the absorption maximum occurs at shorter wavelengths; they are also stable to aqueous alkalis. Hamer and coworkers[181] prepared trimethinecyanine dyes with an anilinomethyl group in the *meso*-position‡; these are used as intermediates for preparing trinuclear dyes. The method can be illustrated as follows:

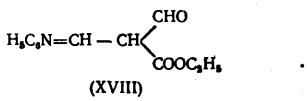


N-Ethylquinaldinium iodide reacts with $C_6H_5NHCCl_2$ to form a *meso*-substituted trimethinecyanine with the anilino-group in the 10-position[182]. Methods have been developed for the preparation of carbocyanines with the CN group in the polymethine chain[183,194].

(c) Pentamethinequinocyanines (dicarbocyanines). Pentamethine dyes are the vinyl analogues of the trimethines, and are used as sensitisers for photographic emulsions in the infrared region. They were first obtained by König[185] by condensing the quaternary salts with β-ethoxyacrolein acetal (XVII), the vinyl analogue of orthoformic ester. The acetal may be substituted in the α- or β-position, when chain-substituted pentamethinecyanine dyes are obtained[186]:

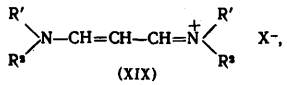


Kendall and Edwards[187] replaced compound (XVII) by its thio-analogue $C_2H_5SCH{=}CHCH(SC_2H_5)_2$. Compound (XVIII) reacts with quinaldinium salts to form dicarbocyanines with the ethoxycarbonyl group in the methylene chain[188].



(XVIII)

β-Formyl-β-chloro-α-phenoxyacrylic acid reacts with 1-ethylquinaldinium iodide in ethanol in the presence of triethylamine, giving off CO_2 and forming a dye[189]. The use of β-anilinoacrolein anil can give symmetrical or asymmetrical pentamethinequinocyanines[190-192]. The anil can be replaced by its derivative:



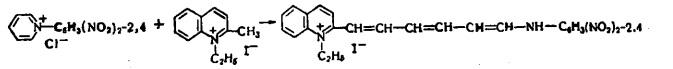
(XIX)

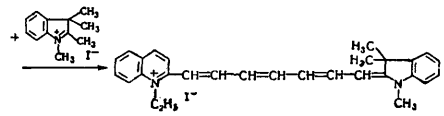
in which case the reaction is carried out in alcoholic solution in the presence of pyridine or piperidine[193]. Asymmetrical dicarbocyanines can be obtained from (XIX) in acetic acid[194] or β-anilinoacrolein anil hydrochloride in pyridine solution[195]; this last method can provide dicarbocyanines with an alkyl group on the polymethine chain[196].

‡ Presumably the authors are referring to the 3-ethyl-2-(dianilinoisopropylidene)benzothiozoline at this point (Ed. of Translation).

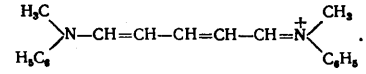
Quinaldinium and lepidinium salts also form dicarbocyanines with 1,1,3,3-tetraalkoxypropane or 1,1,3,3-tetraacyloxypropane in pyridine[197]; good yields are obtained. Methods are also known for preparing dicarbocyanines with a CN group in the *meso*-position[183,184].

(d) Heptamethinecyanine dyes (tricarbocyanines) of the quinoline series can be prepared by condensing quinaldinium or lepidinium salts with compounds containing five methine groups and having, at the ends of the chain, groups which are readily split out; or with compounds which can react during the condensation to form a pentamethine group. Wahl[198] used pyridine salts which can decompose to form derivatives of glutaconic aldehyde; symmetrical and asymmetrical dyes can be produced, since the reaction takes place in two stages:





Best results are given by using, instead of the pyridinium salts, their amine reaction products, *e.g.* (XX):[191]



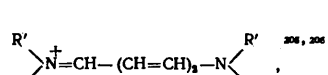
(XX)

The condensation is carried out in alcoholic solution in the presence of inorganic[199] or organic[200] bases.

4,4′-Tricarbocyanines (xenocyanines) are said to be obtained by condensing 2 moles of a lepidinium salt with 1 mole of glutaconic aldehyde hydrohalide in the presence of an organic base stronger than pyridine[201]. The dianilide may be substituted in the polymethine chain[202]. Dyes of this type, and also their 2,2′-analogues, have been prepared from lepidinium or quinaldinium salts and benzoxazolepyridinium chloride[203], which decomposes during the reaction to produce the polymethine chain.

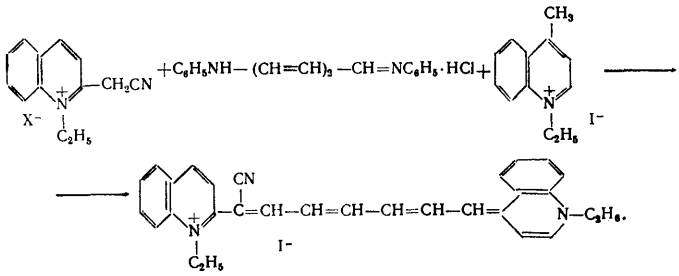
Tricarbocyanines can also be formed by the action of quinaldinium or lepidinium salts on the reaction product of 1-ethyl-2-iodoquinolinium iodide with pyridine, 1-ethyl-2-(1-pyridinium)quinolinium diiodide[204].

Asymmetrical heptamethinecyanines can be obtained analogously to the pentamethinecyanines by condensing a quinaldinium salt and another heterocyclic quaternary salt in two stages with

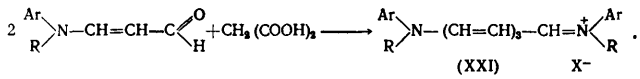


pyridylpyridinium chloride[205], glutaconic aldehyde tetraacetal[206], or a salt thereof[209]. Similar dyes can be obtained by condensing a heterocyclic pentamethine aldehyde with a heterocyclic quaternary salt containing a methyl group[210].

Kendall and Doyle[183,184] prepared tricarbocyanines with a CN group on the polymethine chain:

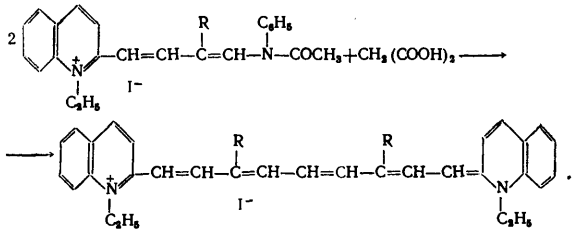


Tetra- and penta-carboquinocyanines, which show a sensitisation maximum at 940 and 1120 mμ respectively, have also been prepared, using a compound of type (XXI) for forming the bridge[212-214]:

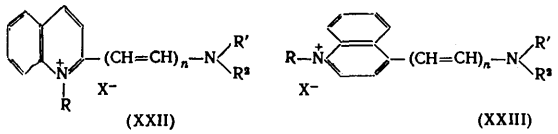


(XXI)

Ogata[215] developed a method for preparing nonamethine-quinocyanines:

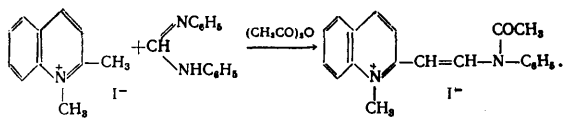


(e) Hemiquinocyanine dyes have structure (XXII) or (XXIII):



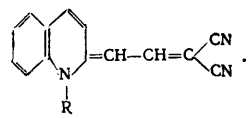
(XXII) (XXIII)

A special case is when $n = 1$, *i.e.* the aminovinyl derivatives, which are intermediates in the production of asymmetrical carbocyanines. They were first obtained by heating a quinaldinium salt with diphenylformamidine in acetic anhydride[216,217]:



Takahashi and coworkers[218-221] prepared a series of aminovinyl compounds by fusing quinaldinium salts with formamidine; the products have been used as pharmaceutical dyes. Heating quinaldinium or lepidinium salts with a diarylformamidine in the presence of orthoformic ester in an alcoholic medium produces the aminovinyl derivatives in higher yields[222,223]. Analogous aminovinyl compounds can be obtained by heating the quaternary salts with orthoformic ester and a primary or secondary amine[224-227]. The production and investigation of a number of aminovinylquinolinium derivatives have been reported[228-230]. Similar studies by Japanese chemists were carried out to find the optimum conditions for preparing these compounds and to investigate their pharmacological properties[156,231-233].

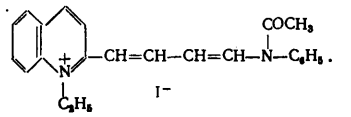
The condensation of phenylhydrazine or *N*-ethylphenylhydrazine with ethyl orthoformate and quinolinium salts produces the phenylhydrazinovinyl derivatives. Pilyugin and coworkers[234] obtained the anilinovinyl derivatives of *N*-arylquinolinium salts by reacting diphenylformamidine with *N*-phenylquinaldinium perchlorate and with *N*-phenyl-5,6-benzoquinaldinium iodide. The acetanilidovinyl derivatives react with malononitrile in the presence of an organic base to form (XXIIIa), which is used as a supersensitiser for silver halide emulsions[235]:



(XXIIIa)

The arylamino- and acylarylamino-vinyl derivatives are hydrolysed in aqueous alcohol to the formylmethylene compounds[236-238].

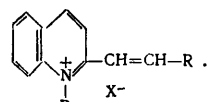
By replacing diphenylformamidine by its vinyl analogues (*e.g.* $C_6H_5NH-CH=CH-CH=NC_6H_5$), quinolinium compounds with a longer chain in the 2- or 4-position can be obtained[190-192]:



To obtain a hexamethine chain, the quaternary salts are condensed with the product obtained by first condensing the salt with *N*-dinitrophenylpyridinium chloride[198].

(f) Styrylquinolines. Quinostyryl dyes can be considered as derivatives of styrene, from which they are in fact named.

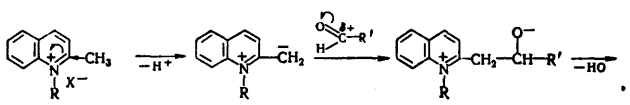
Quinostyryl compounds with a quaternary nitrogen atom (XXIV) are cyanine dyes:



(XXIV)

They were first obtained by Kaufmann and Vallette[239] from quinolinium salts containing an active methylene group and aromatic aldehydes in alcoholic solution in the presence of piperidine; pyridine or acetic anhydride can also be used

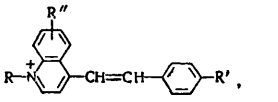
as reaction medium. Mills and coworkers[159] have studied the mechanism of this reaction. Electronically, the reaction can be represented:



(XXIV)

The preparation of these dyes has been much studied, since they are used as sensitisers, supersensitisers, and desensitisers for photographic emulsions, and are also physiologically active. In 1934 Atabekova *et al.*[240] prepared 6-ethoxy-1-methyl-2-(*m*-nitrostyryl)quinolinium methyl sulphate (Pinakryptol Yellow), which has a desensitising action. Mikhailov and Pryanishnikov[241] proposed the production of analogous compounds by condensing various quinaldinium salts with 3-nitrobenzaldehyde or 4-dimethylamino-3-nitrobenzaldehyde in the presence of alcohols containing more than two carbon atoms; there is also an analogous American patent[242]. Maurin[243] showed that *N*-methyl- and *N*-ethyl-4-hydroxyquinaldinium iodide forms styryl dyes with *p*-dimethylaminobenzaldehyde, cinnamaldehyde, vanillin, and anisaldehyde in the presence of piperidine; benzaldehyde does not react. Meyer and coworkers[244] carried out a similar condensation of 6- and 8-methyl-4-hydroxyquinaldinium salts and the corresponding 4-alkoxy- and 4-chloro-derivatives with salicylic, cinnamic, and anisic aldehydes, and with piperonal, vanillin, and dimethylaminobenzaldehyde in the presence of traces of piperidine or diethylamine, but in the absence of a solvent. 3-Dialkylaminostyrylquinolinium salts have been obtained by condensing 3-dialkylaminobenzaldehydes with quinaldinium salts in piperidine[245].

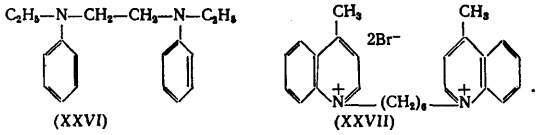
The condensation of 1-methyl-4-phenoxyquinaldinium iodide with piperonal in the presence of triethylamine produces 1-methyl-2-(3,4-methylenedioxystyryl)-4-phenoxyquinolinium iodide[246]. If a secondary amine, *e.g.* piperidine, is used as catalyst, the phenoxy-group is replaced by the amino-group. 2-Amino-4-styrylquinolinium compounds have been prepared and their pharmacological properties studied[247]. Stanek and Zvěřina[248] showed that 1-methylquinaldinium iodide reacts with benzaldehyde in the presence of piperidine or morpholine to form 1-methylstyrylquinolinium iodide. Doja and Sinha[249,250] prepared styryl compounds by condensing *p*-dimethylamino- and *p*-diethylamino-benzaldehyde with 6-amino-, 6-formamide-, 6-acetamido-, 6-chloro-, 6-bromo-, and 6-iodo-1-ethylquinaldinium iodides; the 1-ethyl-6-formamido- and -acetamido-styrylquinaldinium iodides were found to be very good sensitisers. *cis*- and *trans*-isomers of 2-styrylquinolinium compounds have been prepared[251]: condensing quinaldinium salts with aromatic aldehydes in the presence of piperidine gave the *trans*-isomers; reacting the quinaldines with the aldehydes in acetic anhydride gave the *cis*-2-styrylquinolines, which were then quaternated. Ito and Matsumura[252] obtained a high yield of the iodide of *trans*-1-(1′-ethylquinol-2′-yl)-2-(8″-hydroxyquinol-5″-yl)ethylene by heating an equimolar mixture of 5-formyl-8-hydroxyquinoline and 1-ethylquinaldinium iodide in acetic anhydride or propan-2-ol in the presence of piperidine. Heating quinaldine with 5-formyl-8-hydroxyquinoline in acetic anhydride gives 1-(8-hydroxyquinolyl)-2-(quinol-2-yl)ethylene, which with an alcoholic solution of ethyl iodide produces the *cis*-isomer, which is not converted into the *trans*-isomer by boiling with acetic anhydride. The *cis*- and *trans*-isomers of 1-ethyl-2-(3′-methoxy-4′-hydroxystyryl)quinolinium iodide were obtained similarly from vanillin and 1-ethylquinaldinium iodide or quinaldine. The condensation of 1-methylquinaldinium iodide with veratryl aldehyde in the presence of morpholine gives 1-methyl-(3,4-dimethoxybenzylidene)-quinaldinium iodide, which is hydrogenated to *d,l*-cuspareine in the presence of platinum[253]. Bahner and coworkers[254] prepared a number of 1-alkyl-4-(*p*-dimethylaminostyryl)quinolinium iodides (XXV) to study their anti-tumour activity:



(XXV)

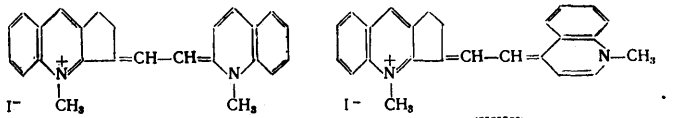
where R′ = $(CH_3)_2N$, CH_3CONH, NO_2, or F, and R″ = H, 6-I, 3-CH_3, 8-CH_3, or 8-C_6H_5.

Styrylquinolinium compounds containing two or more styryl groups have been prepared by condensing compounds of type (XXVI) with 2- or 4-methylquinolinium salts[255], or condensing substituted monoarylaldehydes with alkylene-bis-quinolinium salts of type (XXVII):[256]



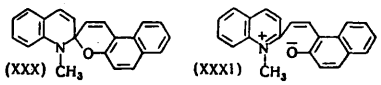
(XXVI) (XXVII)

Lal and Petrow[257] condensed 2,3-dihydroquinindene ethyl iodide with 2- or 4-(2-anilinovinyl)-1-methylquinolinium iodide to obtain the quinostyryl analogues (XXVIII) and (XXIX):



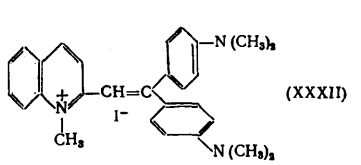
(XXVIII) (XXIX)

The reaction between *N*-methylquinaldinium methyl sulphate and 2-hydroxy-1-naphthaldehyde in the presence of piperidine has produced 1-methyl-α-(2-hydroxy-1-naphthylidene)quinaldinium perchlorate, which is converted by ammonia into the compound of structure (XXX) or (XXXI):[258]



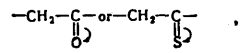
(XXX) (XXXI)

Philips[259] prepared styrylquinolinium analogues by condensing cinchoninic aldehyde with 2- or 4-methylquinolinium salts. Michler's ketone does not react with quinaldinium salts in acetic anhydride, but the methyl sulphate salt of the *N*-methyl derivative of the corresponding thioketone has given the dye (XXXII) with maximum absorption at 538 mμ:[260]



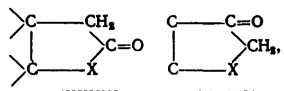
(XXXII)

(g) Non-ionic dyes. Meroquinocyanines. Cyclic (including heterocyclic) compounds containing the group



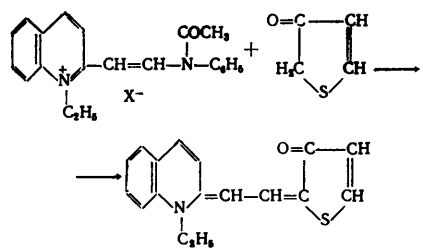
possess labile hydrogen atoms and therefore readily react with quinolinium compounds containing active groups, to form non-ionic polymethine dyes known as merocyanines. These are highly soluble in non-polar solvents and exhibit solvatochromism [261].

Kendall [262] first prepared a number of meroquinocyanine dyes in 1933 by reacting organic compounds of the formula (XXXIII) or (XXXIV):

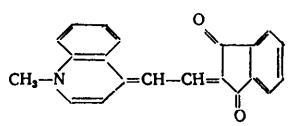


(XXXIII) (XXXIV)

where X = C, S, or O, with quinolinium salts substituted in the 2- or 4-position by halogen atoms or thioether, seleno-ether, aminovinyl, or methyl groups, usually in the presence of basic catalysts:



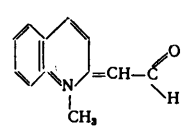
Heating acetanilidomethenylindane-1,3-dione with 1-methyllepidinium iodide in pyridine gave the dye (XXXV):



(XXXV).

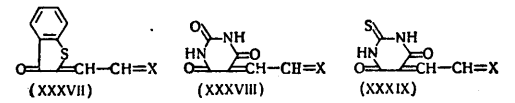
As ketomethylene component there may also be used rhodanine, thiohydantoin, etc. [263] Quinolinium salts substituted in the 2- or 4-position by halogeno-, cyano-, or thio--ether groups react with keto- or thioketo-methylene compounds to form dyes not containing methine groups [264-268].

Formylmethylene bases such as (XXXVI) also form merocyanines with ketomethylene-substituted cyclic compounds [269]:



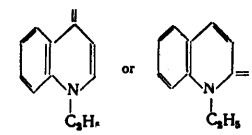
(XXXVI).

Brooker [270] has prepared a series of dimethinerhodanines (XXXVII)–(XXXIX) by reacting quinolinium salts 2- or 4-substituted by an *N*-arylaminovinyl group, with 2(1)-thionaphthenone, thioindoxylic acid, or barbituric acid or its derivatives:



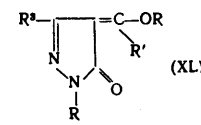
(XXXVII) (XXXVIII) (XXXIX)

where X =



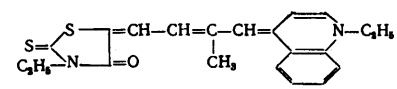
Improved yields are obtained by using alkali metal hydroxides, carbonates, or alkoxides as condensing agents [271].

Compounds (XL), obtained by boiling the pyrazolone derivative with the ortho-ester of a monocarboxylic acid, react with *N*-ethylquinaldinium iodide to form dimethine-merocyanines substituted on the methine chain [272]:

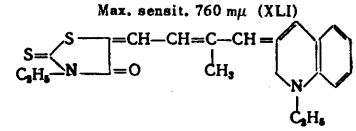


(XL)

The patent literature also refers to the preparation of the tetramethinemeroquinocyanines (XLI) and (XLII), which show maximum sensitising activity in the infrared [273]:

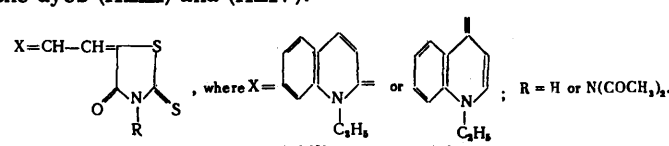


Max. sensit. 760 mμ (XLI)



Max. sensit. 730 mμ (XLII)

The production of oxazolone dyes is described in another patent [274]. Reacting ethylrhodanine with the product obtained from diphenylformamidine and 7-acetamido-1-ethyl--2,4-dimethylquinolinium iodide produces a mixture of isomers, the relative proportions of which depend on the condensation conditions [158]. Sytnik *et al.* [275] have prepared the dyes (XLIII) and (XLIV):



(XLIII) (XLIV)

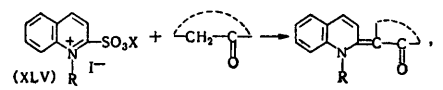
A number of di-, tetra-, and hexa-methinemeroquinocyanines in which the second ring is a rhodanine ring have also been prepared [276]. Similar quinomerocyanines, imidazoline-2-thione-4-one derivatives, were prepared by Jeffreys [277].

Zenno [278] obtained meroquinocyanines by reacting 3-phenyloxazol-5-one, 3-ethylrhodanine, 3-phenylrhodanine, 1-methyl-3-phenylpyrazolone, and 3-hydroxythionaphthenone with 2,2-(*NN'*-diphenylhydrazino)divinylquinoline dimethiodide or diethiodide. The reaction of barbituric acid, thiobarbituric acid, 1,2-diaryl-3,5-dihydroxypyrazolidines, or other heterocyclic diketomethylene compounds

with orthoformic ester and quinaldinium salts also produces meroquinocyanine dyes[279,280]. With malonic ester only symmetrical quinocarbocyanines are obtained[279]. Using acetic or benzoic anhydride instead of the orthoformic ester produces merocyanines methyl- or phenyl--substituted on the polymethine chain[280]. Merocyanines are also obtained if orthoformic ester is condensed with barbituric or thiobarbituric acid, and the resulting dye reacted with 1-methyl- or 1-ethyl-quinaldinium salts[281].

If merocarbocyanines are heated with quinaldinium salts, there is an exchange of heterocyclic nuclei and quinomerocyanines are produced[282].

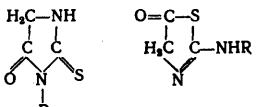
Compounds of type (XLV) react fairly readily with cyclic ketomethylene or thioketomethylene compounds to form merocyanines[283]:



(XLV)

where X = H or Na.

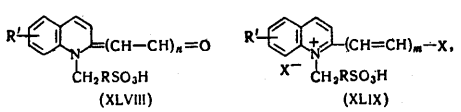
Jeffreys[284] prepared merocyanines from quinolinium salts and (XLVI) or (XLVII):



(XLVI) (XLVII)

Meroquinocyanines with an alkoxy-group on the methine chain are known[285].

Quinomerocyanines with an acylamino-group in the ketomethylene ring have also been prepared[286]. Brooker and Heseltine[287] have obtained merocyanines containing the sulphonic acid group by condensing quinolinium salts having active groups which are readily split out, with a ketomethylene compound $H_2C-SO_2-X-C=O$ (where X represents the atoms making up a five-membered ketomethylene ring). Bach and Brunken[288] prepared merocyanines containing the sulphonic acid group by condensing a quinolinium compound (XLVIII) or (XLIX):

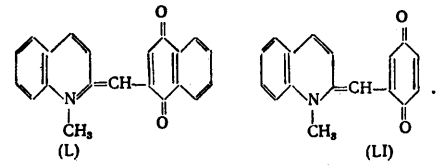


(XLVIII) (XLIX)

where X = alkyl, halogen, SR", or OR", with the five- or six-membered heterocyclic ketomethylene compounds rhodanine, 2-thiohydantoin, 2-thiooxazolid-4-one, pyrazol-5-one, 3-hydroxythionaphthene, barbituric acid, or 2-thiobarbituric acid.

Sytnik and others[289,290] prepared di- and tetra-methinequinomerocyanines containing an electropositive substituent in the α-position, in order to study their optical properties.

(h) Other types of non-ionic dyes. In 1937 Kröhnke[291] described the reaction of *N*-methylquinaldinium iodide with 2,3-dichloro-1,4-naphthoquinone in alkaline medium. Gates[292,293] mixed benzene solutions of 1,4-naphthoquinone and the methylene base derived from *N*-methylquinaldinium iodide to obtain (L):

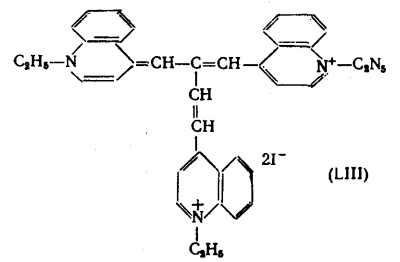


(L) (LI)

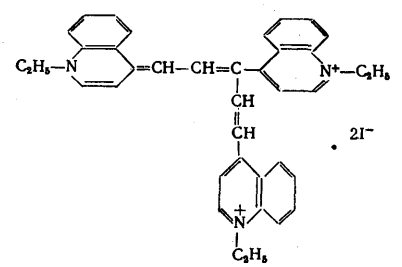
Kiprianov[294] showed that in the presence of alkalis quinaldinium salts react with benzo- and naphtho-quinones to form dyes such as (L) and (LI); the reaction mechanism was given.

Zenno[295] showed that quinaldinium and lepidinium salts react readily with alloxan and 5,5-dibromobarbituric acid to form dyes; with acetylisation, isatin β-anilide and *NN'*-diphenyl-3,5-dioxopyrazolidine, indigo dyes are formed.

(i) Trinuclear quinocyanine dyes. In the production of bis(1-ethylquinol-4-yl)trimethinecyanine iodide from *N*-ethyllepidinium iodide and triethyl orthoformate, small amounts of another dye were formed; this was named Neocyanine[296]. Its structure was investigated by Hamer[297] and König[298], who suggested formulae (LIII) and (LIV):



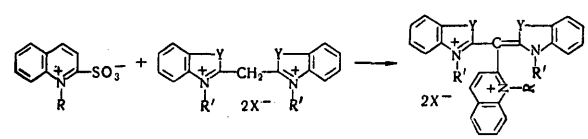
(LIII)



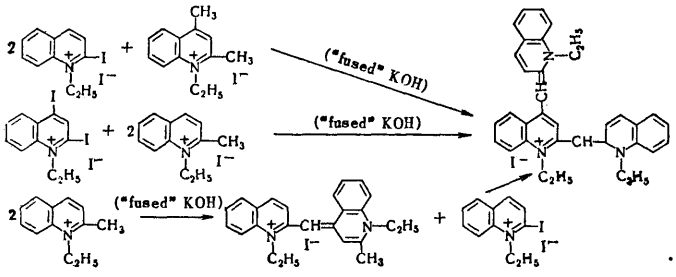
(LIV)

Neocyanine was found to be a very effective infrared sensitising agent for photographic emulsions and to be physiologically active, and it has accordingly been much studied to find optimum conditions for its formation and for the preparation of related dyes with three heterocyclic nuclei[299-317].

Larivé and Collet[318] prepared trinuclear quinocyanine dyes by the reaction:

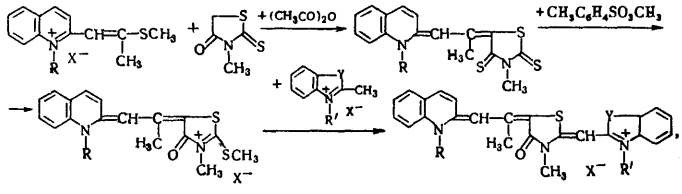


Trinuclear cyanine dyes have been prepared in which the polymethine chain is substituted in the *meso*-position by a pyrrole, pyrrocoline, or indoline nucleus[319]. Trinuclear pentamethinecyanines can be obtained by using the 2-acetanilidovinylquinolinium compound instead of the 2-methylmercapto-derivative. Brooker and Smith[320,321] prepared trinuclear dyes by the reactions§:



It is interesting that the absorption spectra and sensitising action of these compounds consist of two bands separated by a region of full transmission.

A number of trinuclear quinocyanine dyes have been prepared by condensing lepidinium or quinaldinium salts with five-membered heterocyclic thioketomethylene compounds, followed by methylation of the resulting merocyanine and condensation with a quaternary salt, in accordance with the reactions[322,323]:

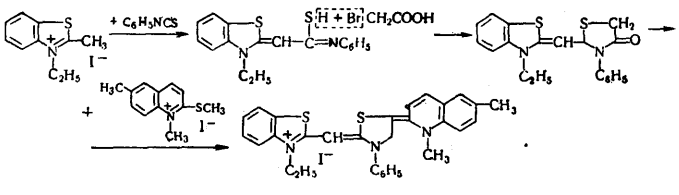


where Y = S, Se, O, or $-CH=CH-$.

Similar dyes are obtained by condensing 5-anilinomethylene-substituted monomethinecyanine derivatives of thiazolin-4-one or pyrazolone with quinaldinium or lepidinium salts[324,325].

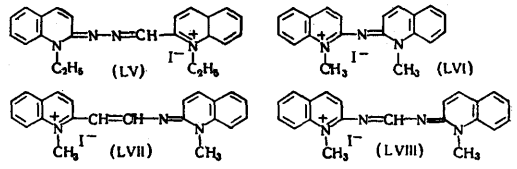
Dyes with a central thiohydantoin nucleus have been prepared[326], and are used in colour photography. Dyes with a central oxadiazole, thiadiazole, or triazole nucleus have also been proposed as sensitisers for colour photography[327-329].

Thompson[330] has prepared a series of trinuclear dyes by the interesting method:

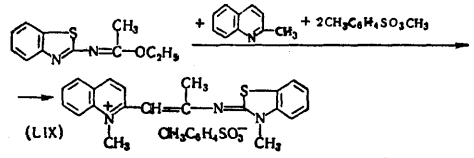


The reaction of thiazolone cyanine dyes with diphenylformamidine, β-anilinoacrolein anil hydrochloride, or glutaconic aldehyde dianil hydrochloride gives anilino- (or acetanilido-) methine derivatives, which produce trinuclear dyes with quinaldinium and lepidinium salts[331]. The optical and photographic properties of such trinuclear dyes (merocyaninecarbocyanines) have been studied by Levkoev and coworkers[332,333].

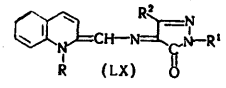
(j) Quinolinium dyes with hetero-atoms in the polymethine chain. Fuchs and Grauaug[334] obtained quinolinium dyes (of the cyanine type) in which the $-CH=CH-$ group is replaced by nitrogen, *e.g.* (LV), by reacting quinolinium hydrazines with appropriate heterocyclic 2-aldehydes. Kendall[335,336] and Hamer[337] prepared the similar dyes (LVI), (LVII), and (LVIII):



Kendall and Fry[338] developed a method for the production of the asymmetrical *meso*-substituted dyes (LIX) by reacting the amino-compounds with ortho-esters and condensation of the intermediates with quinaldine with simultaneous quaternation:

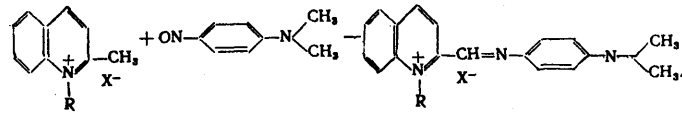


The preparation of the azamerocarbocyanine dyes of the quinolinium series (LX) has been described[339]:



where R^1 and R^2 are H, alkyl, or aryl and R is *n*-alkyl of 1–4 carbon atoms.

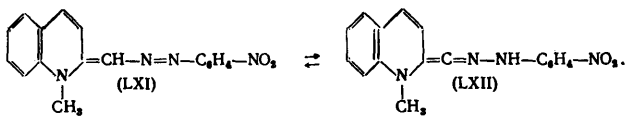
(k) Styryl analogues (azomethines). Hamer[340] obtained a styryl analogue with a nitrogen atom in place of a methine group by reacting a quinaldinium salt with *p*-nitrosodimethylaniline:



The formation of azomethine dyes has been studied in more detail by Katayanagi[341]; they are also produced by condensing quinaldinium or lepidinium salts with 1-ethyl-2-phenyl-3-nitrosoindole[342].

§ "Fused" KOH is not mentioned in either of the papers cited, although one[320] refers to powdered KOH (Ed. of Translation).

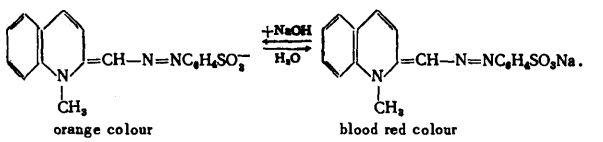
Monoazo-compounds of quinaldinium salts, such as (LXI), are obtained by the reaction of diazonium salts with the methylene bases (derived from quinaldinium salts) in neutral ether[343]:



(LXI) (LXII)

This dye was found to be identical with (LXII), which was prepared from 1-methyl-ω-bromoquinaldinium bromide and *p*-nitrophenylhydrazine[344]. The existence of a tautomeric equilibrium is indicated.

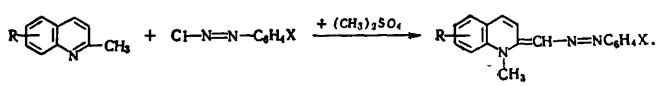
N-Methylquinaldinium iodide and phenyldiazonium chloride react analogously. Under analogous conditions diazotised sulphanilic acid also forms a dye:



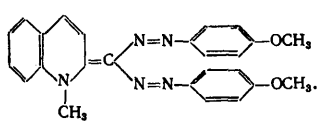
orange colour blood red colour

Good yields of the dyes are obtained in each case.

Humphries[345] prepared monoazo-compounds by the action of *p*-nitrophenylnitrosamine or the anti-diazotate on quinaldinium or lepidinium salts. Königs and Büren[346] obtained 1-methylphenylazomethylene-1,2-dihydroquinoline and certain of its derivatives by reacting a quinaldine with a diazo-compound in the presence of dimethyl sulphate in an alkaline medium; there is simultaneous alkylation and azo-coupling:



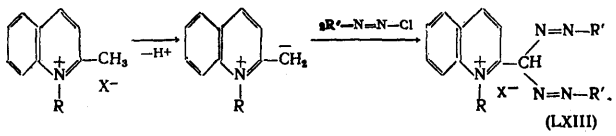
Lepidine reacts analogously. The reaction of 1-methylquinaldinium methyl sulphate with a *p*-methoxyphenyldiazonium salt produces the bis-azo-dye:



These azo-dyes have shown *in vitro* bactericidal activity against staphylococci. It is of interest that 1-methyl-2-methoxylepidinium and 1-methyl-4-methoxyquinaldinium methyl sulphates do not couple with phenyldiazonium chloride in alkaline medium.

Seyhan[347] prepared the two methylene-azo-dyes of the quinoline series 4-(4-nitrophenylazomethylene)- and 4-(2,4-dinitrophenylazomethylene)-1-ethyl-dihydroquinoline, by the action of concentrated potassium hydroxide solution on the 4-nitro- and 2,4-dinitro-phenylhydrazones of quinoline-4-aldehyde. In solution the colour of both dyes depends on the solvent used.

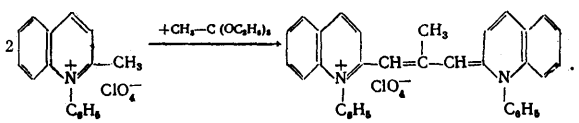
Wahl and Le Bris[348] showed that in alkaline medium quinaldinium and diazonium salts react to form the bis-azo-dyes (LXIII). They suggest that both diazo-groups couple simultaneously, since no monoazo-dye could be isolated.



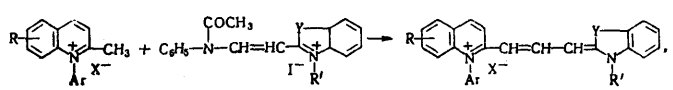
(LXIII)

A simple method for the production of methyleneazo-dyes has been proposed, by the reaction of quinaldinium or lepidinium salts with antidiazotate in aqueous or alcoholic solution[349].

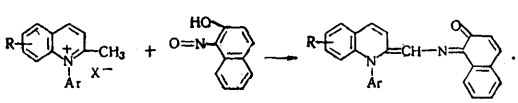
(1) *N*-Arylquinocyanines. The preparation and study of quinocyanines containing aryl radicals on the nitrogen heteroatom have become possible only by the development of general methods for the production of *N*-aryl-quinolinium, -quinaldinium, and -lepidinium salts. The presence of the electron-withdrawing aromatic radical on the nitrogen in conjugation with a methyl group in the 2- or 4-position renders the methyl group more active than in the corresponding *N*-alkyl compounds. Thus even *N*-aryl-benzoquinaldinium iodides react with orthoformic ester, and not just the sulphonates, as is the case with the *N*-alkyl analogues. Also reaction occurs with orthoacetic ester, which is not the case with the *N*-alkyl compounds[350]:



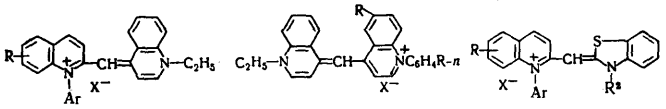
N-Aryl-quinaldinium and -lepidinium salts, as already stated, react with orthoformic and orthoacetic ester to produce symmetrical quinocarbocyanines[14,22,37,41-47,350,351]; they also react with acetanilidovinyl-substituted heterocyclic compounds to produce asymmetrical carbocyanines[14,23,24,41-46,234,351,354]:



where Y = $-C-(CH_3)_2$, $-S-$, or $-CH=CH-$; with aromatic aldehydes to produce styrylquinolinium dyes[14,22-24,37,41,44-46,351,355]; with nitroso-compounds to produce azomethines, the styryl analogues[350,351,356,357]; and with nitrosophenols to produce non-ionic azomethines which exhibit solvatochromism[353]:

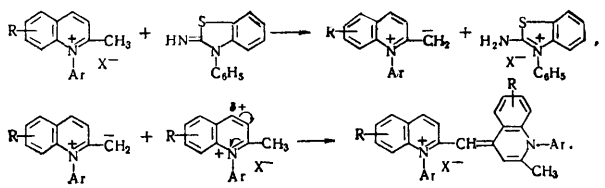


N-Aryl-quinaldinium and -lepidinium salts have also been used[22-24,37,42-44,46,358,359] to prepare monomethinecyanines of the types:

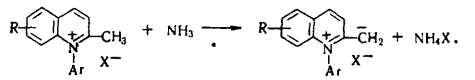


where R = C_2H_5 or C_6H_5.

In the preparation of monomethinecyanines containing the benzothiazole ring, isocyanines are obtained as by-products, possibly by the reactions:



The first stage of methylene base formation can also be effected by ammonia:

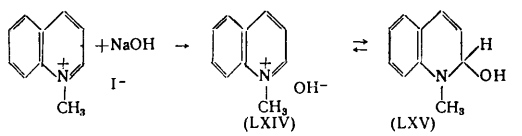


5,6-Benzoquinaldinium salts do not form isocyanines in this reaction, because of steric hindrance; this can presumably be used to prove the structure of the arylquinaldinium salts obtained by cyclisation of asymmetrical diarylamines such as phenylnaphthylamine.

Mono-[360] and bis-azo-dyes[361] have been obtained from *N*-arylquinaldinium salts.

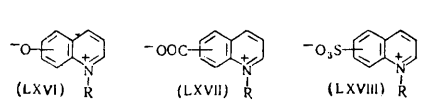
4. Other Reactions

(a) Ion exchange reactions. Quinolinium salts, like ammonium salts, are ionic; they are readily soluble in water, dissociating into an organic cation and, usually, an inorganic anion. The aqueous and alcoholic solutions are fairly good conductors of electricity. In addition to normal ion-exchange reactions, these salts also exhibit certain specific reactions; thus when caustic alkalis react with quinolinium salts, there is first an exchange of ions, with the formation of the ammonium base (LXIV), which is as strong as caustic alkalis; on standing, however, the conductivity of the aqueous solutions falls (LXIV) changing into the pseudobase (LXV):



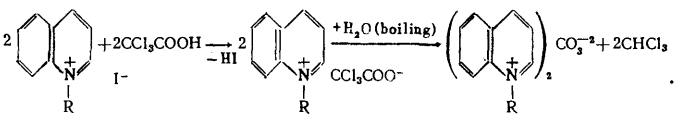
This effect was first studied by Hantzsch and Kalb[362]; Aston and Lasselle[363] studied the kinetics of this reaction.

As stated, the reaction of quinaldinium and lepidinium salts with alkali produces the so-called methylene bases (VIII) and (X), which are bipolar ions of the betaine type. The action of caustic alkalis on quinolinium salts containing OH, COOH, or SO_3H groups produces the betaine-like compounds (LXVI), (LXVII), and (LXVIII)[364-366]:



Simonov[367] has studied in detail the conversion of 6-amino-substituted 1-alkylquinolinium salts in the presence of bases. Harris[368] has shown that mixing boiling acetone solutions of $NaCu_2I_3$ and methylquinolinium iodide produces *N*-methylquinolinium cupriodide, which is also obtained by treating *N*-methylquinolinium iodide with solutions of NaI and Cu_2I_2. Alkali metal salts of complex acids, *e.g.* $K_4[Fe(CN)_6]$, $K[HgI_3]$, $Na_3[Co(CN)_6]$, $Na_3[Co(NO_2)_6]$, $K[BiI_4]$, and $K_4[Mo(CN)_8]$, in aqueous solution react with quinolinium salts to precipitate the corresponding quinolinium salts of the complex acids[369-376]. The colour of these precipitates and of quinolinium salts with other anions has been discussed[377,378]. Treatment of an aqueous solution of a quinolinium salt with hydrochloric acid (1 : 1) and ferric chloride precipitates the chloroferrates, which may be used instead of the picrates, chloroaurates, and chloroplatinates for the identification of the quaternary salts[379].

With thionyl chloride in acetic anhydride at 0° quinolinium salts produce dichloroiodides, a 2-iodo-atom being replaced by chlorine[380]. Vilsmeier[381] formed quaternary ammonium (including quinolinium) carbonates as follows:



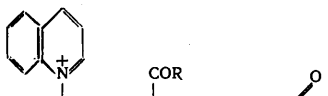
The products are valuable as additives when dyeing with indigo dyes, and as intermediates for the production of other salts, *e.g.* tartrates and citrates of the quaternary bases. Knowing that certain aliphatic amine nicotinates are therapeutically active, Simon[382] prepared *N*-methyl-*N*-ethyl-, and *N*-propyl-quinolinium nicotinates by reacting the corresponding halide with an aqueous suspension of silver nicotinate.

(b) Elimination reactions. When quinolinium salts with an alkyl or aralkyl radical on the nitrogen atom are heated above their melting point, the substituting radical is split out as the halide, leaving the quinoline; this has been used to separate mixtures of quinoline and pyridine bases having very similar boiling points, *e.g.* quinoline, isoquinoline, and methylquinolines, the decomposition temperatures of the corresponding quaternary salts being relatively far apart. The method can also be used to separate mixtures of halides otherwise difficult to separate, *e.g.* *o*- and *p*-chlorobenzyl chloride[383]. Later Menzl[384] developed a method for the decomposition of the quaternary salts by heating with ethanolamines or other alkanolamines, which again produces the quinoline and the alkyl halide. Kursanov and coworkers[385-387] investigated the reaction of 1-alkoxymethylquinolinium salts with alcohols and carboxylic acids and their salts and esters; in each case the alkoxymethyl radical is split out. Raison[388,389] found that of *m*- and *p*-aminobenzyl-substituted quinolinium salts, only the former are stable; the *p*-isomers are readily decomposed to form quinoline, and are stable only in the presence of mineral acid or as the acyl derivatives.

IV. USES OF QUINOLINIUM COMPOUNDS

(a) Quinolinium salts. Quaternary ammonium salts, including quinolinium salts, form the main type of cationic surface-active substance, and are employed in washing, disinfecting, and stabilising compositions used in the food and medicinal industries[235,390-399]. They are efficient emulsifying, dispersing, and wetting agents[400], and are used as textile treatment additives[381,401-405].

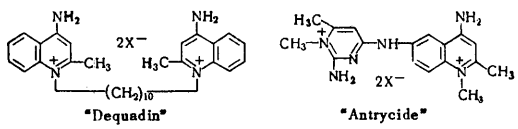
Compounds (LXIX) are used to break oil emulsions and as wetting agents when filling exhausted oil-bearing strata with water[406]:



(LXIX)

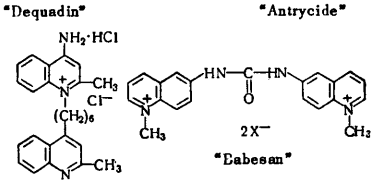
where RCO is an acyl radical containing not more than five carbon atoms, and R'CO is an acyl radical containing not more than 18–32 carbon atoms.

Some quinolinium salts have been recommended as additives in bright nickel plating[407-409], and others as bactericides and fungicides, especially against agricultural plant pests[397,410-419]. Good antibacterial and chemotherapeutic properties are possessed by "Dequadin"[419-425], "Antrycide" (Pyraldin)[426-430], "Tosocide"[428], and "Babesan"[431], which are used for treating various illnesses of domestic animals.



"Dequadin"

"Antrycide"



"Tosocide"

"Babesan"

Bis-quinolinium salts of some types exhibit a strong ganglio-blocking and hypotensive activity[6,7,432,433].

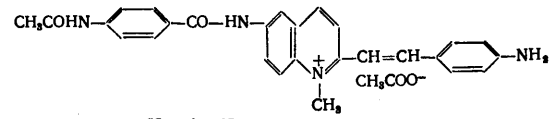
Quinaldinium salts have been suggested as azo-coupling agents for diazotype light-sensitive paper[434]. Quinolinium salts are very sensitive reagents for the micro-determination of bismuth[370,371] and persulphate ion[435].

(b) Quinolinium dyes. The use of quinocyanine dyes in the cinematographic industry as sensitisers, desensitisers, and supersensitisers for photographic emulsions and filter and antifogging dyes is well known[101-105]. Although ordinary cyanine dyes are fairly sensitive to light, with certain inorganic heteropoly-acids, such as tungsto-molybdophosphoric acid, they form very light-stable lakes suitable for use in dyeing[436,437]. Some types of quinocyanine and azo-dyes have been recommended for stable dyeing of fibres[438-448].

The quino-azo-dyes are particularly interesting. They have a high affinity for polyacrylonitrile fibre, give very deep shades of yellow, red, claret, violet, and blue colours, are very stable to light, and are unaffected by change of pH. Because of these properties, investigations have been started to develop convenient methods for the production of these dyes and their use in dyeing[447-449].

Quinocyanine dyes have been successfully used in fine histochemical investigations[450-452] and also for studying the mechanism of action of antibiotics on microbes[453]. Pinacyanol[454], Cyanine (Quinoline Blue)[455], and Neocyanine[456,457] are strong bactericides and have been recommended for clinical use.

Certain quinocyanines, derivatives of pyrrole and pyrimidine, are effective anthelminthics[458-463]. Quinostyryls, lepidinium derivatives, possess anti-tumour activity towards lymphoma 8 and some types of sarcoma[464-468]. "Styryl 430" has interesting radiomimetic properties, but they have not yet been sufficiently investigated[469-471]:



"Styryl 430"

Quinocyanines and quinostyryls have been recommended as plant growth regulants[472-478]. Hirshberg[479,480] suggests the use of the quinospirans (XXX) and their analogues as a photochemical memory unit in cybernetic machines.

Cyanines, particularly 1,3'-diethyl-6'-nitro-2-quinothiacyanine iodide, increase the sensitivity of certain light-sensitive polymers which become insoluble when irradiated and are used for obtaining linogravures by an optical method[481]. Cyanine dyes of the quinolinium series can be used to determine Hg^{2+}, Ag^{+},[482,483] and Mg^{2+},[484,485] to detect primary and secondary amines in tertiary amines[486], and for other analytical purposes[487].

A method has been suggested for the analysis of mixtures of anionic and cationic soaps, using Pinacyanol as indicator[488,489]. Particular attention is directed to the use of cyanine dyes, including quinolinium derivatives, as good models for studying the relationship between the structure and colour of a dye, and so to their importance in developing a theory of colour[22-25,35,37,40-47,102,105,350-359,490-506].

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MECHANISM OF THE CATALYTIC REDISTRIBUTION OF HYDROGEN IN UNSATURATED CYCLIC HYDROCARBONS

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1. INTRODUCTION

The catalytic redistribution of hydrogen in hydrocarbons has been studied for more than half a century. The interest taken in these reactions is due to the important part they play in many processes, both in the chemical and petroleum-processing industries and in Nature, for example, in any enzymic oxidation.

The amount of work done on simultaneous hydrogenation and dehydrogenation on metal catalysts has been especially large. The redistribution of hydrogen among molecules of the same substance, going practically to completion without the evolution of gaseous hydrogen, was discovered by Zelinskii and Glinka[1]. Such changes undergone by various hydrocarbons on palladium catalysts were subsequently investigated by Wieland[2] and by Zelinskii and his school[3-10]. On nickel catalysts the conversion was less complete[11] than on palladium catalysts, and it was usually accompanied by hydrogen evolution. With platinum catalysts higher temperatures are required for the redistribution of hydrogen than with palladium catalysts. In many cases this process is accompanied by isomerisation. For example, copper and iron catalysts[12] behave similarly to oxide catalysts[13] towards cyclohexene. Conversion into benzene and cyclohexane has been observed only when a mixture of cyclohexene and hydrogen is used[12]. On metallic rhenium[14] the conversion of cyclohexene at certain temperatures is not accompanied by the evolution of hydrogen, the ratio of benzene to cyclohexane in the products corresponding to that found on palladium catalysts. However, the proportion of cyclohexene which has undergone such reaction on rhenium does not exceed 32% at 300°, whereas on palladium catalysts this process goes to completion at far lower temperatures.

Comparison of these results shows that hydrogen redistribution in unsaturated hydrocarbons takes place differently on different metal catalysts. Insufficient attention has been paid in the literature to the reasons for this, and a possible explanation is suggested below for the decrease in activity, with respect to the redistribution of hydrogen, for the series: palladium, nickel, platinum.

The mechanism of hydrogen redistribution in cyclohexadiene, cyclohexene, and decalin hydrocarbons having an unsaturated bond in the side-chain has been elucidated by Levina[15,16], but the changes undergone by hydrocarbons having an unsaturated bond in the ring are interpreted in two different ways.

Balandin[17] suggested models in which transformations of cyclohexene or cyclohexadiene are effected by direct intermolecular transfer of hydrogen atoms. This scheme is examined in detail in Section 3, as also the closely similar views of Linstead and his collaborators[18,19].

A different view of the mechanism of catalytic hydrogen redistribution was held by Zelinskii[1,3] and Wieland[2], who

regarded this process as the net effect of two simultaneous and opposite reactions, those of dehydrogenation and hydrogenation of the starting material. The redistribution of hydrogen was subsequently interpreted in a similar manner by other workers (see, for example, Shcheglova and Kagan[20]). However, no experimental evidence was given in these papers for the independent occurrence of dehydrogenation and hydrogenation during the redistribution of hydrogen.

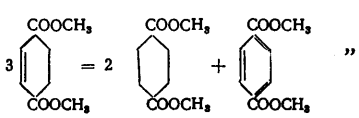
Fresh results[21-38] on the changes undergone by cyclohexene and cyclohexadiene on platinum and palladium films, obtained by spectroscopic, kinetic, adsorption, and conductimetric methods (see Section 4), allow the redistribution of hydrogen to be regarded as a combination of dehydrogenation and hydrogenation reactions. The extent to which these reactions balance one another is governed by thermodynamic factors, the nature of the catalyst (especially its ability to retain hydrogen in a form which is active in hydrogenation), and competitive adsorption of the starting material and its conversion products. Such a view, as will be shown below, provides explanations of several experimental results which had not previously been interpreted.

In spite of the marked differences in hydrogen redistribution on metallic, oxide, and aluminosilicate catalysts, main stages can be found which are common to all these systems, as will be shown in Sections 6 and 7.

Since reviews have been published on reactions involving the redistribution of hydrogen in hydrocarbons[39-43], the present paper will contain mainly new results and information which is essential for determining the mechanism of the process.

2. REDISTRIBUTION OF HYDROGEN AS A COMBINATION OF DEHYDROGENATION AND HYDROGENATION

In 1911 Zelinskii and Glinka discovered[1] that the hydrogenation of dimethyl tetrahydroterephthalate in the presence of palladium black at room temperature is accompanied by its dehydrogenation. They concluded that the second process is linked with the first, since with this catalyst it does not take place in the absence of hydrogen: "The reaction is initiated by palladium hydride, after which the role of palladium as catalyst is in effect to redistribute hydrogen among three molecules of the tetrahydroterephthalic ester[1]:



The reaction is far slower with platinum black than with palladium black.

The important part played in redistribution by hydrogen dissolved in the palladium was noted also by Wieland[2]. He pointed out that, when a large quantity of palladium black is used at room temperature, dihydronaphthalene is almost exclusively dehydrogenated, or this reaction at least predominates. With a small amount of palladium black, however, dehydrogenation is followed by hydrogenation. Unfortunately, no experimental evidence was given to prove that dehydrogenation and hydrogenation take place independently in the redistribution of hydrogen. Wieland[2] regarded the two reactions as two equilibria involving an unstable addition product:

$$\begin{matrix} -R-R- \\ H\ PdH \end{matrix},$$

the conventional formula HPdH (or PdH_2) being used to denote a solid solution of hydrogen in palladium. It was supposed that the unstable complex is formed in the first stage of dehydrogenation, and that the hydrogen absorbed by the palladium then adds on at the double bond in the molecule which is capable of hydrogenation

$$\begin{matrix} -R-R- \\ H\ H \end{matrix} + Pd \rightleftarrows \begin{matrix} -R-R- \\ H\ PdH \end{matrix} \rightleftarrows -R{=}R- + PdH_2.$$

It is readily seen that, according to this mechanism, the redistribution of hydrogen between molecules of an unsaturated hydrocarbon consists of separate dehydrogenation and hydrogenation stages.

On palladised asbestos at temperatures below 130° in a current of carbon dioxide, the following changes involving cyclohexadiene:

$$2C_6H_8 = C_6H_{10} + C_6H_6, \quad (1)$$

and cyclohexene:

$$3C_6H_{10} = 2C_6H_{12} + C_6H_6, \quad (2)$$

go almost to completion[3,4] and without the evolution of hydrogen. Zelinskii and Pavlov[3] considered that these processes consist in the simultaneous occurrence of two reactions, dehydrogenation and hydrogenation, the catalyst distributing the mobile hydrogen among the molecules of the starting material in such a way that a more stable system is formed. However, these workers left open the question as to whether redistribution is accomplished by combining individual dehydrogenation and hydrogenation stages or by the direct intermolecular transfer of hydrogen atoms.

Shcheglova and Kagan[20] put forward the hypothesis that cyclohexene molecules oriented with the double bond towards the catalyst surface are hydrogenated by hydrogen atoms split off from cyclohexene molecules adsorbed at the saturated carbon atoms. While assuming that dehydrogenation and hydrogenation occur simultaneously, they also noted that hydrogen could appear in the adsorbed layer. The evolution of hydrogen into the gas phase was regarded as impossible under the conditions of hydrogen redistribution. This mechanism is represented schematically as follows:

$$C_6H_{10}\,(gas) \longrightarrow C_6H_{10}\,(ads),$$
$$C_6H_{10}\,(ads) \longrightarrow C_6H_8\,(ads) + 2H,$$
$$C_6H_{10}\,(ads) + 2H\,(ads) \longrightarrow C_6H_{12}\,(ads) \longrightarrow C_6H_{12}\,(gas),$$
$$C_6H_8\,(ads) \longrightarrow C_6H_8\,(ads) + 2H\,(ads),$$
$$C_6H_{10}\,(ads) + 2H\,(ads) \longrightarrow C_6H_{12}\,(ads) \longrightarrow C_6H_{12}\,(gas).$$

There was no experimental confirmation of this scheme. These workers[20] cited the previously discovered[4] stepwise character of the transformation of cyclohexadiene in support of the assumption that hydrogen redistribution consists of two successive stages. However, the models[17] to be described below enable this result to be explained on the basis of the direct intermolecular transfer of hydrogen atoms.

3. DIRECT INTERMOLECULAR TRANSFER OF HYDROGEN ATOMS

In 1929 Balandin[17] attempted to explain peculiarities in the redistribution of hydrogen in cyclohexadiene and in cyclohexene on the assumption that the former reaction takes place on a triplet, *i.e.* on three atoms of the metal catalyst, and the second reaction on two triplets (see Fig. 1). According to these models, two hydrogen atoms pass directly from one cyclohexadiene molecule to another, as do four hydrogen atoms from a cyclohexene molecule to two others. The models were consistent with the experimental results available at that time. The absence of hydrogen evolution in the "irreversible catalysis" of cyclohexene and cyclohexadiene[3,4] could be interpreted as indicating that the hydrogen atoms passing from one molecule to another did not interact with the catalyst atoms. As can be seen from Fig. 1, the direction of movement of the hydrogen atoms, indicated by arrows, is governed mainly by the fact that the C=C bond is stretched owing to two-point adsorption, while the C–C bond in the other molecule is shortened owing to both carbon atoms being attracted to one surface atom of the metal catalyst The planar orientation of the original molecules required by the model is difficult with the *trans*-forms of disubstituted cyclohexenes and cyclohexadienes. In fact, formation of only the hexahydro-*cis*-terephthalic ester was observed in the early work[1]. It is true that still earlier[44] a small amount of hexahydro-*trans*-terephthalic ester had been obtained together with the predominant *cis*-form on heating dimethyl dihydroterephthalate with palladium black, but in these experiments the process took place under quite severe conditions and was accompanied by the evolution of hydrogen.

The rate of conversion of cyclohexadiene into cyclohexene and benzene exceeds that of the "irreversible catalysis" of cyclohexene[4]. This was explained by the above models, since the presence of two triplets side by side and in a definite orientation is less probable than the presence of one triplet.

A scheme of direct intermolecular hydrogen transfer was used[18,19] to explain the low concentration of cyclohexa-1,3-diene found during the redistribution of hydrogen in cyclohexene. This reaction was regarded as termolecular, taking place in a single step with the simultaneous transfer of four hydrogen atoms from one cyclohexene molecule to two others. The kinetic data were regarded as inconsistent with the view that redistribution of hydrogen takes place in two independent stages involving dehydrogenation and hydrogenation. As a proof of direct intermolecular transfer of hydrogen, the fact is cited that the stoichiometric equation of "irreversible catalysis" is satisfied even with a low metal/cyclohexene ratio and boiling tetrahydrofuran as medium, when it could be expected that chemisorbed hydrogen would be removed. However, it has since been shown[34] that, even at 20°, the redistribution of hydrogen in cyclohexene and cyclohexadiene may be accompanied by hydrogen evolution (see next Section). Furthermore, a mechanism involving direct intermolecular transfer of hydrogen atoms does not provide an explanation of why the redistribution of hydrogen in cyclohexene is accelerated by hydrogen chemisorbed on the catalyst. While giving a scheme of "termolecular disproportionation", which is very close to the model of Balandin[17] (*cf.* Figs. 2 and 1*b*), Braude *et al.*[19] also suggest the scheme of termolecular disproportionation in the presence of chemisorbed hydrogen illustrated in Fig. 3. It is readily seen that the resemblance between the mechanisms in Figs. 2 and 3 is quite superficial. Whereas in Fig. 2 the elimination of the particular hydrogen atoms indicated by the letters H can still be explained by hydrogenation of the unsaturated bonds in other cyclohexene molecules, it is not clear in Fig. 3 why only one cyclohexene molecule loses four hydrogen atoms and just two other molecules add on four hydrogen atoms. The statement[19] that chemisorbed hydrogen diminishes the degree of approach of cyclohexene molecules necessary for reaction contradicts the mutual independence of the processes of dehydrogenation and hydrogenation of cyclohexene molecules which clearly follows

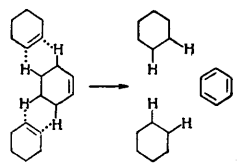


Fig. 2. Termolecular redistribution of hydrogen in cyclohexene[19].

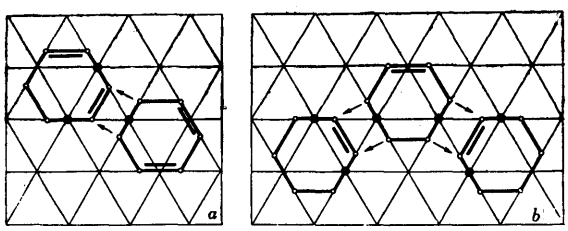


Fig. 1. Arrangement of molecules of (*a*) cyclohexadiene and (*b*) cyclohexene on a metal surface during hydrogen redistribution[17]. The black circles denote metal atoms constituting active centres (triplets), and the arrows indicate movements of hydrogen atoms.

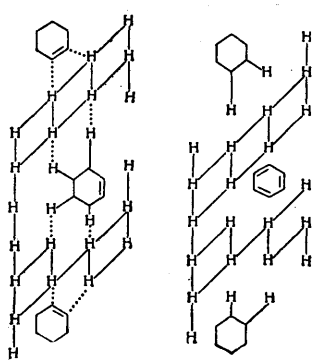
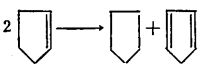


Fig. 3. Termolecular redistribution of hydrogen in cyclohexene involving chemisorbed hydrogen[19].

from Fig. 3. The complete balancing of these processes shown in Fig. 3 requires the additional artificial assumption that the amount of hydrogen retained by the catalyst remains unchanged during the redistribution. Measurements of the electrical conductivity of platinum films during the transformation of cyclohexene and cyclohexadiene on them[33] have shown the limited character of such a treatment (see Section 4). Kinetic studies of the redistribution of hydrogen in cyclohexene on palladium and platinum films[28,37] are also inconsistent with a mechanism of direct intermolecular transfer of hydrogen atoms.

The activity of iron catalysts observed[12] towards reaction (2) could not be expected on the basis of the models[17], since the crystal lattice of iron does not permit formation of two triplets oriented as indicated in Fig. 1*b*. On the other hand, palladium and platinum, which have the same type of lattice, similar atomic radii, and similar metal–carbon and metal–hydrogen bonding energies, differ substantially in their activity with respect to hydrogen redistribution, as had been noted in several papers, and has recently been shown on platinum and palladium films[36]. The models[17] also provide no explanation of the redistribution of hydrogen between five-membered rings, which have no elements of symmetry in common with any crystal lattices. Yet it has been shown[46,47] that cyclopentene is converted into cyclopentane and cyclopentadiene on palladium at 200°



It has recently been discovered[48] that a similar process takes place with dihydromethylfuran on a palladium catalyst.

Thus a mechanism involving direct intermolecular migration of hydrogen atoms in hydrogen redistribution reactions has proved suitable for interpreting some experimental results, but is inconsistent with many others.

4. NEW DATA ON CHANGES UNDERGONE BY SIX-MEMBERED CYCLIC HYDROCARBONS ON PALLADIUM AND PLATINUM FILMS

Since the mechanism of hydrogen redistribution had not been sufficiently elucidated, an investigation was undertaken of the reactions of cyclohexene and cyclohexa-1,3-diene, as well as of the adsorption of these compounds and of the products formed from them[21-38]. The adsorbents and catalysts used were palladium and platinum films prepared by evaporating the metal in a high vacuum, since on them the interaction of the hydrocarbon molecules with the metal surface could be studied by various physicochemical methods, including spectroscopic[22-26,28] and conductivity[29-33] techniques. The investigation of adsorption on metal films is difficult because of their small specific surface, but improvements[35] in the method of feeding the vapour through a capillary have enabled these difficulties to be overcome. The kinetics of the catalytic changes undergone by cyclohexene and cyclohexadiene have been studied both on films of palladium and platinum invisible to the naked eye and on specular layers of the metals. Experiments were made at temperatures between 0° and 600° and vapour pressures of the hydrocarbons differing by a factor of almost a million (between 30 mm and 5×10^{-5} mm).

Since no data had been published on hydrogen redistribution on vacuum-sublimed palladium or platinum films, it was necessary to ascertain whether the composition of the reaction products, for example, from cyclohexa-1,3-diene, was the same on the metal films as on the metal catalysts used previously. Analysis based on the infrared absorption spectra showed[21] that, with palladium films of low catalytic activity or small geometrical surface area, the molecular ratio of benzene to cyclohexene in the products of catalysis was close to unity. This is consistent with the equation[4] for reaction (1) occurring rapidly on palladium black. On palladium films of larger surface at the same temperature (50°), reaction (2) was observed as well as reaction (1). Hence palladium films do not differ substantially from other palladium catalysts.

Calculation of the limiting quantity of hydrogen which the palladium films could contain before entry of cyclohexadiene vapour showed[21] it to be less than the quantity of hydrocarbon used in the experiment by a factor of 10^8. This result also agreed with Zelinskii's data[8] on the catalytic activity of palladised asbestos freed from hydrogen by being heated to 300° in a current of carbon dioxide.

It was found[23] from the infrared spectra that the catalytic activities of transparent palladium films towards hydrogen redistribution in cyclohexadiene vary inversely with the stable adsorption of the starting material observable spectroscopically. Films with an effective thickness of ~100 Å, deposited on quartz or fluorite, show appreciable catalytic activity, while stable adsorption of cyclohexadiene on these films is not revealed by spectroscopic methods. A less dense film of palladium on fluorite possessed a far smaller activity, and the cyclohexadiene which was not removed from the film by evacuating to 10^{-3} mm gave an absorption band. A still less dense palladium film deposited on rocksalt proved catalytically inactive, while the spectrum of cyclohexadiene firmly adsorbed on it remained at a residual pressure of 10^{-4} mm, after the reaction vessel had been evacuated for many hours and had been swept out with benzene vapour.

Fig. 4 shows that the spectrum of cyclohexadiene firmly adsorbed on palladium[24,25] has several absorption bands in common with its spectrum in the vapour state. In particular, the bands in the 1000–1450 cm^{-1} range, corresponding to vibrations of $\rangle C-H$ bonds, remain, but the bands at 750 and 925 cm^{-1}, representing vibrations of $\rangle C-H$ bonds, are not found in the spectrum of the adsorbed cyclohexadiene. This cannot be attributed to rupture of π bonds, since absorption is observed in the range 1600–1700 cm^{-1}, which is characteristic of C=C stretching vibrations. If the spectral differences between firmly adsorbed cyclohexadiene and its vapour are due to molecular changes resulting from interaction with the palladium film, it must be supposed that hydrogen atoms are split off mainly from $\rangle C-H$ groups in the cyclohexadiene.

All these results indicate that the stable absorption of cyclohexadiene detectable from the infrared spectrum does not form an intermediate stage in the catalytic transformation. Elimination of hydrogen is detected also in the stable adsorption of benzene vapour on platinum films, manometrically and from the change in their electrical conductivity[30,49]. A characteristic feature of such stable adsorption is that the elimination of hydrogen atoms from

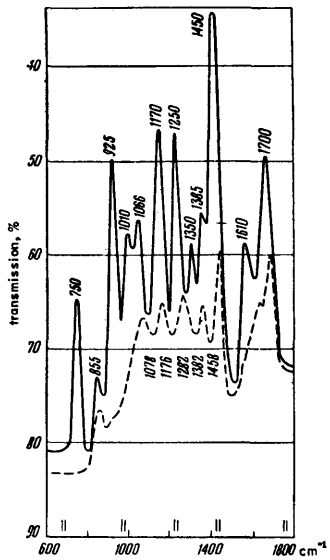


Fig. 4. Infrared absorption spectrum of cyclohexadiene firmly adsorbed on transparent palladium film[23] (broken curve), and absorption spectrum of cyclohexadiene vapour.

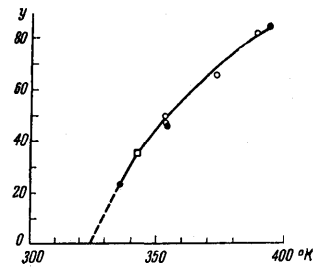


Fig. 5. Temperature variation of proportion of cyclohexene converted when reaction ceases to be of zero order. The full and open circles denote results of experiments on two platinum films[28], and the square indicates a result from Schwab and Lorenzen[50].

>C–H or >C–H groups does not yield simple dehydrogenation products, but may constitute the initial stage of processes of dehydrocondensation and polycondensation (see Section 8), resulting in deactivation of the catalysts owing to their surface becoming covered with resinous or tarry substances.

The kinetics of hydrogen redistribution in cyclohexadiene and cyclohexene on palladium and platinum films has been studied[26,28] under static conditions by a spectroscopic method, in which the changes in absorption in a definite spectral range, due to the decrease in concentration of the starting material or the accumulation of one of the products, are automatically recorded during the reactions. By means of calibration graphs these curves were used to find the variation with time of the partial pressure of the corresponding reactant. A manometric method could not be employed, since with initial vapour pressures of cyclohexene or cyclohexadiene exceeding 1 mm Hg the total pressure remained unchanged during the reaction.

The kinetic results for hydrogen redistribution in cyclohexadiene on palladium films show that a scheme of direct intermolecular transfer of hydrogen atoms does not enable all the experimental data to be explained. Still more marked discrepancies between this scheme and experiment were observed with the kinetics of hydrogen redistribution in cyclohexene. On palladium films this reaction is of zero order until a certain degree of conversion has been reached, this proportion diminishing as the temperature is lowered (Fig. 5). Study of the adsorption of all the reactants on palladium films showed that the change in reaction order was due to competitive adsorption of cyclohexene and benzene. An equation was obtained for the temperature variation of the percentage conversion of cyclohexene up to which the reaction is of zero order at a given total pressure, based on the fact that the adsorption coefficients of these hydrocarbons depend in different ways on temperature owing to differences in their heats of adsorption on the catalytically active surface. The curve calculated by means of this equation satisfactorily reproduces our experimental results and the data given by Schwab and Lorenzen[50] (see Fig. 5). Extrapolation of this relationship shows that the reaction is not zero order at temperatures below 50°. Actually, an analysis[17] of Zelinskii and Pavlov's kinetic experiment[4] at 35° showed that a reaction order of 1.5 gave the most constant values for the rate constant. At higher temperatures (105°–124°) zero order was observed in the redistribution of hydrogen in cyclohexene[20], which also agrees with the curve in Fig. 5. Thus all these results can be explained on the same basis.

An important fact in evaluating the mechanism of hydrogen redistribution is that the reaction order of 1.5, which has been regarded in the literature as an argument in support of the hypothesis that three molecules of cyclohexene undergo transformation on two active centres (triplets), applies only at low temperatures.

Comparison of data on the changes undergone by cyclohexene and cyclohexadiene on palladium and platinum films prepared in the same way has revealed[36] substantial differences in the catalytic action of these films. On palladium films, redistribution of hydrogen was already taking place at 20°, and at pressures exceeding 1 mm was not accompanied by hydrogen evolution. On freshly prepared platinum films no reactions of cyclohexadiene or cyclohexene were observed at temperatures up to 200°, and at higher temperatures it was mainly dehydrogenation of these hydrocarbons which occurred. In subsequent experiments with the same platinum films, hydrogenation was observed as well as dehydrogenation, since the pressure of the hydrogen fell. It is interesting that, after a few experiments in which cyclohexene was dehydrogenated, redistribution of hydrogen in cyclohexadiene on the same platinum film was no longer accompanied by evolution of hydrogen into the gas phase.

Thus dehydrogenation and hydrogenation of cyclohexene and cyclohexadiene are observed on platinum films above 200°. In order to ascertain whether these reactions can occur at lower temperatures, and to study the nature of the interaction of six-membered cyclic hydrocarbons with the platinum surface, measurements were made of the effect

of adsorption of the vapours of benzene, cyclohexadiene, cyclohexene, and cyclohexane and of hydrogen at 20° on the electrical conductivity of the platinum films.

Adsorption was measured by a method involving flow through a capillary with automatic recording of the results. Since the vapours of these hydrocarbons are adsorbed on the glass walls of the apparatus, a technique has been developed[35] for determining their rate of accumulation, which is appropriate under these conditions and does not involve the assumption of molecular flow.

As a result of the varying influence of adsorption of the vapours of these hydrocarbons and of the sorption of hydrogen on the conductivity of platinum films, the conductivity method combined with adsorption measurements proved very useful in elucidating the nature of the interaction between the hydrocarbon molecules and the metal surface. It has been found[29-33] that the first admission of the vapour of any six-membered cyclic hydrocarbon to a freshly prepared platinum film at 20° is accompanied by stable adsorption, together with the evolution of hydrogen. At the same time an unstable adsorption takes place, which can be removed by evacuation at room temperature. The adsorbed molecules gradually redistribute themselves over the surface of the metal film in conformity with the adsorption potential. In the course of unstable adsorption, when the hydrocarbon may be removed by evacuation at room temperature, benzene and cyclohexane remain unchanged, but with cyclohexene and cyclohexadiene hydrogen is split off however many times admission of hydrocarbon vapour and evacuation are repeated.

Curves *I* and *IV* in Fig. 6 represent the variation in the resistance of the platinum films during the first and second admissions of cyclohexene vapour[33]. On the first contact between the vapour and the film prepared by sublimation in a high vacuum, the resistance of the film increases sharply, whereas during the second inflow the resistance increases slightly, passes through a maximum, and then falls below its initial value. Curves *II* and *III* are copies of the traces, on the chart of the potentiometric recorder, of the pressure in the vessel containing the platinum film, made at the same time as the variations in its resistance. *H* denotes the instants at which entry of cyclohexene vapour begins in the first and second experiments, *T* the cessation of entry of vapour, and *B* freezing of the hydrocarbon vapours at the temperature of liquid nitrogen. After entry of vapour had stopped, the pressure remained unchanged with time (section *TB* of curve *II*), and freezing lowered the pressure slightly. This last fact means that the gas phase comprised mainly hydrogen split off from the cyclohexene molecules. After evacuation of the vessel containing the film to a residual pressure of 10^{-7} mm, introduction of cyclohexene vapour had little effect on the resistance of the platinum film because most of the sites on the surface, adsorption on which would involve stronger electronic interaction with the metal, were occupied by reaction products of the cyclohexene, predominantly benzene, as is shown by other experiments. Consequently, the second and subsequent admissions of cyclohexene vapour are no longer accompanied by stable adsorption on the platinum film, but by temporary adsorption with evolution of hydrogen into the gas phase: after freezing (*B* on curve *III*) the pressure does not drop to the very low value observed in the absence of hydrogen.

Further repetitions of evacuation and admission of cyclohexene or cyclohexadiene vapour have practically the same influence on the resistance of the platinum film, as can be seen from Fig. 7, which gives curves similar to those in Fig. 6 but obtained during the fourth and tenth influxes of cyclohexadiene vapour[33].

If the supply of cyclohexene or cyclohexadiene vapour is periodically interrupted, and the hydrocarbon vapour frozen out of the gas phase, the quantity of hydrogen formed passes through a maximum. In particular, curve *1* in Fig. 8 was obtained with cyclohexene, while curve *2* shows the dependence of the ratio between the numbers of hydrogen and cyclohexene molecules $N_{H_2}/N_{C_6H_{10}}$ on the number of cyclohexene molecules admitted. Analogous results were obtained with cyclohexadiene, but only about half the hydrogen is evolved compared with adsorption of

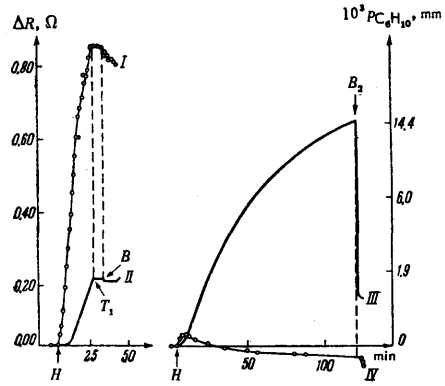


Fig. 6. Variation in resistance of platinum film (curves I and IV) and pressure over it (curves II and III) during first (left-hand half of diagram) and second admissions of cyclohexene vapour[33]. *H* = start of entry of vapour; *T* = termination of entry of vapour; *B* = freezing of hydrocarbon vapours.

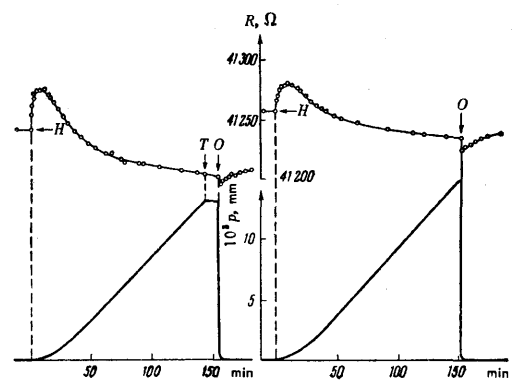


Fig. 7. Dependence of resistance of platinum film (upper curves) and of vapour pressure over it on time of inflow of cyclohexadiene vapour in fourth (left-hand half of diagram) and tenth experiments[33]. *H* = start of inflow; *T* = termination of inflow; *O* = evacuation.

the corresponding amount of cyclohexene. Experiments in which the same quantity of cyclohexene was admitted at a constant rate into a vessel containing a platinum film and different quantities of hydrogen showed that, with a certain amount of the latter, it is neither adsorbed nor evolved during entry of the unsaturated hydrocarbon. Dehydrogenation takes place with a smaller amount of hydrogen, and hydrogenation with a larger amount. Cyclohexadiene, too, can be both dehydrogenated and hydrogenated at 20°.

These results show that hydrogenation and dehydrogenation, both of cyclohexene and of cyclohexadiene, take place simultaneously on platinum films at 20°. If the rates of these processes were made equal, the quantity of hydrogen in the vessel would reach a certain value and then remain unchanged with further entry of hydrocarbon. But actually the quantity of hydrogen passes through a maximum (see curve *1* in Fig. 8). Hence dehydrogenation had predominated at first, and then hydrogenation had become dominant. Such a change in relative velocities may be caused by selective blocking by reaction products of those portions of the platinum surface on which dehydrogenation takes place. It was established in separate experiments that cyclohexane has practically no influence on the transformation of cyclohexene, whereas benzene, which is not hydrogenated under these conditions, actually suppresses the dehydrogenation of cyclohexene. On the other hand, continuous removal of reaction products from cyclohexene markedly increases the yield of hydrogen.

Thus dehydrogenation and hydrogenation of cyclohexene and cyclohexadiene are observed under conditions of hydrogen redistribution in these hydrocarbons. At the start, dehydrogenation predominates. The accumulation of hydrogen and of benzene, the latter preferentially blocking the active centres for dehydrogenation, causes a diminution in the velocity of this process, while the rate of hydrogenation increases. Therefore with increasing amount of unsaturated hydrocarbon the hydrogen content of the gas phase decreases, and the composition of the reaction products is more and more closely represented by Eqns. (1) and (2), although the latter do not reflect dehydrogenation and hydrogenation stages. In spite of the greater capacity of palladium compared with platinum for sorbing hydrogen, evolution of hydrogen is observed also in the conversion of cyclohexene on palladium films, and its amount passes through a maximum. Hence even on the metal most

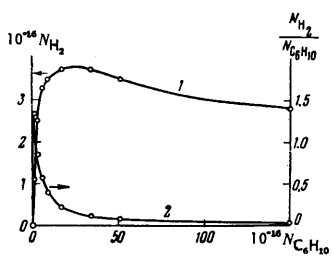


Fig. 8. Dependence of amount of hydrogen formed N_{H_2} (curve 1) and of ratio $N_{H_2}/N_{C_6H_{10}}$ on number of cyclohexene molecules $N_{C_6H_{10}}$ admitted to vessel containing platinum film.

favourable to "irreversible catalysis", the redistribution of hydrogen in cyclohexene and in cyclohexadiene passes through dehydrogenation and hydrogenation stages, and is not effected by direct intermolecular transfer of hydrogen atoms.

A thermodynamic calculation[38] of the maximum partial pressure of hydrogen in the equilibrium mixture formed from cyclohexene at various temperatures has shown that at 20° it is 10^{-3} mm, which is the value found at the end of the experiment represented by curve *1* in Fig. 8. At 120° this pressure is close to 3 mm, which is less than 0.005 atm, and it becomes clear why at this temperature and atmospheric pressure hydrogen evolution was not observed[3] during the conversion of cyclohexene. A rise in temperature at atmospheric pressure favours the dehydrogenation of cyclohexene, whereas an increase in total pressure suppresses it. This latter fact may explain the marked difference[45] in the extent of hydrogen redistribution in cyclohexene at 1 and at 10 atm. Thus it is possible to indicate the conditions under which detectable quantities of hydrogen will be evolved into the gas phase during hydrogen redistribution, and on the other hand when the composition of the reaction products approaches that corresponding to the stoichiometric equations (1) and (2).

Hence the absence of hydrogen evolution accompanying reactions involving the redistribution of hydrogen merely constitutes a particular case, observable when the stages of dehydrogenation and of hydrogenation just balance one another.

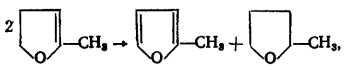
5. DEPENDENCE OF CATALYTIC ACTIVITY TOWARDS HYDROGEN REDISTRIBUTION ON ABILITY OF METAL TO ABSORB HYDROGEN

On the basis of the results reported in Section 4 on the redistribution of hydrogen as a combination of dehydrogenation and hydrogenation, it could be expected that the mutual balancing of these reactions would be facilitated on those metals which are capable of absorbing the hydrogen split off from the dehydrogenated molecules, retaining it in an active form for hydrogenation, and transferring it to the molecules of the original hydrocarbon to be hydrogenated. It has been noted several times in the literature[1,3] that palladium catalysts, which dissolve hydrogen readily, are more active than platinum catalysts for the redistribution of hydrogen. Interesting results have been obtained in a study[51,52] of the changes undergone by cyclohexa-1,3-diene dissolved in heptane and in alcohol on platinum, nickel, and palladium catalysts at 25°. Hydrogen redistribution in cyclohexadiene ("irreversible catalysis") and its hydrogenation to cyclohexene occur simultaneously on all three metals, but the velocity ratio for these reactions is close to 0.4 : 1 on platinum black, 1.5 : 1 on Raney nickel, and 3 : 1 on palladium black. From our point of view this means that on platinum black the hydrogenation of cyclohexadiene is far more rapid than its dehydrogenation, while the opposite is the case on palladium black. Raney nickel occupies an intermediate position between these two catalysts.

For the reasons mentioned in Section 3, direct transfer of hydrogen atoms between cyclohexadiene molecules does not explain the differences in the relative rates of hydrogen redistribution and hydrogenation on palladium, nickel, and platinum. If, however, the redistribution is regarded as taking place in two stages, the above results[51,52] indicate

that with cyclohexadiene the balancing of the dehydrogenation and hydrogenation stages, which is required for Eqns. (1) and (2) to be satisfied, is associated with the ability of the metal to dissolve the hydrogen eliminated by dehydrogenation of the hydrocarbon. Catalytic activity is not a simple function of the hydrogen content of a metal (see for example Refs. 53–57), and the hydrogen content is markedly dependent on the conditions of preparation of a metal catalyst and of its saturation with hydrogen. This is probably governed by the kinetics of the sorption and diffusion of hydrogen in a metal, which is sensitive to the surface state and degree of dispersion of the specimen. Therefore for a qualitative comparison let us utilise data on the equilibrium solubility of hydrogen in the massive metals. Below 600° the solubility of hydrogen is[58] a maximum in palladium, lower in nickel, and still lower in platinum. This can explain why the dehydrogenation and hydrogenation of unsaturated hydrocarbons are especially readily balanced on palladium, even with a supply of gaseous hydrogen, whereas this is more difficult on nickel, and still more difficult on platinum.

The above enables us to understand why platinum catalysts are usually inferior to palladium for hydrogen distribution reactions, and are employed at higher temperatures. It has recently been found[48] that, on a palladium catalyst at 200°, dihydromethylfuran is smoothly converted into 2-methylfuran (sylvan) and tetrahydrosylvan



which is completely analogous to the "irreversible catalysis" of cyclohexene. In experiments with a platinum catalyst under the same conditions, the initial portions of the products contain smaller amounts of sylvan than of a ketone formed by isomerisation of tetrahydrosylvan. This difference in the reactions undergone by dihydromethylfuran in the presence of palladium and platinum catalysts is explained[48] by a difference in properties of the hydrogen adsorbed on palladium and on platinum. In particular, it is assumed that hydrogen adsorbed on palladium is incapable of hydrogenating dihydromethylfuran. However, the same paper refers to the high activity of palladium for the hydrogenation of the double bonds in the furan ring. From our point of view these results are due to the greater difficulty of balancing hydrogenation and dehydrogenation on a platinum than on a palladium catalyst, owing to the smaller capacity of platinum for sorbing hydrogen.

In this connection it is interesting that[59] the promoter action of palladium on a Raney nickel catalyst increases the activity of the latter for the hydrogenation of 2-methylbut-3-en-2-ol, whereas platinum decreases it. The reaction velocity was increased with the potential of the catalyst remaining constant, which indicates that hydrogenation is effected by dissolved hydrogen. The diminution in the rate of hydrogenation after 40% coverage of the nickel surface with platinum was not linked[59] with the lower solubility of hydrogen in platinum than in nickel, although such an explanation is quite probable in view of what has been said above.

Since palladium and platinum catalysts are not usually prepared by completely identical procedures, and since specimens can contain different amounts of hydrogen depending on the mode of preparation, it was of interest to compare the catalytic activity of films of these metals prepared under identical conditions of vacuum sublimation and practically free from hydrogen before contact with the vapour of the test substance. Experiments with cyclohexene and with cyclohexadiene showed[36] that on the palladium film, products corresponding to Eqn. (1) and (2) are already obtained at 20°, and appreciable amounts of hydrogen are not evolved. On platinum films below 200° no reaction could be detected spectroscopically, and at higher temperatures the main reaction was dehydrogenation of the cyclohexene and cyclohexadiene. Redistribution of hydrogen in cyclohexadiene on the platinum film was observed only after dehydrogenation of cyclohexene had taken place repeatedly on it. These results indicate that the velocity ratio of the simultaneous dehydrogenation and hydrogenation of the initial hydrocarbon is different on platinum from that on palladium. As several workers have shown[53–55], an important part in the hydrogenation of unsaturated hydrocarbons is played by hydrogen dissolved in the metal. Platinum sorbs hydrogen far more feebly than does palladium, and therefore on the former metal hydrogenation can take place more slowly than dehydrogenation. If after a series of experiments, however, the benzene formed by dehydrogenation of cyclohexene covers part of the surface on which dehydrogenation takes place, the rates of dehydrogenation and hydrogenation will approach one another, and the content of hydrogen in the reaction products will fall. In the limiting case of dehydrogenation and hydrogenation being in balance, the composition of the reaction product will correspond to Eqns. (1) and (2).

6. PECULIARITIES OF HYDROGEN REDISTRIBUTION ON OXIDE CATALYSTS

The redistribution of hydrogen in unsaturated hydrocarbons is different on oxide catalysts from that on metals, and requires higher temperatures. Petrov[60] studied the condensation of cyclohexene in the presence of aluminium oxide under pressure at 400°–440°, and obtained a gas (31% hydrogen and 60% alkanes) together with a tarry liquid containing benzene and cyclohexane. The formation of benzene was attributed to pyrogenic dehydrogenation of the cyclohexene as a side-reaction accompanying the formation of cyclohexane and other polymethylene hydrocarbons. Later Plate[46] showed that neither benzene nor cyclohexane is obtained from cyclohexene on aluminium oxide at the atmospheric pressure and 450°. An investigation by Topchieva[61] of the kinetics of the transformation of cyclohexene on aluminium oxide showed that at 350° only skeletal isomerisation takes place, while neither hydrogen redistribution nor polymerisation occurs.

Goldwasser and Taylor[13] studied the conversion of cyclohexene and cyclohexadiene on chromic oxide. They found that at 305° cyclohexene is 60% converted, without hydrogen evolution, into a mixture of benzene and cyclohexane in the molecular proportions 1 : 2, which corresponds to Eqn. (2). When the temperature is lowered to 163°, the extent of conversion of the cyclohexene drops to 3%, but the ratio of benzene to cyclohexane in the products is maintained. Cyclohexadiene is already 50% converted at 95° into a mixture of benzene and cyclohexane in molecular proportions 2 : 1, and at 137° the extent of conversion reaches 65%. Thus on chromic oxide the redistribution of hydrogen in cyclohexene and cyclohexadiene occurs similarly to that on palladium and platinum, but with lower yields and at somewhat higher temperatures than on these metals. Zelinskii and Arbuzov[62] observed, with cyclohexene on chromic oxide at 400° and 450°, the formation of benzene

and a small amount of cyclohexane accompanied by hydrogen evolution. They noted that at 450° chromic oxide effects the dehydrogenation of methylcyclohexene accompanied by hydrogenation of a small proportion of its molecules by the hydrogen evolved. On aluminium oxide containing silica as impurity at 450°, as also on beryllium oxide and silica gel, cyclohexene merely isomerises to methylcyclopentene[63]. Titanium dioxide at 350°–450° produces, together with this reaction, dehydrogenation of cyclohexene to benzene. On thorium dioxide, zirconium dioxide, vanadium trioxide, and manganous oxide, only partial dehydrogenation of cyclohexene to benzene was observed[62]. It was later shown[64] that, on beryllium oxide at 400°, cyclohexene yields mainly 1-methylcyclopentene together with 3-methylcyclopentene and methylcyclopentane.

A study of the reactions of cyclohexene in the presence of vanadium oxide on aluminium oxide at 450°–500° established[46] that the main products are methylcyclopentene, methylcyclopentane, cyclohexane, and benzene. Under the same conditions cyclopentene is converted into cyclopentane and cyclopentadiene, and also gives some naphthalene. It was suggested that benzene and cyclohexane are formed probably as a result of hydrogen redistribution, although at the temperatures used dehydrogenation of cyclohexene to benzene is also possible. Furthermore, the hypothesis was put forward that cyclopentadiene and cyclopentane are obtained as a result of a new type of irreversible catalysis of cyclopentene, the cyclopentadiene formed being regarded as the probable source of charring on the catalyst.

Alkenylcyclohexanes and alkylcyclohexenes undergo hydrogen redistribution under conditions of contact isomerisation on an alumina–chromic oxide catalyst at 250°.[65] In particular, allylcyclohexane yields propylbenzene and propylcyclohexane in the proportions 1 : 2.

Erbium oxide and erbium oxide on alumina at 515° dehydrogenate cyclohexene and methylcyclohexene to the corresponding aromatic hydrocarbons, and move double bonds within the cyclohexane ring, but do not cause redistribution of hydrogen[66].

The main reactions of 1-methylcyclohexene on a catalyst containing 90% of alumina and 10% of ferric oxide at temperatures between 250° and 450° are isomerisation with migration of the double bond in the six-membered ring, and dehydrogenation of the starting material and of the resulting 4-methylcyclohexene to toluene. Redistribution of hydrogen with the formation of methylcyclohexane and toluene is also regarded[67] as possible. Isomerisation to five-membered hydrocarbons is not observed.

On crystalline α-chromic oxide redistribution of hydrogen in cyclohexene has been observed[68] at temperatures between 210° and 350°, but accompanied at 210°–250° by hydrogenation of the cyclohexene to cyclohexane, and at 280° and above by dehydrogenation of the cyclohexene to benzene. Among the reaction products was detected methylcyclopentane, the amount of which increased with rise in temperature. The products of catalysis between 209° and 235° contained methylcyclopentene. As already mentioned, formation of methylcyclopentene and of methylcyclopentane from cyclohexene has been observed[46] on an alumina–vanadium oxide catalyst.

Valuable results have been obtained from an investigation[69] of the dehydrogenation of cyclohexane containing radiocarbon-labelled cyclohexene on chromic oxide[70] and on rhenium on carbon[71]. It was concluded that irreversible catalysis is not the main reaction of cyclohexene on chromic oxide at 450°, and it does not take place at all on rhenium at 336°. On chromic oxide the rate of formation of benzene from cyclohexene greatly exceeds that of cyclohexane, but on rhenium the opposite is true.

The possibility of dehydrogenation and hydrogenation taking place independently during the redistribution of hydrogen at lower temperatures has been shown previously[34] on platinum films.

Thus the concept of the redistribution of hydrogen as a combination of dehydrogenation and hydrogenation, developed in this paper, is applicable not only to metallic but also to oxide catalysts.

Since oxides are far less capable than metals of retaining atomic hydrogen and transferring it from hydrocarbon molecules undergoing dehydrogenation to those undergoing hydrogenation, the lower activity of oxide catalysts towards reactions involving redistribution of hydrogen becomes explicable. Impairment of the link between dehydrogenation and hydrogenation makes balancing of these processes difficult, and hydrogen redistribution on oxide catalysts is accompanied by hydrogenation below 250°,[68] and by dehydrogenation at higher temperatures[62–64,66–68]. The predominance of the latter process over hydrogenation above 450° and at atmospheric pressure is due to thermodynamic causes.

The conclusion that irreversible catalysis does not occur on rhenium[69] constitutes evidence against a mechanism of direct transfer of hydrogen atoms between cyclohexene molecules, but does not fundamentally affect results[14] showing that, at temperatures between 215° and 300° on two rhenium catalysts prepared in different ways, cyclohexene is transformed, without evolution of gas, in conformity with the equation:

$$3C_6H_{10} = C_6H_6 + 2C_6H_{12}.$$

At higher temperatures hydrogen containing 6–8% of methane is evolved. In those experiments in which appreciable hydrogen evolution was observed, the reaction velocity was approximately two-thirds of the rate obtained by extrapolating the Arrhenius plot representing results obtained at low temperatures. The lower rate was explained by the greater degree of conversion (60–75%) under these conditions, and a possible deviation from zero order.

It is noteworthy that on the catalyst Re-2, which was more active in the conversion of cyclohexene, the rate of evolution of gas at 316° was 1.4 ml min^{-1}, and the corresponding point of the Arrhenius equation lay on the straight line representing experiments in which no gas was evolved. With the catalyst Re-1, on the other hand, the point corresponding to an experiment with a rather lower rate of gas evolution (1.3 ml min^{-1}) lay on the straight line representing all experiments in which gas was evolved. This shows that gas evolution is not the distinguishing factor between the two regions obtained on the assumption that zero reaction order is maintained throughout the range of temperatures and degrees of conversion studied.

On the view of the redistribution of hydrogen as a combination of dehydrogenation and hydrogenation, the evolution of hydrogen must be regarded as a breakdown, in favour of dehydrogenation, of the balance between these two processes. At not too high temperatures, when hydrogenation predominates owing to the conditions of thermodynamic equilibrium, the achievement of preferential dehydrogenation requires that special measures should be taken to

prevent blocking of the sites for dehydrogenation, as discussed above. The results[14] suggest a higher surface concentration of dehydrogenation centres on the catalyst Re-2 than on Re-1. This is consistent with data[72-74] indicating that Re-2 is more active also towards the dehydrogenation of cyclohexane, and with the absence from the reaction products of cyclohexene, which is detected in the products of the dehydrogenation of cyclohexane on Re-1. This last fact was explained by edge dehydrogenation, which occurs to a slight extent together with sextet dehydrogenation.

An interesting confirmation that hydrogen redistribution represents a combination of dehydrogenation and hydrogenation, in which the former reaction governs the rate of the overall process, is the agreement between experimental values for the energies of dehydrogenation of cyclohexane and of the disproportionation of cyclohexene for the two rhenium catalysts[14,73].

The results obtained on rhenium catalysts have been discussed in this Section because of the great similarity in the changes undergone by cyclohexene on them and on chromic oxide. It is interesting that substantially different indications of the nature of hydrogen redistribution in cyclohexene are obtained with different specimens of chromic oxide: Balandin and Rozhdestvenskaya[68] did not observe the applicability of the equation

$$3C_6H_{10} = C_6H_6 + 2C_6H_{12}$$

which had been found previously[13]. A chromic oxide gel catalyst[13] had a higher activity than crystalline chromic oxide[68], especially at 210° and below. The peculiarity of chromic oxide[13] is indicated also by the absence, among the conversion products of cyclohexene, of five-membered cyclic hydrocarbons, which were found in experiments with crystalline chromic oxide[68] and with other oxide catalysts[61-63]. Isomerisation of six-membered into five-membered cycloalkenes is observed also in hydrogen redistribution on aluminosilicate catalysts.

7. REDISTRIBUTION OF HYDROGEN ON ALUMINOSILICATE CATALYSTS

Hydrogen redistribution in unsaturated hydrocarbons on natural aluminosilicates was investigated by Lebedev and Koblyanskii[75] and by other workers. Synthetic aluminosilicate catalysts were also employed in many researches.

Frost[76] showed that migration of hydrogen atoms occurs in alkenes on a synthetic aluminosilicate at 250°, the accumulation of unsaturated polymers being accompanied by the appearance of saturated compounds. The hypothesis that the latter are formed from the alkenes by depletion of the hydrogen of the polymers was verified experimentally on activated clays[77,78]. Investigation of the transformation of cyclohexene[79] over an activated clay showed that the action of aluminosilicate catalysts is different from that of metals. The absence of benzene from the light fractions led to the conclusion that on aluminosilicates the hydrogen required to convert cyclohexene into cyclohexane and methylcyclopentane is derived from condensation products. The kinetics of redistribution in unsaturated petroleum derivatives on aluminosilicates has been studied in a series of papers[80-85].

Alkenes having a double bond linking a tertiary carbon atom undergo stronger saturation by hydrogen redistribution on an aluminosilicate catalyst than do other alkenes[86]. On a synthetic aluminosilicate catalyst under conditions excluding cracking, cyclohexene is converted into methylcyclopentane, and 4-methylcyclohexene mainly into methylcyclohexane[87]. Aromatic hydrocarbons were not detected in the monomer fractions, which agrees with other results[79]. Petrov and Frost[88] ascertained, from an investigation of hydrogen redistribution in a series of alkenes and cycloalkenes on an aluminosilicate catalyst, that with no single substance did the monomer fraction of the catalysate contain products containing less hydrogen than the original hydrocarbon. Aromatic hydrocarbons were detected only in the high-boiling polymeric fraction. However, the polymeric fraction contained as many saturated products as did the monomeric fraction, and was able to yield the 9–16% of hydrogen necessary for the observed saturation of the monomeric fraction. On the other hand, formation of condensation products on the catalyst grew in proportion to the quantity of saturated hydrocarbons formed. It was concluded from these results that the chief source of hydrogen for the saturation of olefinic hydrocarbons by hydrogen redistribution is the formation of condensation products (char) on the catalyst[88]. On the assumption that part of the condensation products containing relatively less hydrogen, probably polymers, can split off from the catalyst in the form of aromatic hydrocarbons, the appearance of the latter in the high-boiling fractions was attributed to processes secondary to hydrogen redistribution. In particular, further confirmation was obtained of the earlier conclusion[79] that the action of aluminosilicates on cyclohexene is different from that of metals leading to "irreversible catalysis".

An examination of the kinetics of the changes undergone by cyclohexene on aluminosilicate catalysts of different compositions showed[61] that at 350° hydrogen redistribution and polymerisation take place only on the active centres of the aluminosilicate, while isomerisation to methylcyclopentene occurs also on the active centres of aluminium oxide, reaching its greatest extent with the pure oxide. Hydrogen redistribution resulted in hydrogenation of cyclohexene and methylcyclopentene to the corresponding naphthenic hydrocarbons.

It was suggested[89] that, on aluminosilicate catalysts, dehydrogenation of a six-membered ring to an aromatic ring can occur only together with the formation of polymers, and polymerisation is necessarily linked with isomerisation of one of the rings. This hypothesis was based on experimental results indicating that, on an aluminosilicate catalyst at a temperature excluding cracking, cyclohexene is converted into a mixture of saturated and unsaturated hydrocarbons, the monomeric fraction containing cyclohexane, cyclohexene, methylcyclopentane, and methylcyclopentene, and the polymeric fraction comprising mainly the dimer, cyclohexylmethylcyclopentane, and phenylmethylcyclopentane. It is significant that benzene is absent from the monomeric fraction, and bicyclic hydrocarbons containing two six-membered rings from the polymeric fraction.

However, there are indications that the transformation of cyclohexa-1,3-diene and cyclohexene hydrocarbons having a double bond in the side-chain results, on aluminosilicate catalysts, in the formation of light aromatic hydrocarbons, as also on palladium, but complicated by polymerisation and skeletal isomerisation.

Heating *p*-mentha-1,8-diene with an activated clay at 160°–180° causes polymerisation of this hydrocarbon and its isomerisation products. The unpolymerised residue

contains 1-isopropyl-4-methylcyclohexa-1,3-diene, formed by migration of the double bond from the side-chain into the ring, the hydrogenation product 1-isopropyl-4-methylcyclohexene, and also *p*-isopropyltoluene[90]. It is interesting that a similar transformation of this terpene has been observed also on Raney nickel[91]. On activated gumbrin at 270°–275°, 3-methyl-5-propenylcyclohexene yields[92] a mixture of *m*-propyltoluene and 1-methyl-3-propylcyclohexane in the proportions 2 : 1. This process is characterised as "irreversible catalysis" occurring after migration of the double bond from the side-chain into the ring.

In the presence of gumbrin at 300°–310°, cyclohexa-1,3-diene is partly converted into a mixture of benzene and cyclohexane in proportions close to 2 : 1, and is partly isomerised into methylcyclopentene and methylcyclopentane; it is assumed[93] *via* the formation of cyclohexene by stepwise hydrogenation. These changes are accompanied by the evolution of gaseous products, considerable "charring" on the catalyst, and polymerisation of the cyclohexadiene. Cyclohexane hydrocarbons having unsaturated side-chains yield on gumbrin[87], together with polymerisation products, mixtures of aromatic and cycloalkane hydrocarbons in the proportions 2 : 1. With several of the hydrocarbons investigated, hydrogen redistribution by "irreversible catalysis" is accompanied by hydrogenation by hydrogen evolved in the simultaneous dehydropolymerisation. Thus with gumbrin the type of hydrogen redistribution in cyclohexadiene which is usual for palladium catalysts is combined with that observed for cyclohexene and several other alkenes on aluminosilicate catalysts.

It can be concluded from what has been said that the redistribution of hydrogen, which on aluminosilicate catalysts and on oxides yields a larger number of products than in the case of palladium, nevertheless retains the same basic features. The distinction, even contradistinction, met in some papers between processes of hydrogen redistribution on metallic catalysts on the one hand, and on oxide or aluminosilicate catalysts on the other, was caused by the limited character of the experimental data. As shown above, metals differ markedly from one another in their catalytic behaviour towards hydrogen redistribution reactions, mainly because of their varying ability to absorb hydrogen and transfer it from molecules of the initial hydrocarbon undergoing dehydrogenation to those undergoing hydrogenation. The more feebly developed is this ability, the less active is the metal towards hydrogen redistribution and the higher its isomerising activity. For example, only hydrogen redistribution takes place on palladium, whereas platinum is far less active towards this process, and produces isomerisation, as do aluminosilicates and several oxides. Metallic rhenium is far closer to oxides than to palladium or nickel as regards the character of the hydrogen redistribution processes occurring on it. On the other hand, on some oxides and aluminosilicates processes involving hydrogen redistribution can occur in a similar manner as on metal catalysts, but accompanied by side-reactions.

It can be concluded from what has been reported above that the redistribution of hydrogen in unsaturated hydrocarbons on metal, oxide, and aluminosilicate catalysts represents a combination of dehydrogenation and hydrogenation reactions. Stable adsorption of unsaturated six-membered hydrocarbons on the catalyst surface is probably accompanied by the elimination of hydrogen atoms mainly from $\diagdown\!\!\diagup C-H$ groups. The work of Eischens and Pliskin[94] also indicates dissociative adsorption in the absence of hydrogen and retention of double bonds in chemisorbed molecules of ethylenic hydrocarbons. Study of the effect of the adsorption of hydrocarbon vapours on the electrical conductivity of platinum films has shown[29] that adsorption first takes place on portions of the metal surface having different adsorption potentials. A hydrocarbon molecule adsorbed on the surface of a metal catalyst moves along it until adsorption accompanied by the elimination of hydrogen atoms becomes possible at a site of sufficiently high adsorption potential. Cyclohexane splits off hydrogen only at sites having the highest adsorption potential, *i.e.* with stable adsorption. On the other hand, cyclohexene and cyclohexadiene undergo this change at sites of moderate adsorption potential, from which the dehydrogenation products escape more rapidly than from those centres on which hydrogen is split off from cyclohexane or benzene. The more strongly the metal catalyst absorbs hydrogen, the more strongly is the supply of atomic hydrogen facilitated through the metal layer to centres of low adsorption potential, on which the unsaturated hydrocarbon is adsorbed without elimination of hydrogen but is sufficiently activated for hydrogenation to occur. Hence formation of H_2 molecules occurs only when dehydrogenation and hydrogenation are out of balance; and it is especially important for the redistribution of hydrogen, in contrast to ordinary dehydrogenation, that the catalyst should retain hydrogen in a suitably active form for hydrogenation of the initial hydrocarbon.

On oxide and aluminosilicate catalysts, which display activity towards hydrogen redistribution at higher temperatures than do metals, dehydrogenation of the initial hydrocarbon is often accompanied by its isomerisation and polymerisation. Without attempting to discuss these complicated cases in detail, especially as various opinions have been expressed[95-97] on the nature of the active centres in aluminosilicate catalysts, we give the mechanism of hydrogen redistribution in alkenes on such catalysts suggested by Petrov and Frost[88]. A molecule of the initial alkene, by combining with an active centre on the catalyst (HA), reacts with another molecule to form a dimer

$$CH_2{=}CH{-}R + HA \longrightarrow CH_3{-}CHA{-}R,$$

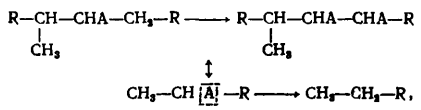
$$CH_3{-}CHA{-}R + CH_2{=}CH{-}R \longrightarrow R{-}\underset{\displaystyle CH_3}{CH}{-}CH{=}CH{-}R + HA,$$

$$R{-}\underset{\displaystyle CH_3}{CH}{-}CH{=}CH{-}R + HA \longrightarrow R{-}\underset{\displaystyle CH_3}{CH}{-}CHA{-}CH_2{-}R.$$

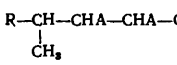
The molecule of the resulting dimer can again react with the catalyst.

By interaction of the dimer molecule linked to the catalyst and a molecule of the original substance, also combined with the catalyst, formation of a dimer molecule becomes possible which is linked no longer with one, but with two, active centres on the catalyst. The two hydrogen atoms which were originally linked to these active centres add on to the alkene. If on desorption of the dimer linked with two active centres, one hydrogen atom remains on each centre, which according to this mechanism[88] is necessary for the maintenance of catalytic activity, the molecule passing into the gas phase contains two hydrogen atoms less than did two molecules of the original alkene. If the

process of depletion of the dimer or other polymer molecules with respect to hydrogen is continued, resinous products (char) are obtained:



and further with formation of a new hydrocarbon molecule and a polymer–catalyst complex which contains still less hydrogen:



Resinification occurs also on metal catalysts, but to a less extent than on aluminosilicates or on oxides, probably owing to the higher activity of metals towards reactions involving hydrogenation. In fact, when benzene is pyrolysed on fire-clay, dehydrocondensation reactions take place, biphenyl being formed at first, and then terphenyls, triphenylene, and resinous and tarry products. On copper at the same temperatures carbon formation is insignificant, and far less hydrogen is evolved than in the experiments with fire-clay[98]. The initial stage in carbon and resin formation may also be the splitting off of hydrogen atoms from $\diagdown\!\!\diagdown$C–H and $\diagup\!\!\diagup$C–H groups in the hydrocarbons[23-25,30,38]. The mechanism of carbon formation has been investigated[99,100] in the decomposition on silica gel of homologues of benzene, and also of alkanes and cycloalkanes containing six and seven carbon atoms. In all the cases studied, carbonisation represents a multistage dehydrocondensation either of the original hydrocarbons or of products formed by their preliminary transformation. In addition to cracking reactions, destructive hydrogenation of the cycloalkanes and alkanes is effected by the hydrogen evolved.

If on a given catalyst elimination of hydrogen from the original alkene takes place more readily than its polymerisation, resinification can be expected to diminish, and the composition of the hydrogen redistribution products will approach that corresponding to the stoichiometric equations of "irreversible catalysis". If, however, dehydrogenation is preceded by polymerisation, "irreversible catalysis" is impossible, but the dehydrogenation and hydrogenation stages are retained as in the case of metal catalysts.

Thus the hypothesis that the redistribution of hydrogen in unsaturated hydrocarbons takes place in stages enables the results obtained on metallic, oxide, and aluminosilicate catalysts to be considered from a single point of view. The nature of the reaction products depends on the extent of balancing of dehydrogenation and hydrogenation, which is facilitated by the retention, on the surface or in the adjacent layer of the catalyst, of hydrogen in a suitably active form for hydrogenation. The subsidiary processes of isomerisation and polymerisation of the original hydrocarbon indicate that under these conditions precatalytic adsorption results not only in the elimination of hydrogen atoms but also in the rupture of carbon–carbon bonds.

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INFRARED SPECTRA OF SALTS AND COMPLEXES OF CARBOXYLIC ACIDS AND SOME OF THEIR DERIVATIVES

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1. INTRODUCTION

Many of the organic reagents used for the separation and masking of metal ions are carboxylic acid derivatives. Great interest is shown in studying the structure of the compounds which are formed. Yet chemists have hardly any direct methods at their disposal which would enable them to determine with what functional groups a metal is combined. Indirect methods often do not give an unambiguous answer.

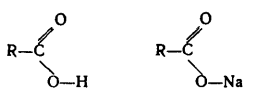
Infrared spectroscopy provides a direct method enabling the presence of a bond between a metal and a functional group to be established immediately.

The purpose of the present survey is to show, on the basis of a systematic comparison of published results, what evidence of the bonding of functional groups is provided by infrared spectra. In view of the meagre data available for comparison, only a few conclusions can be reached concerning the characteristic features of the infrared spectra of particular functional groups in different classes of acids and concerning the criteria of chelate ring formation in complexes.

Let us examine the characteristics of the infrared spectra of carboxylic acids and their salts taking the simplest representatives, monocarboxylic acids, as example.

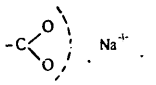
2. MONOBASIC CARBOXYLIC ACIDS AND THEIR SALTS

The characteristic functional group of carboxylic acids is the carboxyl group, the hydrogen in which is replaced by a metal on formation of a salt. Up to now chemists have held the view that such an acid and its salt can be represented quite correctly by formulae such as



However, it is assumed in several cases that the hydrogen in the carboxyl group of the acid belongs to some extent to both oxygen atoms, whereas the metal is linked to only one oxygen atom. Examination of the infrared spectra of carboxylic acids and their salts has shown that the latter view is incorrect.

According to infrared spectroscopic data, the carboxyl group has an unsymmetrical structure: the proton, owing to its small size, is located within the electron shell of one of the oxygen atoms [1]. All acids contain a band due to the carbonyl group C=O in the neighbourhood of 1700 cm^{-1}, which is present also in the spectra of aldehydes, ketones, and esters. Salts of carboxylic acids have no carbonyl band at about 1700 cm^{-1}, but contain a characteristic band in the range 1510–1650 cm^{-1} and a series of other characteristic bands due to the COO^- ion, which has a symmetrical structure in which the metal atom is associated equally with the two oxygen atoms and the O–C–O angle is 110°–130°: [1,2]



The symmetrical structure of the COO^- group is proved also by the close similarity between the spectra of carboxylates and of nitro-compounds [1,2]. Thus the Raman spectrum and the infrared absorption spectrum of disodium oxalate are very similar to those of N_2O_4, [2] while the spectrum of sodium benzoate resembles that of nitrobenzene [1].

Flett examined sixty carboxylic acids in their normal state of aggregation, solid or liquid, at room temperature [3], and found that the carboxyl group has five characteristic frequencies, at 2500–2700, ~1700, ~1400, 1200–1300, and 900 cm^{-1}, with relative intensities of 1 : 5 : 2 : 3 : 1. Table 1 gives the assignment of the frequencies. The most characteristic among them are considered to be the O–H stretching vibrations, at 2500–2700 cm^{-1}, of carboxyl groups present in dimers, and the C=O stretching band at ~1700 cm^{-1} when carboxyl-containing compounds are absent. The position of the carbonyl band may be somewhat displaced depending on the nature of the substituents in the organic radical [3–5]. Thus passage from aliphatic to aromatic acids is accompanied by a shift in the carbonyl band to longer wavelengths (1690 cm^{-1} in benzoic acid) [3].

TABLE 1. Characteristic frequencies of the carboxyl group.

Frequency, cm^{-1}	Intensity*	Assigned to	Ref.
2500–2700	w.	O–H stretching vibrations, linked into COOH dimers	3
~1700	v.s.	C=O stretching vibrations	3
~1400	m.	C–O stretching vibrations or	7,8
1200–1300	s.	O–H deformation vibrations	
~900	w.	O–H deformation vibrations (non-planar) in COOH	7

* Intensities arbitrarily denoted as: s. = strong, v.s. = very strong, m. = medium, w. = weak.

TABLE 2. Characteristic frequencies of the carboxylate ion.

Frequency, cm^{-1}	Intensity	Assigned to	Ref.
1510–1650	s.	asymmetric COO^- stretching vibrations	1, 8, 9
~1400	s.	one of them = symmetric COO^- stretching vibrations	1, 9, 10
1280–1350	s.		
800–950	s.	COO^- deformation vibrations	1

The presence of electronegative substituents in the organic radical causes a shift to shorter wavelengths. Thus in aliphatic acids the band is usually located at 1705–1720 cm^{-1},[3] in monochloroacetic acid it is at 1735 cm^{-1},[3] and in 2-chloropropionic acid at 1730 cm^{-1}.[6]

The characteristic frequencies of the carboxylate ion are altogether different. There are four of them, at 1510–1650, ~1400, 1280–1350, and 800–950 cm^{-1},[1,8-10] their assignment being given in Table 2.

Thus the identification of carboxylic acids and their salts from the infrared spectra presents no difficulties: the acids have a weak band at 2500–2800 cm^{-1} and an intense band due to C=O stretching vibrations at 1700 cm^{-1}; the spectra of the salts do not contain these bands, but do show an intense band due to asymmetric COO^- stretching vibrations at 1560–1600 cm^{-1}.

These characteristic frequencies can be utilised also for identifying carboxylic acids and their salts in aqueous solution[8], by placing a drop of the test solution between plates of fluorite, silver chloride, BaF_2, or As_2S_3. Since ordinary water absorbs strongly around 1600 cm^{-1}, solutions in heavy water can conveniently be employed, as they do not absorb in this region.

3. POLYBASIC CARBOXYLIC ACIDS AND THEIR COMPOUNDS WITH METALS

Polybasic carboxylic acids differ little from the monobasic acids with respect to the position of the carboxyl band[3]. Thus the C=O stretching vibrations are at 1712 cm^{-1} in acetic acid, 1690–1710 cm^{-1} in oxalic acid, 1700 cm^{-1} in succinic acid, and 1740 and 1710 cm^{-1} in malonic acid[3]. If all the carboxylic groups are combined with a metal, the carbonyl band disappears, and a band due to asymmetric stretching vibrations of the carboxylate ion appears in the range 1510–1650 cm^{-1}.[11,12] If, however, one of the carboxyl groups remains uncombined, or if the combined carboxyl groups are not equivalent, two or more bands are observed in the range 1560–1640 cm^{-1}.[11,12]

Lecomte and his collaborators carried out a detailed investigation of the infrared spectra of the oxalates of fifty metals[2]. Comparison of the infrared and Raman spectra showed that with many oxalates they have no bands in common. According to the principle of mutual exclusion, this indicates the presence of a centre of symmetry in dipotassium and diammonium oxalates and in $K_2[TiO(C_2O_4)_2]$. In the case of $K_3[Al(C_2O_4)_3]$ the same bands are present in the Raman and in the infrared spectra, and hence the molecule has no centre of symmetry[2].

Guided by the formal criterion of the presence of two different metals in the formula of a complex oxalate and of one metal in a molecule of a simple oxalate, Lecomte concludes that the characteristic features of the infrared spectra of oxalates are that simple oxalates contain two intense bands in the range 1100–1600 cm^{-1} and one in the range 700–900 cm^{-1}, whereas complex oxalates contain three and two bands respectively. The reasons for this are probably quite different. The researches of other workers on oxalates[13-15] led Fronæus and Larsson to suggest[14] that the appearance of new bands in concentrated aqueous solutions of ferric oxalate is due to the formation of polynuclear complexes, whereas the spectra of solutions containing one, two, and three $C_2O_4^{2-}$ ions per atom of iron or aluminium coincide with the bands of solid $Fe_2(C_2O_4)_3$.

All that has been stated above concerning the great similarity in the spectra of oxalates applies to molecules which are not combined with water of crystallisation. The presence of a hydrate sheath about the metal atom has a definite effect on the symmetry of the oxalate ion[11,16,17] and also on that of other anions, for example, SO_4^{2-}.[17] In the compound $U(C_2O_4)_2.5H_2O$ the oxalate ion possesses symmetry of type D_{2h}, but in $K_4[U(C_2O_4)_4].4H_2O$ its symmetry is C_{2v}.[16] The infrared spectrum of oxalates is affected not only by the number of molecules of water of crystallisation but also by differences in crystal form. For example, anhydrous calcium oxalate, the monohydrate, and the three different forms of the trihydrate have different spectra[11].

Unfortunately the peculiarities of the infrared spectra of the simplest normal and hydrogen oxalates have not been discussed in the literature. The acid oxalate for some reason does not contain the carbonyl band, which would indicate the presence of a free carboxyl group, while in disodium oxalate the frequency of the asymmetric COO^- stretching vibrations is higher than in salts of other dicarboxylic acids[2,12].

Frequencies in compounds formed by malonic, succinic, glutaric, and other acids with metals are assigned to vibrations of the carbon chain by a comparison of the spectrum of the salt with that of the corresponding acid[12,15,18,19]. They should not be greatly displaced on passing from the acid to the salt. Like the oxalate series, the spectra of malonates[1,12,15], succinates[1,12,15], and phthalates[1] of different metals have much in common, since in each series they are due to the same anions.

In contrast to potassium hydrogen oxalate, the corresponding phthalate has a clearly defined band at 1669 cm^{-1} due to the free carboxyl group[20,21].

Comparison of the spectra of disodium malonate, succinate, glutarate, etc. shows that the succinate has a smaller number of bands than the other salts, which is due to the presence of a centre of symmetry in this molecule[12]. Rather surprisingly, the compounds formed by copper with oxalic, malonic, succinic, and other aliphatic acids have spectra which are very similar to those of the corresponding disodium salts[12,15]. It is true that, in all cases other than the malonate, the asymmetric stretching vibrations of the carboxylate ion are at shorter wavelengths in the copper salts than in the sodium salts[12]. This can be explained by the bond in the latter being ionic in character, whereas in the copper salts it is more covalent (see Table 3), by analogy with the compounds of ethylenediaminetetraacetic acid (EDTA)[22-25] and of amino-acids[26-29]. However, Kuroda and Kubo[12] have a different explanation — coupling between copper atoms in the salts of all dibasic acids other than malonic acid — as a result of which the magnetic moment associated with one copper atom is less than that

TABLE 3. Frequencies (in cm^{-1}) of acids, salts, and complexes.

	Acid					Normal salt					Complex				
	formula	stretching vibrations C=O	stretching vibrations of other functional groups	other groups	ref.	formula	stretching vibrations COO^- asymmetric	stretching vibrations of other functional groups	other groups	ref.	formula	stretching vibrations COO^- asymmetric	stretching vibrations of other functional groups	other groups	ref.
Monobasic carboxylic acids	CH_3COOH	1712			3	CH_3COONa	1600			8					
	C_6H_5COOH	1685			3	C_6H_5COONa	1600			21					
Polybasic carboxylic acids	COOH—COOH	1690—1710			3	COONa—COONa	1635			12		1665		CH_2 rock	12
	COOH—CH_2—CH_2—COOH	1700		CH_2 rock 808	3,2	COONa—CH_2—CH_2—COONa	1567		CH_2 rock 808	12		1608		881, 893	12
		1695			3		1603			21					
Halogenated acids	$ClCH_2$—CH_2—COOH	1730			3	$ClCH_2$—CH_2—COONa	1635			6					
Hydroxy-acids	COOH—CHOH—CHOH—COOH	1750	δ1097		30							1634	1080 1063		30
		1665	3230		3,53		1603	нет		21					
EDTA	$H_2CN(COOH)_2$ $H_2CN(COOH)_2$	1697		CH stretch. 3020 3030	25	$H_2CN(COONa)_2$ $H_2CN(COONa)_2$	1510		C—H 2800 2810	22	$Ba[CoEDTA_2].4H_2O$	1638		CH stretch. 2900—3000	24, 25
Amino-acids	$H_3\overset{+}{N}CH_2$—COO^-	1603	3160		8	H_2NCH_2COOK	1575	3380, 3360		29		1575	3330, 3260		29
		1660	3361		3		1575	3410		26		1603	3280		26

predicted theoretically, and the band is displaced to shorter wavelengths. In copper and sodium malonates the position of the bands is the same, and the magnetic moment of the copper compound has its usual value.

The linking of two carboxyl groups in a dicarboxylic acid by a metal involves the presence of only one band due to asymmetric COO^- stretching vibrations provided that the polarity of the COO^-–M^{n+} bond and their separation in the crystal lattice are equal for the two carboxylate ions[12]. Such cases are given in Table 3 (copper oxalate and succinate).

The linking of the two carboxyl groups in succinic acid by a metal with formation of a ring results in deformation of the $-CH_2-CH_2-$ bond, causing splitting of the 808 cm^{-1} CH_2 rocking band and its displacement to shorter wavelengths[12] (see Table 3). In complexes with other dicarboxylic acids the deformation of the carbon chain is less pronounced[12].

Thus the absence of the carbonyl band in the region of 1700 cm^{-1} indicates that all the carboxyl groups in a polybasic acid are combined with a metal. The presence of only one asymmetric COO^- stretching band in the range 1560–1600 cm^{-1} indicates that all the combined groups are equivalent, and the presence of more than one band that they are not equivalent or that an uncombined carboxyl group is present.

4. HALOGENATED ACIDS AND THEIR SALTS

Replacement of hydrogen by a halogen or by CN in the organic radical of an aliphatic acid increases the frequency of the carbonyl stretching vibrations. Flett points out[3] that the shift to shorter wavelengths is greater with substitution in the α-position than in the β-position. The C=O band is displaced to shorter wavelengths with increasing number of halogen atoms in the acid molecule[31,32], and the shift in the C=O stretching vibrations also increases in the sequence I^-, Br^-, Cl^-, F^-.[31,33] Analogous results for the sodium salts of chlorinated propionic acids have been published by Potts[8].

5. ETHYLENEDIAMINETETRAACETIC ACID AND ITS COMPOUNDS WITH METALS

Sawyer and his coworkers have made a detailed investigation of the infrared spectra of ethylenediaminetetraacetic acid (EDTA) and its compounds with fifteen metals[22-24,34] over the range 700–3400 cm^{-1}. In EDTA the C=O stretching vibrations occur at 1697 cm^{-1} for all four carboxyl groups. Salt formation is accompanied by the appearance of bands in the range 1550–1650 cm^{-1} (see Table 3). The C–H stretching vibrations are sensitive to the formation of chelate complexes. In the acid and its disodium salt they occur at 3020–3030 cm^{-1}, in the tri- and tetra-sodium salts at 2800–2810 cm^{-1}, and in complexes with bivalent and multivalent metals at 2900–3000 cm^{-1}. This last frequency is characteristic of chelation in EDTA compounds[22-24,34].

The position of the band due to asymmetric COO^- stretching vibrations indicates the nature of the bond between the metal and COO^-: absorption in the range 1510–1550 cm^{-1} is brought about by complexes in which the bond is predominantly ionic (Na^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, Ce^{3+}, and Bi^{3+}), and in the range 1630–1650 cm^{-1} by complexes having a predominantly covalent bond (Pb^{II}, V^{III}, Cr^{III}, Fe^{III}, Co^{III}, V^{IV}, Ti^{IV}, Th^{IV}, Mo^{V}, and Mo^{VI} [34]). The difference in frequency between the asymmetric and the symmetric COO^- stretching vibrations (at 1510–1650 cm^{-1} and 1350–1450 cm^{-1} respectively) may serve as a measure of covalency. For an ionic bond Δ = 150 cm^{-1} (sodium acetate, tetrasodium salt of EDTA); the bond is covalent if $\Delta > 225$ cm^{-1} (with Cr^{III} Δ = 280 cm^{-1}).

With increasing radius of the metal the frequency of the asymmetric COO^- stretching vibrations shifts to longer wavelengths in the sequence: Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}. The ionic character of the bond becomes stronger in the same sequence (from left to right), and the complexes become less stable[24,34]. However, correlation between the position of the band and the stability of the complexes is rarely observed.

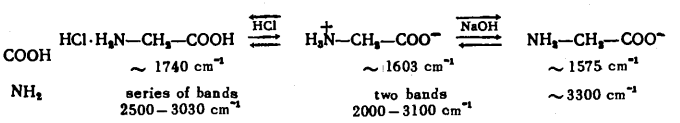
Comparison of the infrared spectra with results obtained by other physicochemical methods led Sawyer *et al.* to conclude that one narrow band in the range 1550–1630 cm^{-1} indicates a coordination number 6 with most bivalent metals[24]; a wide band in the range 1630–1660 cm^{-1} suggests that EDTA is also a sexidentate ligand in its complexes with Fe^{III}, Co^{III}, and Mo^{V}.[23] Bailar considers that in $Na[Co^{III}BrEDTA]$ the EDTA is a quinquedentate ligand[25]. In spite of the ability of EDTA to form chelate complexes and the presence of a metal–nitrogen coordinate bond (as demonstrated by X-ray structural analysis)[24], and of both Sawyer and other investigators[22-25,34-37] having obtained data on C–N vibrations, it has not yet proved possible to find criteria of metal–nitrogen bonding in the infrared spectra. It has, however, been noted that the C–N band shifts to longer wavelengths with increasing ionic radius of the metal.

The presence of one narrow band in the region of the asymmetric COO^- stretching vibrations indicates that all the carboxyl groups are linked with the metal. Thus $Ba[CoEDTA_2].4H_2O$ has one band at 1638 cm^{-1}, and hence all the carboxyl groups are equally linked with the metal; $Na[Co(NO_2)EDTA].H_2O$ has bands at 1628 and 1723 cm^{-1}, *i.e.* one free carboxyl group[25]. The presence of three bands in the titanium compounds of EDTA allows us to accept for it the formula $TiOEDTA.H_2O$ with two uncombined groups[23,24]. With the titanium compound the bands are observed at 1700–1720 cm^{-1}, so that they can be confidently assigned to a free carboxyl group; in the case of the Mo^{V}, Mo^{VI}, Th^{IV}, and other compounds, more than one band is observed below 1650 cm^{-1}, so that they can be assumed to contain either a free carboxyl group or non-equivalent combined carboxyl groups[24,25,34].

Other studies have been made[25,36] of compounds formed by Co^{III} with EDTA, including the effect of water of crystallisation on the infrared spectrum[38], and also of the Cu^{II},[30] Pt^{II}, and Pd^{II} [37] compounds. Thus the linking of the carboxyl groups in EDTA by a metal produces similar changes in the infrared spectrum to those with the other acids. Formation of a chelate ring is accompanied by a shift in the C–H stretching vibration to the 2900–3000 cm^{-1} range.

6. AMINO-ACIDS AND THEIR COMPOUNDS WITH METALS

Amino-acids are usually in the form of zwitter-ions, and therefore do not exhibit the bands due to the free carboxyl group at ~1740 cm^{-1} or the free NH_2 at 3300 cm^{-1}.[8,29,39] If sodium hydroxide is added to an aqueous solution of an amino-acid[8], bands due to the carboxylate ion and free NH_2 appear; addition of hydrochloric acid at first causes the appearance of NH_3^+ bands in the range 2000–3000 cm^{-1} and the associated COO^- band at 1603 cm^{-1}, whereas a high concentration of hydrochloric acid produces a band at ~1740 cm^{-1} due to the free carboxyl group and an almost continuous series of bands in the range 2500–3030 cm^{-1}, characteristic of compounds formed by amines with hydrochloric acid[8,29]. With glycine this equilibrium can be represented thus:



Quagliano and his collaborators examined the infrared spectra of the compounds formed by about ten metals with glycine and its derivatives, alanine, sarcosine, and other amino acids[9,10,26-29,40-42]. They showed that the complexes contain an ionic bond between the metal and the carboxylate ion (band in the range 1550–1630 cm^{-1}) and a coordinate link with the amino-group, the corresponding band being displaced to longer wavelengths compared with the sodium salt (see Table 3)[26,29]. As with the EDTA compounds, the frequency of the asymmetric COO^- stretching vibrations gives a measure of the covalency of the bond with the metal: for a purely ionic bond the frequency is 1570–1580 cm^{-1} (Zn^{2+}, Co^{2+}, Cu^{2+}, and Ni^{2+} diglycinates), and for a covalent bond above 1610 cm^{-1} (with Pt diglycinate 1640 cm^{-1})[26,29]. A characteristic sign of a coordinate link between a metal and an amino-group is a sharp increase in intensity of the NH stretching band at 3300 cm^{-1}.[9] An increase in the number of coordinated ligands containing NH_2, and in particular an increase in the number of coordinated ammonia molecules in ammines, shifts this band to longer wavelengths[9].

If the spectra of the solids are determined, the form of the N–H stretching bands may give information on the structure of the complex[9]. Thus one narrow band in complexes containing two molecules of amino-acid combined with one atom of copper indicates that these molecules have a *trans*-coplanar configuration. A wide band given by the bis(salicylideneimine) complex of zinc indicates a tetrahedral configuration; and an intense narrow band at 3297 cm^{-1} and a broad band at 3160 cm^{-1} indicate that the tris(salicylideneiminato)iron(III) complex has an octahedral configuration[9]. In the case of a *cis*-coplanar configuration, the narrow NH stretching band is split into two. The splitting of bands into two in the case of the *cis*- compared with the *trans*-configuration is a general characteristic of the infrared spectra of such compounds.

The relation between the position of the NH band and the stability of the complexes is a matter of controversy. Thus in the glycinato-complexes the NH frequency diminishes in the sequence K^+, Cu^{2+}, Co^{3+}, Pt^{2+}, H^+,[9] and in the salicylideneimine complexes in the sequence Zn^{2+}, Be^{2+}, Cu^{2+}, Ni^{2+}, Fe^{2+},[9] it being assumed that a shift to a longer wavelength corresponds to strengthening of the M → N bond. However, this is not always confirmed by other methods.

Anthranilic acid behaves similarly to other amino-acids[9,26,43]. Thus in copper anthranilate the NH band is at longer wavelengths (3280 cm^{-1}) than in sodium anthranilate (3410 cm^{-1})[9] (see Table 3). Anthranilates have the advantage over other complexes formed by metals with organic reagents that, for Cu^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Hg^{2+}, Ag^{+}, Pb^{2+}, Na^{+}, and Ba^{2+}, it has proved possible to find[43] specific bands from which one metal can be conveniently determined quantitatively in the presence of another. However, the error in such a determination is 2–3%.[43]

Thus the linking of a carboxyl group with a metal in amino-acids shows the same features as in the other acids. The presence of a coordinate bond with the amino-group is characterised by a strengthening of the NH stretching vibration in the region of 3300 cm^{-1}.

7. HYDROXY-ACIDS AND THEIR COMPOUNDS WITH METALS

The presence of a hydroxyl group in a hydroxy-acid produces only a slight displacement of the carbonyl band to shorter wavelengths[44], the stretching vibrations of the C=O group in glycollic and the isomeric hydroxypropionic and hydroxybutyric acids lying between 1700 and 1725 cm^{-1}. The presence of a hydroxy-group in an acid is most readily established by means of an intense band in the region of O–H stretching vibrations at about 3440 cm^{-1}, and also from weak bands at 6700 cm^{-1} (first overtone) and 5150 cm^{-1} (combination frequency)[44]. The region of O–H deformation vibrations at ~1050 cm^{-1} is convenient for determining the relative positions (α, β, or γ) of the hydroxyl and carboxyl groups. Ordinary acids, too, show a band in this range, due to O–H deformation vibrations in the COOH group, but in hydroxy-acids the band is more intense, being displaced to shorter wavelengths by an α-hydroxyl group but not shifted by a β-hydroxyl[44]. Thus O–H deformation vibrations are located at 1040 cm^{-1} in butyric acid, 1060 cm^{-1} in lactic acid, and at 1042 cm^{-1} in 3-hydroxybutyric acid[44].

Interesting data on the structure of copper tartrate trihydrate $CuC_4H_4O_6.3H_2O$ have been obtained by Kirschner[45], who has shown that one narrow band at 1634 cm^{-1} proves that the two coordinated carboxyl groups are completely equivalent. In the complex the band at 1097 cm^{-1} due to deformation vibrations of the equivalent free hydroxyl groups in free tartaric acid is split into two (1080 and 1063 cm^{-1}), which indicates their non-equivalence. Although the hydrogen in them has not been replaced by copper, one of the hydroxyl groups is more closely linked with the copper atom than is the other. The influence of the water of crystallisation on the spectrum of Rochelle salt has been studied by Bernard[46].

Some work has been done on the salts of pyruvic acid, most of which show a band due to stretching vibrations of the carbonyl group, both in the solid state and in aqueous solution, *i.e.* they are derivatives of the keto-form $CH_3.CO.COOM$.[47,49] The lithium salt in the solid state, and according to some investigators also the sodium salt[49], show no band corresponding to C=O, but are derived from the diol form of the acid, $CH_3.C(OH)_2.COOLi.nH_2O$.[47–49] Contradictory data have been obtained concerning the presence of a band due to C=O in aqueous solutions of lithium pyruvate.

Goulden has investigated aqueous solutions of salts having the composition $M^{2+}\{HO.CR_2.COO^-\}_2$ formed by Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, and Cu^{2+} with glycollic, lactic, and 2-hydroxy-2-methylpropionic acids[50–52]. Owing to the strong absorption by water, the region of the asymmetric COO^- stretching vibrations was not examined; the deformation vibrations of the hydroxy-group were investigated. Goulden assigned the band at 1390 cm^{-1} in compounds formed by bivalent metals with glycollic and lactic acids to vibration of the hydroxy-group combined in a chelate complex[50]. This band increases in intensity as the complex becomes more stable in the sequence $Sr^{2+} < Ca^{2+} < Mg^{2+} < Zn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} \ll Cu^{2+}$, while the band at 1275 cm^{-1}, assigned to the hydroxy-group in a free lactate ion, and the band at ~1080 cm^{-1} diminish. All the lactates investigated, including those of lithium, sodium, and potassium, have bands at 1390, 1275, and 1080 cm^{-1}, and all conclusions concerning chelation were made merely from a comparison of the intensities of these bands, which is unconvincing[51]. It is also not clear why Goulden assigned the shoulder of the 1360 cm^{-1} band in calcium and strontium 2-hydroxy-2-methylpropionates to an uncombined hydroxy-group (1330 cm^{-1}), while the 1360 cm^{-1} band itself, observed in calcium and copper 2-hydroxy-2-methylpropionates, was assigned to a hydroxy-group linked to copper in a chelate complex.

Other salts of hydroxy-acids have been studied by Parker[53].

Thus the previous generalisations relating to the carboxyl group remain valid for the compounds formed by hydroxy-acids with metals. The stretching vibrations and overtones of the hydroxy-group have not been investigated, while the deformation vibrations do not always show marked differences in chelate complexes and in simple salts having an uncombined hydroxy-group.

Salicylates

The band corresponding to C=O stretching vibrations in salicylic and 3-hydroxy-2-naphthoic acids is at longer wavelengths (down to 1660 cm^{-1})[3,54,55] than in acetic acid (1712 cm^{-1}) and benzoic acid (1685 cm^{-1})[3], while the hydroxyl stretching band is in the neighbourhood of ~3200 cm^{-1} owing to the presence of a strong intramolecular hydrogen bond[54–57]. In methoxybenzoic acid, where a hydrogen bond is impossible, the O–H stretching vibration occurs at 3400 cm^{-1}.[21] The reason for the unusual stability of this bond, which has been termed a "chelate and conjugate hydrogen bond", has formed the subject of much detailed investigation[54–57]. It is due to the superposition of three effects: ring formation (chelation), the presence of the conjugated bond O=C–C=C, and hydrogen bond formation –O–H...O=C– between hydroxyl and carboxyl groups located close to one another.

Lecomte and coworkers[1] examined the compounds formed by salicylic acid with six metals over the range 650–1500 cm^{-1}, and showed the great similarity in the infrared spectra of the salicylates of different metals. The compounds formed by salicylaldehyde and methyl salicylate with Na^+, Cu^{2+}, Ti^{4+}, Mg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, and Cd^{2+} have been investigated by Yamada[58], Yamamoto and Kambara[59], and Bellamy and Branch[60]. They showed that the presence of a coordinate link with the C=O group produces a shift in the corresponding band to longer wavelengths compared with free salicylaldehyde and methyl salicylate, together with a considerable increase in its intensity. In contrast to many other complexes (with acetylacetone[60], benzoylacetone[60], tropolone[61]) the position of the C=O stretching band (1668 cm^{-1}) and its shift to longer wavelengths in the salicylaldehyde complexes vary linearly with the logarithm of the instability constant of the complex. The frequency of the C=O stretching vibrations falls in the sequence $Mg^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Ti^{4+} > Cu^{2+} > Cd^{2+}$,[58,60] while the stability increases from left to right. The frequencies in this sequence are 1681, 1659, 1656, 1652, 1637, 1608, and 1585 cm^{-1} respectively. Ayers and Land have identified

the Nb=O band in the sulphosalicylic complex of niobium[62]. Hales *et al.*[21] showed that, in monosodium and disodium salicylates, the band due to asymmetric vibrations of the carboxylate ion is located at 1603 and 1590 cm^{-1} respectively, which is similar to what is found with the salts of all carboxylic acids. They suggested[21] that the monosodium salicylate will differ from the disodium compound in the O–H stretching band in the range 3100–3400 cm^{-1}. However, with neither salt was any band detected in this range[21]. The reason for the absence of bands due to the hydroxy-group in monosodium salicylate is completely obscure. Cardinaud considers[63] that the absence of O–H stretching vibrations in *o*-nitrophenol is due to a strong hydrogen bond between the OH and NO_2 groups, as a result of which the O–H band disappears from the 3100–3400 cm^{-1} range. He observed that dissolution of the compound in dioxan considerably increases the intensity of the 3200 cm^{-1} band[63], which can therefore be assigned to vibrations of the hydroxyl group. Since the spectrum of *o*-hydroxynitrobenzene should be similar to that of sodium salicylate, the latter would be expected to have a band at 3200 cm^{-1}, but this is not the case. An interesting fact in this connection is that the very stable hydrogen bond formation in 5-hydroxyflavones is accompanied by the disappearance of the band due to O–H stretching vibrations, whereas a less stable hydrogen bond in 3-hydroxyflavones gives a weak band at 3200 cm^{-1}.[64]

Thus the infrared spectra of metal salicylates have been little investigated. Judging from the spectra of the sodium salicylates, the asymmetric COO^- stretching vibrations have the usual frequency, but the disappearance of the hydroxyl band from the range 3100–3400 cm^{-1} has not been explained in the literature.

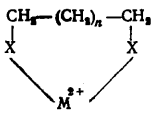
8. CRITERIA OF THE LINKING OF FUNCTIONAL GROUPS AND OF CHELATE RING FORMATION

From the results obtained by several investigators the changes in the infrared spectrum occurring when hydrogen in a carboxyl group is replaced by a metal can be attributed to a change in symmetry of the carboxyl group. The bands due to the carboxyl group, located at 2500–2700, ~1700, ~1400, 1200–1300, and ~900 cm^{-1},[8] are replaced by bands due to the carboxylate ion, at 1510–1630, ~1400, 1280–1350, and 800–950 cm^{-1}.[8,16] In order to demonstrate the linking of the carboxyl group with a metal it is sufficient to establish the disappearance of the C=O stretching band at ~1700 cm^{-1} and the appearance of the asymmetric COO^- stretching band in the range 1510–1630 cm^{-1}.[8] In several cases the position of the band due to asymmetric stretching vibration of COO^- depends on the nature of the metal, and several investigators explain this by different degrees of polarity of the metal–COO^- bond[22,24-26,29].

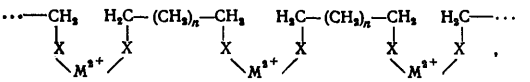
From all that has been said it follows that the linking of a carboxyl group with a metal produces the same spectral changes compared with the acid irrespective of the acid chosen, whether a monocarboxylic acid, an amino-acid, a hydroxy-acid, etc. Splitting of the band due to asymmetric stretching vibration of the carboxylate ion is observed when the molecule contains more than one carboxyl group, forming bonds of different polarity[22,26,29,34].

The presence of other functional groups in an acid results in the appearance of the corresponding bands in the infrared spectrum, while interaction of these groups with the metal (replacement of hydrogen, formation of coordinate bonds) results in corresponding changes in the spectrum.

If a carboxylic acid can act as a bidentate ligand, the linking of both functional groups by a bivalent or a multivalent metal indicates formation of a chelate ring:



where the X are functional groups. Theoretically, compounds can be formed in a different way:



but the existence of such chains has not yet been demonstrated among the compounds which we have been discussing. The formation of chelate rings is proved partly by chemical methods, in particular by the considerable stability of such compounds, in many cases by the formation of intensely coloured compounds, etc.

Summarising the information available in the literature, we can conclude that the infrared spectra give no criterion which is valid for all cases of chelate ring formation. In individual cases chelation can be assessed on the following basis:

1. In all cases in which a carboxylic acid may act as a bidentate ligand, combination of both functional groups with one metal atom may indicate formation of a chelate ring. In particular, this is shown in the infrared spectrum as follows: (a) in a dicarboxylic acid by the presence of only one band due to asymmetric stretching vibration of COO^- at 1510–1630 cm^{-1};[12,21] (b) in a monocarboxylic hydroxy--acid by the disappearance of the C=O stretching vibration at ~1700 cm^{-1} and appearance of the asymmetric COO^- stretching vibration at 1510–1630 cm^{-1}, a shift in the deformation vibration of the hydroxy-group at ~1090 cm^{-1};[8,30] (c) in monocarboxylic amino-acids by the disappearance of the C=O stretching vibration at ~1700 cm^{-1} and appearance of the asymmetric COO^- stretching vibration at 1510–1630 cm^{-1}, an intense band due to NH_2 coordinated with the metal at ~3300 cm^{-1}.[28,29]

2. Direct proof of the formation of a chelate ring may be provided by deformation of the carbon chain of the acid, which in the particular case of the succinates appears in a shift in the CH_2 rocking oscillations at ~808 cm^{-1} to shorter wavelengths[12], and in the case of EDTA complexes a displacement to longer wavelengths of the CH stretching vibrations at 3020 cm^{-1}.[22,24,25] However, an increase or a decrease in the number of carbon atoms in a dicarboxylic acid is accompanied by a smaller displacement of the CH_2 rocking oscillations compared with succinic acid (the shift may even be absent). This may indicate less deformation of the chain[12].

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THE ELECTROCHEMISTRY OF SEMICONDUCTORS

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I. INTRODUCTION

Recent advances in semiconductor physics, and the wide application of semiconductor devices in radio circuits have created a new branch of electrochemistry: the electrochemistry of semiconductors. Over 200 papers primarily concerned with the electrochemical properties of silicon and germanium have been published since 1955. In more recent years, electrochemists have become interested in new semiconducting materials, such as intermetallic compounds, silicon carbide, and various oxides and sulphides.

The development of semiconductor electrochemistry owes its origin to the experiments of Brattain and Garrett. In the Soviet Union, Efimov and Erusalimchik were the first to study semiconductor electrochemistry, but it was not long before the researches of workers at the Institute of Electrochemistry and the Institute of Physical Chemistry of the Academy of Sciences of the USSR, and at the Karpov Physicochemical Institute began to show an awareness of semiconductor problems. Theoretical studies of semiconductor electrochemistry in the USSR were started under the initiative of V.G.Levich.

Gerischer, Green, and Dewald are among those who have made significant contribution to the development of basic ideas in semiconductor electrochemistry.

II. THE SEMICONDUCTOR-ELECTROLYTE SYSTEM AT EQUILIBRIUM

1. Potential Distribution at the Phase Boundary

The equilibrium potential of a semiconductor is the potential difference† in the equilibrium system:

metal M | semiconductor | electrolyte | metal M.

This potential does not depend on the position of the Fermi level in the semiconductor [1,2].

The Galvani potential which appears at the phase boundary between semiconductor and electrolyte is distributed over three separate regions: the diffuse part of the double layer in the electrolyte, the Helmholtz double layer, and the semiconductor‡. Its magnitude is a function of the position of the Fermi level in the semiconductor [1,2,6]. It can be shown (see below) that in the absence of surface states§ the potential drop across the first two regions can be made negligibly small in comparison with the change in potential within the semiconductor. We shall also calculate the thickness of the space-charge layer in the semiconductor.

Consider first Poisson's equation in the form

$$\frac{d^2\varphi(x)}{dx^2} = -\frac{4\pi}{\epsilon}\rho(x), \qquad (1)$$

where $\varphi(x)$ is the potential at the point x, $\rho(x)$ is the space-charge density at the same point, and ϵ is the dielectric permittivity of the medium. The x axis is chosen normal to the phase boundary. Let the semiconductor occupy the region $x > 0$, and the electrolyte occupy the region $x < -d_0$, where d_0 is the thickness of the Helmholtz layer (of the order of 10^{-8} cm).

In an n-type semiconductor with fully ionised donor levels the space-charge density is given by the expression

$$\rho(x) = e[-n(x) + p(x) + N_D],$$

where n, p, and N_D are the concentrations of electrons, positive holes, and donors respectively, and e is the absolute value of the electronic charge. At equilibrium, the concentrations of free current carriers in the presence of an electric field in the semiconductor are given by Boltzmann expressions:

$$n(x) = n_\infty e^{\frac{e[\varphi(x)-\varphi_B]}{kT}} \qquad p(x) = p_\infty e^{-\frac{e[\varphi(x)-\varphi_B]}{kT}}. \qquad (2)$$

The symbols n_∞, p_∞, and φ_B refer to the electron concentration, the hole concentration, and the potential at a point far removed from the space-charge region ($x \to \infty$). An adequate, though qualitative, description of the system can be obtained by considering only small changes in potential. We shall assume, in other words, that $e\varphi/kT$ is much less than unity everywhere in the semiconductor. This enables us to neglect higher terms in the series expansions of the exponentials of Eqn. (2), and to express the space-charge density in the form

$$\rho(x) = \left\{-n_\infty\left[1 + \frac{e(\varphi_{(x)} - \varphi_B)}{kT}\right] + p_\infty\left[1 - \frac{e(\varphi_{(x)} - \varphi_B)}{kT}\right] + N_D\right\}e. \qquad (3)$$

At a point well inside the semiconductor there is no space charge, and $-n_\infty + p_\infty + N_D = 0$. In an n-type semiconductor $n_\infty \gg p_\infty$. Under these conditions Eqn. (3) takes the form

$$\rho(x) = -e^2\frac{[\varphi(x) - \varphi_B]}{kT}n_\infty.$$

Poisson's equation [Eqn. (1)] can now be written in the form

$$\frac{d^2\varphi}{dx^2} = \frac{4\pi e^2[\varphi(x) - \varphi_B]n_\infty}{\epsilon_1 kT}, \qquad (4)$$

where ϵ_1 is the dielectric constant of the semiconductor.

Integration of Eqn. (4) gives

$$\left(\frac{d\varphi}{dx}\right)^2 = \frac{4\pi e^2 n_\infty}{\epsilon_1 kT}[\varphi(x) - \varphi_B]^2.$$

The electric field intensity E is related to $d\varphi/dx$ by the expression $E = -d\varphi/dx$. The field at the semiconductor surface ($x = 0$) is therefore given by

$$E_1 = \frac{\varphi_1}{d_1}, \text{ where } d_1 = \sqrt{\frac{\epsilon_1 kT}{4\pi e^2 n_\infty}}. \qquad (5)$$

The quantity d_1 has the dimension of length and is called the Debye length. Expression (5) can be interpreted as

† Equilibrium potentials for reactions at germanium and silicon electrodes in aqueous solutions have been calculated [3-5]. [More recent values can be found in Holmes [160] [Ed. of Translation).]

‡ Contributions to the Galvani potential arising from adsorption of polar molecules of the solvent (or solute) on the electrode will not be considered.

§ The term surface state [7,8] refers to an electronic energy level localised at the semiconductor surface. These levels appear when the crystal lattice is cleaved to generate a surface (Tamm states), when impurities are adsorbed on the surface, and so on.

follows: the potential drop φ_1 in the semiconductor is concentrated in a region of thickness d_1 (the Debye length) such that the ratio of φ_1 to d_1 measures the intensity of the electric field at the surface of the semiconductor, E_1¶.

As stated above, the value of the Galvani potential can be considered as the sum of three terms: $\varphi = \varphi_0 + \varphi_1 + \psi'$, where φ_0, φ_1, and ψ' denote the potential drop in the Helmholtz layer, in the semiconductor, and in the diffuse part of the electrolyte double layer respectively.

The charge density in a uni-univalent electrolyte is given by

$$\rho = (c_+ + c_-)e, \tag{6}$$

where c_+ and c_- denote the number of cations and of anions per cm^3. By simultaneously solving Poisson's equation (1) and Eqn. (6) for the electrolyte we obtain an expression of the same form as Eqn. (5) for the ψ'-potential[10]. Hence we conclude that the diffuse charge distributions in the semiconductor and in the electrolyte are very similar.

Since the electric field in the Helmholtz double layer is assumed to be constant, *i.e.*

$$\varphi_0 = E_0 d_0,$$

we can express the Galvani potential in the form

$$\varphi = E_1 d_1 + E_0 d_0 + E_2 d_2, \tag{7}$$

where E_2 is the electric field in the solution at $x = -d_0$. If we now assume that the semiconductor surface is free from surface states we can use Gauss' theorem and state that the electrostatic induction does not show a discontinuity at the interface:

$$\varepsilon_0 E_0 = \varepsilon_1 E_1 = \varepsilon_2 E_2, \tag{8}$$

where ϵ_0, ϵ_1, and ϵ_2 denote the permittivities of the Helmholtz layer, the semiconductor, and the electrolyte respectively. The ratio of the potential drops can now be found from Eqns. (5) and (8):

$$\frac{\varphi_1}{\psi'} = \frac{d_1 \varepsilon_2}{d_2 \varepsilon_1}, \quad \frac{\varphi_0}{\psi'} = \frac{d_0 \varepsilon_2}{d_2 \varepsilon_0}. \tag{9}$$

Thus we see that, provided a correction for the difference in permittivity of the two media is made, the ratio of the potential drop in the semiconductor to that in the electrolyte is equal to the ratio of the corresponding Debye lengths. The Debye length of a semiconductor of not too high carrier density usually differs from the thickness of the diffuse layer in an electrolyte by several powers of ten. Thus, in a semiconductor of the germanium type with a density of donor levels $N_D = n_\infty = 10^{14}$ cm^{-3}, $\epsilon_1 = 16$, $kT = 4 \times 10^{-14}$ erg at room temperature, and we obtain

$$d_1 \simeq 10^{-4} \text{ cm}. \tag{10}$$

The thickness of the diffuse layer in an electrolyte, d_2, decreases with increase in concentration, and becomes infinitesimally small in very concentrated solutions. In a normal solution ($c = 10^{21}$ ions cm^{-3}, $\epsilon_2 = 80$) the thickness d_2 is approximately

$$d_2 \simeq 10^{-7} \text{ cm}. \tag{11}$$

The thickness of the Helmholtz layer is approximately 10^{-8} cm. Therefore, using Eqns. (9), (10), and (11), we conclude that in sufficiently concentrated solutions the major part of the Galvani potential drop occurs in the semiconductor. Thus we are justified in considering the semiconductor–solution interface as a capacitor in which the two layers of charge have a diffuse structure. The properties of the interface are determined mainly by the distributed space charge in the semiconductor.

The importance of the assumed absence of surface states on the semiconductor needs to be stressed. In the presence of a large density of surface states the potential difference across the Helmholtz layer can account for a large fraction of the drop in Galvani potential. We shall calculate the potential drop in the Helmholtz region for the case of a density of surface states $N_S = 10^{14}$ cm^{-2}, assuming a degree of ionisation of 0.1. From the formula for a plane parallel-plate condenser, the electric field in the Helmholtz layer is given by the following expression (in which $\epsilon_0 = 3$):

$$E_0 = \frac{4\pi N_s e \, 0.1}{\varepsilon_0} \simeq 10^7 \text{ V cm}^{-1}.$$

In this case the potential drop in the Helmholtz double layer accounts for a few tenths of a volt†.

Experimentally it is found that, as in the case of metallic electrodes, the potential drop across the diffuse part of the double layer in the electrolyte (ψ') is appreciable only in extremely dilute solutions. Recent work[11,12] has shown that the ψ'-potential of a germanium electrode in dilute aqueous solutions is of the order of 20–40 mV and decreases rapidly with increase in concentration.

The difference in potential across the space-charge region of the semiconductor (φ_1) can be deduced from measurements of the surface conductivity (σ) of the semiconductor in contact with the solution. Garrett and Brattain[13] have calculated an expression relating σ to φ_1 for a "dry" semiconductor surface‡. Harten[15] concluded, from a detailed study of the experimental and theoretical curves for a silicon electrode, that a potential applied to the silicon–electrolyte interface will appear almost exclusively within the semiconductor. Krotova showed[16], by the same procedure, that some 15 to 50% of the potential of a germanium electrode close to its steady-state potential appears across the Helmholtz layer. The inference is that germanium surfaces, as normally prepared, contain an appreciable density of surface states; adsorption of traces of copper from the solution can account for some of them[17].

In the zinc oxide electrode, on the other hand, practically the whole of the charge is concentrated within the semiconductor; in other words, this material is free from surface states[18–21].

Illumination of a semiconductor electrode affects the potential drop (φ_1) within the semiconductor, and therefore also the electrode potential. Garrett and Brattain[13] point out that the photopotential (*i.e.* the change in electrode potential upon illumination) must vanish when there is no

¶ We have adopted the terminology of semiconductor physics in calling the quantity d_1 the Debye length. The charge density in a double layer was first calculated, however, by Gouy[9].

† The Helmholtz potential drop can also become appreciable if the space charge in the semiconductor is very large[2].

‡ Myamlin[14] has derived an expression for σ at the semiconductor–electrolyte boundary.

space charge in the semiconductor. The electrode potential (measured against some reference electrode) which corresponds to this state of affairs is called the "flat band potential" because there is no electric field to distort the edges of the energy bands near the semiconductor surface. Measurements of photopotential are therefore a very convenient way of obtaining the value of the flat band potential [21,22]. The influence of free electron concentration on the flat band potential of germanium provides further support for the conclusion that in this material the potential drop in the space-charge region of the semiconductor is comparable in magnitude with the potential drop in the Helmholtz layer [23]§.

The flat band potential of germanium is affected by the method of surface preparation and also by the nature of the electrolyte [23]. In germanium with intrinsic conductivity, for example, the flat band potential is 0.5 V in 1 *N* KOH and 0.13 V in 1 *N* H_2SO_4, showing that even in the absence of space charge within the semiconductor, the Helmholtz potential drop (and therefore also the surface charge) is quite appreciable.

The appearance of surface charge on germanium has been discussed [23,25] in terms of oxidation of the surface. Measurements of charging curves have shown [26-30] that germanium surfaces are normally covered with a monolayer of oxide in non-oxidising solutions. Evidently the surface oxide partly dissociates (*e.g.* by forming $GeOOH^-$ groups in an alkaline medium), the degree of dissociation depending on the pH of the solution. The surface charge thus generated is retained even when there is no space charge in the semiconductor (*i.e.* at the flat band potential) and is balanced by the charge of the ions electrostatically adsorbed from the solution. The double layer present on a germanium electrode at its flat band potential has an obvious similarity to the structure of a mercury surface at the point of zero charge under conditions of specific adsorption of, say, bromide ions¶. The flat band potential should not be confused, however, with the zero-charge potential: the latter corresponds to a situation such that both the space charge and the surface charge must vanish.

The surface recombination velocity†, an important property of semiconductor surfaces, is related to the potential drop across the Debye region of the semiconductor [7]. It has been shown that the surface recombination velocity at a semiconductor–electrolyte interface is a function of potential [39-43], solution composition [44-46], and surface preparation. A characteristic, bell-shaped curve is obtained when the surface recombination velocity is plotted against potential: the situation is therefore analogous to the semiconductor–gas interface [47]. The parameters of the curve can be used to characterise the recombination centres by evaluating the ratio of the capture cross-sections for electrons and for holes [39]. Mild anodic etching of the germanium reduces the rate of surface recombination; strong cathodic polarisation, on the other hand, sharply increases it [39,48,49]. It would appear that additional recombination centres are created, under these conditions, as a result of adsorption of the evolved hydrogen or penetration of the hydrogen into the germanium crystal lattice‡.

§ See also Refs. 16 and 24.

¶ The adsorption of various ions on germanium and silicon has been investigated [31-38].

† See p. 215.

‡ It has been suggested [50] that adsorbed hydrogen can give rise to acceptor levels as well as recombination centres.

2. Differential Capacity

We shall now calculate the capacity of a semiconductor electrode. The differential capacity is defined as $C = |dQ/d\varphi|$, where Q is the total charge and φ is the total potential drop. We can write $Q = Q_1 + Q_S$, where Q_1 is the space charge in the semiconductor and Q_S the charge in the surface states. Allowing for the charge in the donor and the acceptor levels, and making use of Eqn. (2), we write Poisson's equation [Eqn. (1)] in the form

$$\frac{d^2\varphi}{dx^2} = -\frac{4\pi}{\varepsilon_1}\rho; \quad \rho = e(N_D - N_A + p - n). \tag{12}$$

where N_A is the concentration of acceptor levels.

The potential φ_B, deep within the semiconductor and far from the space-charge region, is given by the expression

$$N_D - N_A = 2n_i \sinh\frac{e\varphi_B}{kT}, \tag{13}$$

where n_i is the free electron concentration in the pure (intrinsic) semiconductor.

The last equation is readily integrated and leads to an expression for the total charge in the semiconductor, Q_1. The final result is [51]

$$Q_1 = \pm\sqrt{2}\,\frac{\varepsilon_1}{4\pi}\left(\frac{kT}{eL_D}\right)[\sinh U_B(U_B - U_S) - (\cosh U_B - \cosh U_S)]^{1/2}, \tag{14}$$

where

$$L_D = \sqrt{\frac{\varepsilon_1 kT}{8\pi e^2 n_i}}; \quad U_B = \frac{e\varphi_B}{kT}; \quad U_S = \frac{e\varphi_S}{kT}.$$

In these expressions φ_S is the potential at the semiconductor surface, *i.e.* at $x = 0$. Eqn. (14) gives the total space charge in the semiconductor, Q_1, as a function of the potential difference $\varphi_1 = \varphi_S - \varphi_B$ within the semiconductor, and of the number of donor and acceptor levels.

The next step is to allow for the charge trapped in any surface states which may be present on the semiconductor surface. We shall consider a concrete case and assume that donor levels are present on the surface (*i.e.* levels which are positively charged when empty and neutral when occupied by an electron). Let N_S be the number of surface states per unit area. The electronic occupancy of these states is governed by the Fermi distribution:

$$n_S = \frac{N_S}{1 + \exp\frac{E_S - E_F}{kT}},$$

where E_S is the energy level of the surface states and E_F is the Fermi level. The energy difference $E_S - E_F$ is a function of the potential drop in the space-charge region of the semiconductor. The actual energy of an electron in a surface state is given by

$$E_S^0 - e(\varphi_S - \varphi_B),$$

where E_S^0 is the energy level of the surface states in the absence of space charge in the semiconductor. The charge in the surface states is given by the expression

$$Q_S = e(N_S - n_S) = \frac{eN_S}{1 + \exp\frac{E_F - E_S^0 + e(\varphi_S - \varphi_B)}{kT}}. \tag{15}$$

It is convenient to evaluate the quantity $1/C$,

$$\frac{1}{C} = \left|\frac{\partial(\varphi_1 + \varphi_0 + \psi')}{\partial Q}\right| = \left|\frac{\partial(\varphi_S - \varphi_B + \varphi_0 + \psi')}{\partial Q}\right| =$$

$$= \left|\frac{\partial(\varphi_S - \varphi_B)}{\partial Q} + \frac{\partial\varphi_0}{\partial Q} + \frac{\partial\psi'}{\partial Q}\right| = \frac{1}{C_1} + \frac{1}{C_0} + \frac{1}{C_2}, \tag{16}$$

where C_1, C_0, and C_2 are the capacities of the semiconductor (with allowance for surface states), of the Helmholtz layer, and of the diffuse part of the double layer in the electrolyte, respectively. The capacity of the semiconductor, $C_1 = |dQ/d(\varphi_S - \varphi_B)|$, can be calculated[2] by means of Eqns. (12) and (15):

$$C_1 = \frac{\varepsilon_1}{4\pi\sqrt{2}L_D}\frac{|\sinh U_B - \sinh U_S|}{[\sinh U_B(U_B - U_S) - (\cosh U_B - \cosh U_S)]^{1/2}} + \frac{N_S e^2}{kT}\frac{\exp\left[\frac{E_F - E_S^0 + e(\varphi_S - \varphi_B)}{kT}\right]}{[1 + \exp[E_F - E_S^0 + e(\varphi_S - \varphi_B)]/kT]^2}. \quad (17)$$

The electric field in the Helmholtz part of the double layer is constant, and therefore the capacity C_0 of the Helmholtz region can be calculated from the formula for a parallel-plate condenser:

$$C_0 = \frac{\varepsilon_0}{4\pi d_0} \simeq 10^7 \text{ cm}^{-1} = 10\,\mu\text{F cm}^{-2}.$$

The capacity of the diffuse layer in the electrolyte is given by[10]:

$$C_2 = \frac{\varepsilon_2}{(8\pi^2)^{1/2}}\frac{1}{d_2}\cosh\frac{e\psi'}{2kT}. \quad (18)$$

We have seen that the total capacity of the semiconductor–electrolyte system is determined by the diffuse and the surface charges in the semiconductor, by the Helmholtz layer, and by the diffuse charge in the electrolyte. We shall proceed to evaluate the various contributions to the total capacity for the specific case of an n-type semiconductor ($n_i/N_D \ll 1$) free from surface charge. Under these conditions Eqn. (17) simplifies to

$$C_1 = \frac{\varepsilon_1}{\sqrt{32\pi^2}}\frac{1}{d_1}\left|\frac{1 - e^{\frac{e\varphi_1}{kT}}}{\left[e^{\frac{e\varphi_1}{kT}} - 1 - \frac{e\varphi_1}{kT}\right]^{1/2}}\right|. \quad (19)$$

Terms proportional to n_i/N_D (*i.e.* $\ll 1$) are ignored in the above formula. Green[2] has derived expressions in which these terms are retained. At potentials of the order of $\varphi \simeq kT/e$ the capacities of the semiconductor (C_1) and of the electrolyte (C_2) are found from Eqns. (18) and (19) to be inversely proportional to the appropriate Debye length. Introducing the approximate numerical values of the Debye lengths, and using Eqn. (16), the final result is that the total capacity of the system is controlled by the capacity of the diffuse part of the semiconductor double layer.

Under conditions of appreciable surface charge on the semiconductor (*e.g.* with a density $N_S = 10^{14}$ cm^{-2} of surface states, assumed to be 10% ionised) we have $e^2N_S/kT \simeq$ $\simeq 10^7$ cm^{-1} = 10 μF cm^{-2}. Applying Eqns. (17) and (18) we now find that the capacity of the semiconductor can become comparable with the Helmholtz capacity.

Let us now compute the capacity of a semiconductor electrode without surface states at the flat band potential, *i.e.* with $\varphi_S = \varphi_B$. Applying Eqn. (17), we obtain:

$$C_1 = \frac{\varepsilon_1}{4\pi L_D} = \sqrt{\cosh U_B}\sqrt{\frac{e^2\varepsilon_1}{4\pi kT}}\sqrt[4]{4n_i^2 + (N_D - N_A)^2}. \quad (20)$$

The variation of capacity with potential is shown in Fig. 1. It can be shown[52] that for an intrinsic semiconductor the capacity minimum occurs at the flat band potential. In n-type semiconductors the capacity minimum occurs at more positive potentials, and in p-type semiconductors at more negative potentials, than the flat band potential.

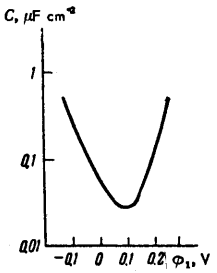


Fig. 1. Variation of differential capacity with potential drop in the space-charge region of the semiconductor, calculated for n-type germanium by Eqn. (17).

Bohnenkamp and Engell's measurements[52,53] of the capacity of the germanium electrode support the ideas outlined above. The capacity *vs.* potential curve shows a minimum, at which, in agreement with theoretical calculations, the capacity is only a few hundredths of a microfarad per cm^2, *i.e.* 2–3 orders of magnitude less than the capacity of a metal electrode. The experimentally observed relationship between capacity and electrode potential fits the theoretical expression for the effect of the potential drop in the space-charge region (φ_1) on the capacity of the electrode, see Eqn. (17)§, whence it can be concluded that changes in φ_1 account for the major part of any change in electrode potential.

The potential of minimum capacity of intrinsic germanium (*i.e.* the flat band potential) varies smoothly with the pH of the solution[52–54]. This confirms our previous conclusions as to the effect of the surface condition on the potential drop in the Helmholtz layer. The capacity minimum of intrinsic germanium lies at 0.5 V (in 1 N KOH solution) and at 0.2–0.3 V (in 1 N H_2SO_4).

Bohnenkamp and Engell's observation of the effect of frequency (between 1 and 160 kc/s) on the capacity and on the potential of minimum capacity is still unexplained¶. The effect may indicate the presence of a frequency-dependent capacity of the type associated with electrode reactions, or alternatively it may be ascribed to surface states with different relaxation times being present on germanium[55].

The capacity of the silicon electrode is somewhat lower than that of the germanium electrode. The electrode capacity is again determined by the space charge in the semiconductor[56–59]. Illumination of the electrode increases the concentration of mobile charges (as a result of the photo-excitation of hole–electron pairs), and the capacity rises towards the characteristic value of metal electrodes (~10 μF cm^{-2}).

§ Eqn. (17) takes no account of the passage of current through the semiconductor–electrolyte interface. It can, however, be applied to germanium because this electrode behaves as an ideally polarisable electrode over a certain range of potentials.

¶ The capacity of a ZnO electrode is independent of frequency[18] between 50 c/s and 100 kc/s.

Efimov and Erusalimchik found a minimum in the capacity of the germanium electrode at a quite different potential: 0.6 V in 0.1 *N* HCl. They call this potential the zero-charge potential of germanium[60]. Their high specific capacity (10–20 μF cm^{-2}), unaffected by the properties of the semiconductor, suggests that these workers were measuring the capacity of the Helmholtz layer. Before each measurement the electrodes were subjected to prolonged cathodic polarisation which, as stated above, can raise the surface recombination velocity very considerably. It would appear that this treatment also makes the semiconductor surface "metal-like". The full significance of Efimov and Erusalimchik's measurements[60], however, is far from clear. These remarks also apply to Efimov and Erusalimchik's[61] anomalously high value for the capacity of a silicon electrode.

III. KINETICS OF ELECTRODE REACTIONS

1. Rate Limitation by the Electrochemical Stage

To give a clearer understanding of the behaviour of the semiconductor–electrolyte interface we shall discuss an electrochemical redox reaction of the type

$$A^+ + e^- \rightleftarrows A. \qquad (21)$$

By analogy with the slow-discharge theory[10] we can write expressions[2,62] for the currents carried by the reduction (i_1) and the oxidation (i_2) reactions:

$$i_1 = k_1 c_{A^+} n(x=0)\, e^{-\frac{\alpha F \Delta\varphi_0}{RT}}, \qquad (22)$$

$$i_2 = k_2 e^{\frac{\beta F \Delta\varphi_0}{RT}}, \qquad (23)$$

where k_1 and k_2 are constants, c_{A^+} is the concentration of A^+ ions in the electrolyte, $n(x = 0)$ is the electron concentration at the plane separating the Helmholtz layer from the semiconductor, F is the Faraday, α and β are constants ($\alpha + \beta = 1$), $\Delta\varphi_0$ is the departure of the potential drop in the Helmholtz part of the double layer from its equilibrium value, and R is the gas constant.

Eqns. (22) and (23) are applicable to reactions, like (21), in which free electrons take part. Eqn. (22) differs from the slow-discharge equation for metallic electrodes[10] by the factor $n(x = 0)$, introduced here because the concentration of free electrons at the semiconductor–electrolyte interface is not constant. This is the fundamental difference between a metallic and a semiconducting electrode surface.

The electron concentration at the interface, $n(x = 0)$, depends on φ_1, the potential drop in the semiconductor, and obeys Boltzmann's distribution law. Applying Eqn. (2) we obtain a new expression for the current:

$$i_1 = k_1 c_{A^+} n_\infty e^{-\frac{e\varphi_1 + \alpha e \Delta\varphi_0}{kT}}. \qquad (24)$$

As we have already pointed out (see p.209) the potential drop in the Helmholtz layer is usually much smaller than the potential drop in the semiconductor. Therefore, ignoring small terms,

$$i_1 = k_1 c_{A^+} n_\infty e^{-\frac{e\varphi_1}{kT}}, \qquad (25)$$

whence

$$\left|\frac{\partial\varphi}{\partial \ln i}\right| = \frac{kT}{e} = \frac{RT}{F}. \qquad (26)$$

If the reaction at the semiconductor surface is of the second order with respect to electrons, Eqn. (22) is modified as follows:

$$i_1 = k_1 c_{A^+} [n(x=0)]^2 e^{-\frac{\alpha F \Delta\varphi_0}{RT}}, \qquad (27)$$

which leads to

$$\left|\frac{\partial\varphi}{\partial \ln i}\right| = \frac{RT}{2F}. \qquad (28)$$

Note that Eqns. (26) and (28) give values of $\partial\varphi/\partial \ln i$ similar to those obtained for metals, but for different reasons.

At high surface charges $\Delta\varphi_0$ becomes greater than φ_1, and the semiconductor electrode tends towards metallic properties. Under these conditions the kinetics of an electrochemical reaction at a semiconductor electrode will be almost indistinguishable from those at a metal electrode.

We shall consider two examples: the anodic dissolution of a semiconductor and the cathodic evolution of hydrogen, the electrochemical stage being assumed to be rate-determining in both cases. Under these conditions the evolution of hydrogen at a germanium electrode is described, irrespective of the conductivity type of the semiconductor, by a Tafel equation with a slope $RT/\alpha F$ of about 0.1–0.12, corresponding to a transfer coefficient of about 0.5.[63–67] The stoichiometric number is $\nu = 1$, the exchange current is $i_0 = 10^{-6}$–10^{-8} A cm^{-2}. Other workers[49,68–70] have reported† $RT/\alpha F = 0.16$, $\alpha = 0.3$, and $i = 10^{-7}$ A cm^{-2}.

Green[2] suggests the following mechanism for the hydrogen evolution reaction by comparing experimental results with $RT/\alpha F$ and ν values calculated for various assumed mechanisms. Hydrogen ion discharge,

$$H^+ + e^- \rightleftarrows H_{ads},$$

occurs relatively fast, and the rate-limiting stage is identified with electrochemical desorption:

$$H^+ + H_{ads} + e^- \rightarrow H_2.$$

The rate of evolution of hydrogen on an *n*-type silicon cathode also increases exponentially with electrode potential: the value of the coefficient $RT/\alpha F$ appears to vary from 0.095[73] to 0.18.[61]

Turning now to the anodic dissolution of germanium, we shall discuss a very characteristic feature of this reaction which stems from the semiconductor nature of germanium: the participation of positive holes. In other words, when a germanium atom goes into solution with a formal valency of +4‡ it gives up some of its electrons to the valence band (see p.215). Brattain and Garrett[76–78] demonstrated that the concentration of holes at the electrode surface depends on the potential§, and that the expression for the reaction overvoltage should include the term $(RT/F)\ln(p/p_0)$, where p and p_0 are the actual and the equilibrium values of the hole concentration at the surface. One method of varying p is to illuminate the electrode: in this way the authors

† The value $RT/\alpha F = 0.23$ has also been reported[71,72].

‡ At very high current densities GeO is formed as well as quadrivalent germanium compounds[74,75].

§ Other workers[79,80] later reached the same conclusion.

were able to show[78] that the current is proportional to the intensity of illumination and therefore that the slow step is kinetically of the first order with respect to holes.

The anodic oxidation of germanium in alkaline solutions consumes hydroxide ions, as shown by the appearance of a limiting current in the polarisation curves obtained in dilute NaOH solutions. The value of the limiting current is determined[81] by the rate of diffusion of OH^- ions to the electrode surface. At still higher potentials the current begins to rise again because a new reaction sets in: the dissolution of germanium, which involves water molecules. Beck and Gerischer[25] studied the effect of alkali concentration on the overvoltage (at currents well below the limiting diffusion current of OH^- ions) and concluded that the slow step in the anodic dissolution of germanium is unimolecular with respect to hydroxide ions. The current–potential relationship is described by a Tafel equation with $\beta = 0.7-0.8$¶ (Fig. 2, curve *1*).

Beck and Gerischer[25] have put forward a reaction mechanism for the anodic dissolution of germanium which accounts for these experimental facts. Germanium atoms at the electrode surface become oxidised with formation of $GeOOH^-$ groups, a process requiring one hydroxide ion and one positive hole. The slow stage is associated with the passage of the $GeOOH^-$ into solution, to give H_2GeO_3.

In the derivation of the kinetic equation (25) we used the Boltzmann distribution to give the electron concentration in the semiconductor during the passage of current. This distribution, however, is strictly applicable only to equilibrium situations, *i.e.* in the absence of external current†. We will now discuss the limitations of this procedure. Consider the expression for the current of electrons in an n-type semiconductor:

$$i = eu_- E(x)\,n(x) + eD_- \frac{dn(x)}{dx} \cdot \qquad (29)$$

Here u_- and D_- are the mobility and the diffusion coefficient of electrons respectively. The term eu_-En describes the drift current of electrons due to the presence of an electric field; the second term, $eD_-(dn/dx)$, is the diffusion current.

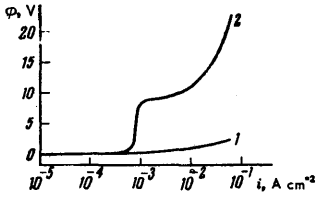


Fig. 2. Polarisation curves for the anodic dissolution of germanium: 1) p-type; 2) n-type.

For $i = 0$, integration of Eqn. (29) leads to the Boltzmann distribution. Even if $i \neq 0$, however, it is possible to have

$$i \ll eu_- En \quad i \ll eD_- \frac{dn}{dx} \cdot$$

so that in Eqn. (29) i becomes negligible in comparison with the much larger terms on the right-hand side. Under these conditions, integration of Eqn. (29) again gives the Boltzmann distribution.

It follows that we can legitimately apply Boltzmann expressions provided that the total current is much smaller than both the drift and the diffusion currents.

But what is the magnitude of expressions of the type eu_-En? Consider, for example, an anodic process at a germanium electrode. We shall assume that the presence of the electrolyte increases the steady-state concentration of holes at the surface, resulting in a Galvani potential of 0.1 V.

The electric field is of the order of φ_1/d_1. Putting $d_1 = 10^{-4}$ cm, we find $E = 10^3$ V cm^{-1}. In germanium of 1 Ω cm resistivity the concentration of free electrons, n_∞, is 2×10^{15} cm^{-3}, and the concentration of holes, p_∞, is 3×10^{11} cm^{-3}. Under these conditions the drift current of holes takes the value

$$eu_+ E p_\infty \simeq 10^{-2} \text{ A cm}^{-2}. \qquad (30)$$

Consequently, hole densities will be accurately described by Boltzmann expressions as long as the anodic current is significantly smaller than the above value†.

These results sometimes prove incorrect when applied to electrodes for which the surface density of carriers is very much less than the carrier density in the uniform bulk of the semiconductor, far from the space-charge region. The concentration of electrons at the interface is given by $n = n_\infty \exp(e\varphi_1/kT)$, and can be very small if the exponential has a low enough value. The Boltzmann distribution ceases to apply when the surface layer of the semiconductor is depleted of free carriers. Two recently published papers have dealt with the calculation of polarisation curves with allowance for a non-equilibrium distribution of carriers.

One of these[82] discusses the current–voltage characteristic of the interface between an electrolyte and an n-type semiconductor. Strong electron depletion at the equilibrium potential is assumed. This produces a surface layer with a low concentration of free carriers, of high electrical resistance, and having rectifying properties‡. When current is passed through such a contact in the forward direction, electrons are injected into it by the field and the resistance decreases. Reverse current, on the other hand, further depletes the contact of electrons and makes its resistance still higher. The donor levels are assumed[82] to be weakly ionised. The rectification at the contact is described by the ratio $\Delta V(+i)/\Delta V(-i)$, where $\Delta V(+i)$ and $\Delta V(-i)$ refer to

¶ Turner finds[26] $RT/\beta F = 0.12$, whence $\beta = 0.5$.

† We are not considering the case of very high charge on the electrode, when the Boltzmann distribution ceases to apply even under equilibrium conditions.

‡ A rectification effect is observed also at metal–solution contacts, *e.g.* when the anodic and the cathodic reaction have widely different overvoltages, or when the rate of one of these reactions is limited by concentration polarisation. We are not concerned here with this type of rectification (although it can occur at semiconducting as well as metallic electrodes), but only with rectification effects specific to the semiconductor–electrolyte interface.

the total potential drop (in the semiconductor and in the Helmholtz layer) under conditions of reverse and forward bias respectively. Its value is given by

$$\frac{\Delta V(+i)}{\Delta V(-i)} = \frac{1}{\beta}\frac{\ln\left(\frac{i}{i_0}\right)(d_1)^2}{d_0 l} \quad (31)$$

where i_0 is the exchange current of the reaction, l is the thickness of the semiconductor. Inserting $l = 10^{-3}$ cm, d_1 (the Debye length) = 10^{-4} cm, $d_0 = 10^{-8}$ cm, and $\ln(i/i_0) = 10$, we find:

$$\frac{\Delta V(+i)}{\Delta V(-i)} = 2\times10^3. \quad (32)$$

Clearly, this system has rectifying properties.

The above treatment[82] has been extended[83] to the case of an n-type semiconductor with current carriers of both types. The authors consider a reaction of type (21), involving carriers of a single type (free electrons). The equilibrium concentrations of electrons and holes in the surface layer are assumed to be much smaller than the concentration of majority carriers (free electrons) in the bulk of the semiconductor. The calculated current–voltage characteristic shows an interesting feature: rectification is present only over a limited range of potentials (of the order of the width of the energy gap) as long as the surface remains depleted of electrons and holes. As soon as the applied field raises the surface density of holes to the level of the bulk electron density a distinctive breakdown phenomenon sets in.

2. Rate Limitation by Minority Carrier Diffusion

We have so far considered systems in which the electrochemical reaction is the slowest step. This happens at low current densities (less than 10^{-4} A cm^{-2} on germanium) or when majority carriers (holes in p-type semiconductors, electrons in n-type semiconductors) are involved in the reaction. If the reaction, however, consumes minority carriers, which are present at low concentration, it is not surprising to find that the current is limited (beyond a certain potential) by the rate of arrival of minority carriers at the electrode surface. We shall discuss the kinetics of reactions of this type, taking the anodic dissolution of germanium as a concrete example[84,85].

As stated above, holes must be supplied to the interface from the bulk of the semiconductor in order that germanium shall dissolve. Part of the reaction current is carried across the phase boundary by free electrons, however, and we may write the ratio of hole to electron current in the form

$$\frac{i_+(x=0)}{i_-(x=0)} = \frac{r}{m}, \quad (33)$$

where r and m are integers. The total current of germanium dissolution is given by

$$i = i_+(x=0) + i_-(x=0) = kp^a e^{\frac{\beta F\Delta\varphi_s}{RT}}, \quad (34)$$

where a is a constant. The germanium surface at its equilibrium potential is assumed to have a high density of excess holes. The current–voltage curve for n-type germanium now takes the form

$$\frac{F\varphi}{RT} = \psi_0 + \frac{1}{\beta}\ln\frac{i}{i_0} + \ln\left(1-\frac{i}{i_{\lim}}\right), \quad (35)$$

where the term ψ_0 includes constants and functions which vary much more slowly than $\ln i$. The value of $i_{\lim}$ is given by

$$i_{\lim} = n_i^2 D_+ e^2 u_- \frac{\rho}{L}\left(1+\frac{m}{r}\right), \quad (36)$$

where n_i is the concentration of free electrons in intrinsic germanium, D_+ is the hole diffusion constant, ρ is the resistivity of the germanium, and L is the hole diffusion length.

Let us examine Eqn. (35) in detail. At currents $i \ll i_{\lim}$ the potential varies with current according to

$$\varphi \simeq \frac{RT}{\beta F}\ln\frac{i}{i_0}, \quad (37)$$

and Tafel's law is obeyed. At currents close to the limiting current the third term of Eqn. (35) becomes predominant:

$$\varphi \simeq \frac{RT}{F}\ln\left(1-\frac{i}{i_{\lim}}\right). \quad (38)$$

When the potential is raised still further a sharply defined limiting current is observed.

An analysis has been given[85] of the distribution of carriers close to the surface. Fig. 3 shows the distribution of holes for currents not very different from the limiting current. In the Debye region ($0 < x < d_1$) the hole density increases rapidly in response to the electric field. Beyond the Debye region there is no field, and the hole concentration falls below its equilibrium value (p_∞) because holes are carried away, across the boundary, by the electrochemical reaction. Under limiting current conditions the hole concentration at the edge of the Debye region effectively vanishes. At points well removed from the boundary the hole density increases, and reaches its equilibrium value (p_∞) at a depth of the order of L, the hole diffusion length. We should note that this distribution is analogous to the distribution of cations in an electrolyte undergoing discharge, at a negatively charged electrode surface under conditions of concentration polarisation: d_1 is equivalent to the thickness of the electrical double layer and L to the thickness of the diffusion layer. The limiting current can be readily evaluated by the following simple arguments. Since the whole of the region $d_1 \leq x < L$ lies beyond the space-charge layer, the supply of holes to the interface occurs mainly by diffusion. The limiting diffusion current of holes will be

$$i_{+\lim} = eD_+\left.\frac{dp}{dx}\right|_{\lim}, \quad (39)$$

where the concentration gradient $\left.\frac{dp}{dx}\right|_{\lim}$ is approximately

$$\left.\frac{dp}{dx}\right|_{\lim} = \frac{p_\infty}{L}. \quad (40)$$

Ignoring recombination in the space-charge region, and using Eqn. (33), we arrive at the total limiting current:

$$i = i_+ + i_- = \left(1+\frac{m}{r}\right)eD_+\frac{p_\infty}{L}. \quad (41)$$

Since the resistivity of the semiconductor is $\rho \simeq 1/en_\infty u_-$, and $p_\infty n_\infty = n_i^2$, Eqn. (36) follows at once. Thus the value of the limiting current is independent of the parameters of the kinetic equation (34), and is also unaffected by any assumptions as to the nature and charge of the surface states.

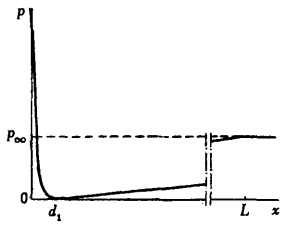


Fig. 3. Hole concentration profile near the surface of *n*-type germanium dissolving anodically under limiting current conditions.

We will now reconsider our assumption that recombination can be neglected, because the limiting dissolution current of germanium can be increased by hole generation in the Debye region. To allow for this effect we use the concept of surface recombination velocity[7], v_S. We shall not attempt to discuss the actual mechanism of hole generation at surface states or in the space-charge region. Following Shockley, we assume a hole generation current i_S proportional to the departure of the hole concentration at the edge of the space-charge region, p_1, from its equilibrium value, p_∞:

$$i_S = ev_S(p_1 - p_\infty). \tag{42}$$

Under limiting current conditions, $p_1 = 0$ and

$$|i_S| = ev_S p_\infty. \tag{43}$$

Therefore the limiting current of positive holes is given by

$$i_{+\lim} = eD_+\frac{p_\infty}{L} + ev_S p_\infty. \tag{44}$$

The hole diffusion length L and the hole lifetime τ are related by the expression $L = (D\tau)^{\frac{1}{2}}$, so that finally

$$i_{+\lim} = ep_\infty\left(\sqrt{\frac{D}{\tau}} + v_S\right). \tag{45}$$

Vdovin *et al.*[85] have discussed one particular generation mechanism, and calculated current–voltage characteristics and limiting current densities on the assumption that hole generation occurs entirely at surface states, and not within the space-charge region.

A limiting current is not observed in the anodic dissolution of *p*-type germanium, because the supply of holes to the surface cannot be diffusion-controlled when holes are the majority carriers.

Curve *2* of Fig. 2 shows an experimental polarisation curve for the anodic dissolution of *n*-type germanium. For current densities up to 10^{-4} A cm^{-2} the current–potential relationship is of the Tafel form (as in the case of *p*-type germanium). At higher potentials the current plateau appears: Flynn[86] states that the value of the limiting current is proportional to the resistivity of the germanium (ρ) and inversely proportional to the hole diffusion length (L), as required by Eqn. (36). It seems clear, therefore, that the diffusion of holes from the bulk of the specimen to its surface constitutes the slow step, and that surface recombination occurs at a negligible rate. The limiting current can be increased by providing more holes at the surface, *e.g.* by illumination of the electrode[78], by hole injection from a *p–n* junction located close to the electrode surface[87], and also by raising the temperature (which raises the bulk concentration of holes in the semiconductor)[88].

Thus in the anodic dissolution of *n*-type germanium the semiconductor–electrolyte boundary behaves very much like a reverse-biased *p–n* junction when *n*-type germanium is subjected to anodic dissolution. Current is carried across the boundary by minority carriers (holes), and the rate at which holes can diffuse from the bulk to the surface of the semiconductor determines the value of the current. The blocking current is therefore diffusional, in contrast to the type of rectification discussed on p. 213–214. Practically the whole of the potential difference applied to the electrode appears across the blocking layer of the semiconductor when limiting current is flowing: only a very small fraction of the potential is dropped across the Helmholtz layer. Since the thickness of the blocking layer is very small (of the same order as the Debye length), the field intensity within the blocking layer can exceed 10^5 V cm^{-1} for a potential of a few volts. Under these conditions hole–electron pair generation can occur by an avalanche process, which produces breakdown in this rectifier-like structure (see curve *2* of Fig. 2). The value of the breakdown voltage depends on the resistivity of the germanium, and can amount to several tens of volts in the case of high-resistivity specimens.

It should be noted that free electrons (as well as holes) can take part in the anodic dissolution of germanium, making the limiting anodic dissolution current larger than the limiting hole diffusion current [see Eqn. (36)]. The ratio $(r + m)/r = \alpha'$ is called the current multiplication coefficient by analogy with the current multiplication which takes place at a transistor collector. Brattain and Garrett[78] devised the following method of measuring α', which was adopted in more recent work[87,89]. The electrode consists of a germanium wafer which is made much thinner than the hole diffusion length (Fig. 4). An annular ohmic contact and a *p–n* junction (prepared, for example, by the indium alloy process) are placed on one side of the wafer; the opposite side is immersed in the electrolyte and acts as the anode. During polarisation of the *p–n* junction in the transmitting direction it serves as a source of holes, which diffuse through the germanium plate and reach the germanium–solution interface, where they participate in the anodic dissolution reaction. The limiting dissolution and hole diffusion currents can be measured simultaneously, and used to calculate α'. Measurements by this (and by other) methods all give[78,89] α' values of the order of 1.65, pointing to the following stoichiometric equation for the anodic dissolution of germanium in alkaline solutions:

$$Ge + 2.4e^+ + 6OH^- \rightarrow GeO_3^{2-} + 1.6e^- + 3H_2O,$$

where e^+ and e^- denote holes and electrons respectively.

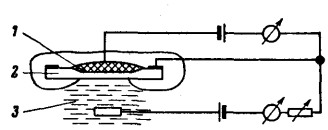


Fig. 4. Electrode for studying the role of free carriers in electrochemical reactions on germanium:
1) *p–n* junction; 2) *n*-type germanium, 3) solution.

The value of α' varies with dissolution conditions (for example, with the current of injected holes)[89-92] and cannot, therefore, be identified with any particular molecular scheme for the reaction. It would appear that when germanium goes into solution electrons have to enter both the valence band (a process which consumes holes) and the conduction band: the ratio of hole current to electron current is a statistical quantity depending on the concentration of holes at the interface, and can be altered by photo-injection of holes or by other means[89,90].

If the thickness of the electrode shown in Fig. 4 is not much greater than the thickness of the space-charge region ($\sim 20\,\mu$, say), the latter can be made to grow and "flood" the entire specimen if a sufficiently high reverse voltage is applied to the p-n junction[93,94]. Under these conditions the hole (and electron) concentrations fall much below their equilibrium values, and the germanium ceases to dissolve anodically as soon as the edge of the depletion region comes into contact with the germanium–electrolyte interface§.[93]

The limiting currents reported in the anodic dissolution of selenium[98] and of n-type cadmium sulphide[99-102] suggest that positive holes may be involved also in these reactions.

The exact mechanism whereby holes participate in the anodic dissolution of the semiconductors is still not clear. Possibly, the rupture of a covalent bond between lattice atoms becomes easier when a hole is localised at a surface atom.

The cathodic evolution of hydrogen at a p-type germanium surface also shows features indicative of minority carrier diffusion from the bulk to the surface of the semiconductor. Brattain and Garrett[78] established that free electrons take part in the reaction, which reaches a limiting rate (~ 1 mA cm^{-2}) at a definite potential. This conclusion was subsequently confirmed by Green[2], Gerischer[49], and Dewald[21]. The limiting diffusion current of electrons is usually less clearly defined than the limiting hole diffusion current: this is because the surface condition of the germanium electrode is gradually altered by the adsorption and penetration of atomic hydrogen into the germanium lattice during the evolution. These phenomena are known (see p.210) to increase the rate of surface generation and recombination of hole–electron pairs[48,86,103,104]. The exact similarity, even at very high current densities, between the polarisation curves for hydrogen evolution from n- and p-type germanium electrodes previously saturated with hydrogen[105] can be explained in the same way. Such electrodes behave like metallic electrodes and effectively lose their semiconductor properties. If the polarisation curve, on the other hand, is determined rapidly, the hydrogen overvoltage on n-type germanium is found to be smaller than on p-type[106].

The observation of Paleolog *et al.*[107] that the rate of hydrogen evolution on p-type germanium, though smaller than on n-type, decreases with increasing germanium resistivity, cannot be reconciled with the views outlined above, which require that the limiting electron current should increase with increase in resistivity — see Eqn. (36). The authors suggest[107] that valence electrons rather than free electrons are concerned in the hydrogen evolution reaction on p-type germanium.

§ A method of producing very thin germanium wafers[95,96] by this technique has been described (see also Albers and Thomas[97]).

All the instances of diffusional control so far outlined apply to electrodes of thickness many times larger than the minority carrier diffusion length, L. Calculations have also been made[108] of the voltage–current characteristic and of the limiting current value for the case of a germanium wafer of thickness $W < L$, in contact with the electrolyte on one side and provided with an ohmic metal contact (which determines the surface recombination velocity v_S) on the other side.

Under these conditions the limiting anodic dissolution current takes the value

$$i_{\lim} = \left(1 + \frac{m}{r}\right) \frac{n_i^2 D_+ e^2 u_- p}{L} \frac{D_+ \sinh \frac{W}{L} + v_S L \cosh \frac{W}{L}}{D_+ \cosh \frac{W}{L} + v_S L \sinh \frac{W}{L}}. \qquad (46)$$

Efimov and Erusalimchik[109,110] have observed, at least qualitatively, a relationship of this type between the limiting current and the resistivity and hole diffusion length of very thin germanium electrodes.

3. Generation of Minority Carriers in the Space-Charge Region

We will now discuss the anodic dissolution of n-type silicon. Eqn. (36) predicts a much smaller limiting dissolution current for silicon than for germanium of comparable resistivity if the dissolution of silicon, like that of germanium, requires holes. The quantity n_i which appears in Eqn. (36) is related to the width of the energy gap, thus:

$$n_i \simeq e^{-\frac{\Delta E}{2kT}}.$$

It follows that n_i, and therefore also the limiting diffusion current of minority carriers, must decrease very rapidly if the width of the forbidden band is increased. Experimentally, however, the dissolution of silicon is found to support currents which are comparable in magnitude to those of germanium anodes. Flynn[86] believes that generation in the space-charge region can provide the holes needed for the dissolution of silicon. One of us[111] has derived a quantitative model for the anodic dissolution of silicon in which allowance is made for generation in the Debye region. The theory of Shockley and Read[112] is used to describe the recombination process. The number of carriers recombining per unit volume and unit time works out to

$$u = \frac{pn - n_i^2}{\tau_{p_0}(n + n_1) + \tau_{n_0}(p + p_1)}, \qquad (47)$$

where

$$n_1 = n_i \exp \frac{E_t - E_i}{kT}; \quad p_1 = n_i \exp \frac{E_i - E_t}{kT}.$$

τ_{p_0} and τ_{n_0} are, respectively, the hole lifetime in a strongly n-type sample and the electron lifetime in a strongly p-type sample containing the same recombination centres as the experimental material; E_t is the energy level of the recombination centres; E_i is the Fermi level of the intrinsic semiconductor. The polarisation curve for silicon dissolution now has the form

$$\varphi = \psi_0 + \frac{RT}{2F}\left(\frac{r}{r+m}\right)^2 \left(\frac{i}{i_1}\right)^2 + \frac{RT}{\beta F} \ln \left|\frac{i}{i_0}\right|. \qquad (48)$$

where ψ_0 is a constant, i_0 is the exchange current of the silicon dissolution reaction, and the current i_1 is given by

$$i_1 = \frac{en_i^2 d_1}{\tau_{p_0} n_1 + \tau_{n_0} p_1}, \quad (49)$$

d_1 being the Debye length of the semiconductor.

At currents $i < i_1$ the second term in Eqn. (48) varies more slowly than the third, and the current–voltage curve approximates to Tafel's law:

$$\varphi = \frac{RT}{\beta F} \ln \left| \frac{i}{i_0} \right| + \text{const.}$$

When the currents i and i_1 are of similar magnitude the parabolic relationship between current and potential becomes predominant, and the potential increases much faster than with the logarithm of the current. The current i_1 characterises the transition to a region of strongly current-dependent potential. From Eqn. (49), i_1 is proportional to the Debye length, and therefore also to the square root of the silicon resistivity:

$$i_1 \simeq \sqrt{\rho} \quad . \quad (50)$$

Eqn. (49) can be obtained by the following semiquantitative argument. We seen from Eqn. (47) that effective generation can occur where $np \ll n_i^2$; $n < n_1$; $p < p_1$. Under these conditions the rate of hole generation per unit volume will be

$$|U| = \frac{n_i^2}{\tau_{p_0} n_1 + \tau_{n_0} p_1} \quad .$$

The total number of holes generated in the Debye region is found by multiplying U by the thickness of the Debye region. This product, multiplied by the electronic charge, gives the corresponding electric current in the form of Eqn. (49).

Theoretical conclusions are in qualitative agreement with experiment. Polarisation curves for the anodic dissolution of n-type silicon, taken in hydrofluoric acid or in hot alkaline solutions (when the silicon surface remains free from passivating films), show two distinct sections. At low anodic polarisations (current density up to 10^{-4} A cm^{-2}) the current–voltage curve is of the Tafel type (as in the case of p-type silicon). At more positive potentials the current increases more slowly with voltage, and approaches a limiting value ($\sim 10^{-3}$ A cm^{-2}). In this region the current density increases with silicon resistivity, as expected from Eqn. (50), and is quite independent of electrode thickness [113,114]. The slower anodic dissolution of n-type silicon as compared with p-type is conclusive proof that holes take part in this reaction.

The value of the current, and its response to changes in temperature and in illumination [115,116], support Flynn's original hypothesis [86] that the rate of anodic dissolution of n-type silicon is determined by field generation of holes in the space-charge region adjacent to the semiconductor surface, and not by the diffusional transport of holes from the bulk to the surface.

Generation of hole–electron pairs in the space-charge region also limits the rate of anodic dissolution of n-type gallium arsenide [117].

The evolution of hydrogen from p-type silicon also appears to be hindered [61,73,118]. Greger concludes [116] that the rate of this reaction is determined by the generation of free electrons in the space-charge region at the silicon–solution interface.

4. The Role of Free and Valence Electrons in Electrochemical Reactions

We have so far been concerned with reactions involving participation of free carriers of a single kind. Thus, Eqn. (22) refers to a reduction reaction in which electrons are transferred from the conduction band to the ions or molecules undergoing reduction. The kinetic equation for an oxidation reaction in which holes are consumed has a similar form. However, we have seen that even in the case of anodic dissolution of germanium free carriers of both kinds may be involved. Dewald [119], Gerischer [120–123], and also Dogonadze and Chizmadzhev [124] have examined quantitatively the relative extents to which the conduction and the valence band can be expected to contribute to the overall charge transfer between the semiconductor and the solution during an electrochemical reaction. We will summarise some of the conclusions of the most recent [124] of the above papers, dealing with the kinetics of redox reactions in which there is no adsorption of reactants and no rupture or deformation of chemical bonds.

The value of the exchange current i_0 (consisting of an electronic component i_0^e and a hole component i_0^p) was calculated by a quantum mechanical method. The ratio of the exchange currents between the solution and the conduction and the valence band is largely controlled by the factor

$$\frac{i_0^e}{i_0^p} \simeq e^{\frac{e\varphi_1}{kT}},$$

where φ_1 is the equilibrium potential drop in the semiconductor, which determines the amount of deformation of the energy bands in the surface region.

The value of φ_1 depends on the redox potential of the system. In strongly oxidising solutions the energy bands are bent upwards at equilibrium ($\varphi_1 < 0$), the surface of the semiconductor becomes richer in holes, and the hole component of the exchange current predominates. In the presence of strong reducing agents ($\varphi_1 > 0$) the conduction band plays the major part in the exchange process.

When the system departs from equilibrium, the anodic current to the conduction band (i_a^e) and the cathodic current from the valence band (i_c^p) are independent of the overvoltage, η, and equal to their respective components of the exchange current, if the potential drop in the Helmholtz layer can be neglected:

$$i_a^e = i_0^e; \quad i_c^p = i_0^p \, . \quad (51)$$

This result is not unexpected: the overvoltage across the Helmholtz layer, which can accelerate the purely electrochemical stage of the process, is assumed negligible, whereas the concentration of charges taking part in the reaction (valency electrons in the valence band or unfilled levels in the conduction band) is large and independent of the overvoltage. The same conclusion was also reached elsewhere [125].

The anodic current to the valence band and the cathodic current from the conduction band are described by equations similar to Eqn. (25):

$$i_a^p = i_0^p e^{\frac{F\eta}{RT}}; \quad i_c^e = i_0^e e^{-\frac{F\eta}{RT}} \quad (52)$$

Thus the components of the current at a semiconductor electrode are formally given by Tafel expressions in which

the transfer coefficients α and β are either 1 — Eqn. (51) — or 0 — Eqn. (52). The overall reaction current is the sum of these partial currents:

$$i = i_0^p(e^{\frac{F\eta}{RT}} - 1) + i_0^e(1 - e^{-\frac{F\eta}{RT}}).$$

We are particularly interested in the ratio of hole current to electron current, which can be measured experimentally. At not too high overvoltages this ratio is given by:

$$\frac{i_a^p}{i_a^e} \simeq e^{\frac{F(\eta-\varphi_1)}{RT}}.$$

The quantity $\eta - \varphi_1$ is simply the potential of the electrode (except for an unknown additive constant).

The more positive the potential, therefore, the higher is the proportion of electrons from the valence band in reduction reactions and the proportion of holes in oxidation reactions.

At very high overvoltages the concentration of free carriers at the semiconductor surface becomes very large, and the surface tends towards metallic properties. In particular, the potential drop at the interface becomes concentrated mostly in the Helmholtz layer, and the above considerations cease to apply. Gerischer has discussed this system [120].

In their study [128] of the anodic dissolution of n-type germanium in solutions of oxidants (alkaline $K_3Fe(CN)_6$; $FeCl_3$), Gerischer and Beck found that the limiting germanium dissolution current increases with the concentration of the oxidising agent. They explain this phenomenon by postulating that the dissolution reaction is accompanied by some reduction of the oxidising agent, in which electrons from the valence band are involved. Thus the reduction reaction injects holes into the valence band of the semiconductor which can be used by the dissolution reaction. Hole injection has also been observed [127] in alkaline solutions of oxygen, in $KMnO_4$, and in $Ce(SO_4)_3$.

Direct experimental evidence [103], and indirect evidence based on polarisation curves [128,129], favours the hypothesis that valency electrons take part in a number of reductions. Even the formation of GeH_4 on a germanium cathode has been shown [130] to involve electrons from the valence band.

Direct measurements of the relative numbers of free and valence-band electrons taking part in reduction reactions have been carried out [131] with the electrode shown in Fig. 4. The reverse-biased p-n junction was used as a hole collector. Any reduction reaction at the germanium–solution interface which interacts preferentially with the valence band will inject holes into the semiconductor. These are able to diffuse across the thin germanium wafer, and are collected by the p-n junction. The ratio of the increase in collector current to the reduction current is effectively equal to γ, the fraction of valence-band electrons in the reduction current.

The value of γ can vary from close to unity ($KMnO_4$ 0.8–0.9, $K_3Fe(CN)_6$ 0.6–0.8) to zero ($K_2Cr_2O_7$ 0.03–0.08, H_2O_2 0). KI_3 and quinone occupy an intermediate position ($\gamma \sim 0.4$). In qualitative agreement with the theoretical calculation, the contribution of the valence band to the reduction current is found [104,132] to increase at more positive electrode potentials.

Oxidation reactions at a germanium electrode have not been studied in detail. The oxidation of bivalent vanadium ions [133], of oxalate ions, and probably also of iodide ions [134,135] does not involve positive holes. The oxidation current of $K_4Fe(CN)_6$ in acid solution [127] and of ethylide ions in a Ziegler electrolyte [136], on the other hand, passes directly into the valence band.

5. Formation of Oxide Layers on the Electrode Surface

If the products of anodic oxidation are insoluble (or sparingly soluble) the anode surface becomes covered with an adsorbed layer or with a relatively thick oxide film, which often has a very high resistance. Silicon electrodes form an oxide film in most aqueous solutions (except HF and KOH), and in some non-aqueous solutions such as methylacetamide [137–139], liquid ammonia, and sulphur dioxide [140,141].

Surface oxide can bring about passivation of the silicon anode. Electrical breakdown of the film is observed at a high enough potential (~15 V). Beyond this point the anodic current is determined by the semiconductor properties of silicon: thus, on a p-type anode the current increases exponentially with potential, whereas n-type anodes show a limiting current [73]. Under certain conditions a layer of amorphous silicon can form on the surface of a silicon single crystal [142].

Germanium oxide is readily soluble in water, but oxide layers can be produced on germanium anodes by using solutions of nitrates in methylacetamide [138,143]. When indium antimonide is oxidised in KOH solutions, the rate of formation and the properties of the oxide film depend on the crystallographic orientation of the electrode surface [144–147].

On the whole, the properties of oxide layers on silicon, germanium, and indium antimonide are relatively unaffected by the semiconducting properties of the underlying electrode material. The electrochemical behaviour of these films (rectifying properties, photo-effect, etc.) is very similar to that of anodic oxide films on aluminium, tantalum, niobium, and other metals.

IV. CHEMICAL ETCHING

Chemical etching of semiconductor surfaces is a standard operation in the radio industry and in laboratory practice (for metallographic, electronic, and other investigations). Etchants contain, as a rule, an oxidising agent, and also a complexing agent whose function is to combine with the semiconductor ions in solution [148]. The view that chemical etching involves chemical oxidation of the semiconductor followed by dissolution of the resulting oxides is widely held [149–152]. However, careful studies of the etching behaviour of germanium and silicon in solutions of the most important oxidising agents (HNO_3, H_2O_2, etc.) have demonstrated that the process is electrochemical in nature. Two complementary reactions take place on the semiconductor surface at identical rates and at a common potential: an anodic half-reaction (dissolution of the semiconductor) and a cathodic half-reaction (reduction of the oxidising agent). The parameters for these two reactions determine the steady-state potential and the corrosion rate [119,153–156].

In some cases (*e.g.* silicon in alkali solutions [73,157–159]) etching can take place by a purely chemical mechanism¶.

¶ Various aspects of chemical etching are discussed in a recent monograph [160].

A more detailed discussion of the electrochemical mechanism of corrosion seems justified. We have already stressed the fact that holes are required for the anodic dissolution of semiconductors like silicon and germanium. These holes can be generated in the bulk or at the surface of the semiconductor. It follows that the rate of corrosion of an n-type semiconductor cannot exceed the limiting rate of diffusion (or generation) of holes. By the same argument, if the cathodic reaction consumes free electrons the rate of corrosion of a p-type semiconductor is determined by the limiting rate of diffusion or generation of free electrons.

However, an additional source of supply of holes is also available to the anodic process. We have seen that many oxidising agents are reduced at a semiconductor by electrons from the valence band. Holes are thus injected into the semiconductor by the cathodic reaction, and are immediately available to the anodic reaction. Under these conditions the cathodic and the anodic reaction are no longer independent: the rate of corrosion ceases to be a function of the semiconductor properties of the sample and is limited by the diffusion of the oxidising agent in solution or by the electrochemical step. In practice the rate of corrosion of germanium in concentrated solutions of oxidising agents is found to be higher than the limiting current of holes to the electrode surface by several powers of ten. These ideas were first put forward by Gerischer and Beck [126], and were further developed by Dewald [119] and Turner [153].

In this way, many oxidising agents can play a dual role in the corrosion of semiconductors: they undergo the cathodic reaction, and they also provide holes for the anodic reaction. When holes are generated faster than the anodic dissolution can use them up, the excess holes (accompanied by an equal number of electrons) diffuse from the surface into the bulk of the corroding specimen [126,153]. This hole current has been experimentally observed by the method described on p.218 . [104,132] This process can raise the bulk (as well as the surface) concentration of holes considerably, and in n-type and in weakly p-type specimens well above the equilibrium value. Since holes are involved in the potential-determining step of the reaction, the steady-state potential (but not the corrosion rate) should be a function of the initial hole concentration in the semiconductor. This effect has been observed by Gerischer and Beck [161] [dissolution of germanium in alkaline $K_3Fe(CN)_6$] and by Turner [153] and Dewald [119] (dissolution of germanium and silicon in HNO_3).

The reduction of nitric acid on germanium consumes electrons from the valence band [119,162]. In concentrated solutions of HNO_3, therefore, germanium and silicon corrode at a high rate (up to 6 A cm^{-2}), independent of the semiconductor properties of these elements. The corrosion rate is determined by the cathodic reaction, and this is found to be autocatalytic. The slow step is the formation of N_2O_4 ($HNO_3 + HNO_2 \rightarrow N_2O_4 + H_2O$), which is further reduced at the electrode. On raising the concentration of HNO_3 the rate of corrosion of germanium increases at first, reaches a maximum for a 6 N solution, and finally decreases as a result of the formation of a thick, passivating film of oxide in very concentrated solutions of HNO_3. Addition of HF destroys the passivity [163,164].

The rate of corrosion of germanium in acid solutions of hydrogen peroxide is decreased by both anodic and cathodic polarisation, suggesting that an electrochemical process is involved. Experimentally measured corrosion rates, however, are significantly higher than the values expected from polarisation curves [154,165]. It is possible that chemical oxidation of germanium by hydrogen peroxide takes place in parallel with the electrochemical corrosion process.

When finished germanium devices, containing various metallic components, are etched in H_2O_2, the anodic and the cathodic reactions become localised in different parts of the device: germanium functions as the anode, copper as the cathode. Indium and tin are usually strongly polarised and have very little effect on the rate of dissolution [166]. Under factory conditions, alkaline solutions of H_2O_2 are used for etching germanium, and the etching rate depends on the concentration of alkali [167].

Germanium is corroded by solutions of electrolytes containing dissolved oxygen, the necessary cathodic reaction being provided by the reduction of O_2. Oxygen concentrations are usually small, and the etching rate (1–10 μA cm^{-2}) is less than the limiting current of minority carriers, and unaffected by semiconductor properties. At low O_2 concentrations the etching rate is determined by the diffusion of oxygen to the reacting surface; at higher concentrations the electrochemical step (reduction of adsorbed oxygen) is rate-limiting. It is important to note that the rate of corrosion depends on the concentration of indifferent electrolyte, and reaches a maximum at a critical concentration (normally less than 0.01 N) which is characteristic of the particular electrolyte. Harvey and Gatos have suggested that the reduction of oxygen is catalysed by anions adsorbed on the germanium surface: when the adsorption of anions becomes excessive, the oxygen coverage of the surface (and therefore also the reaction rate) must decrease [168–170].

Even in the absence of oxidising agents the steady-state potential of germanium and silicon is a corrosion potential [3,171,172]. Measurements carried out under scrupulous conditions of reagent purity have shown that the cathodic process is hydrogen evolution, the anodic process is germanium oxidation to give the brown modification of GeO between pH 0 and pH 4 and the yellow modification between pH 6 and pH 12. GeO_3^{2-} ions may be involved in the potential-determining reaction at pH > 12.5. The measured steady-state potential is practically independent of the germanium conductivity type [3].

When the solution contains salts of metals more noble than silicon or germanium, the cathodic reaction takes the form of electrodeposition of these metals. The so-called "electroless" nickel plating† (followed by heat-treatment) is used to provide ohmic contacts for silicon [173].

The corrosion behaviour of $A^{III}B^{V}$ compounds is very similar to that of germanium. Thus, GaAs corrodes by an electrochemical mechanism [174] in solutions containing dissolved oxygen or $KAu(CN)_2$. In dilute solutions of oxidising agents the rate of corrosion of InSb is determined by diffusion of the oxidant [175,176]; in concentrated solutions, on the other hand, the electrochemical step is rate-determining. The compounds of the $A^{III}B^{V}$ series become passive [177] in concentrated HNO_3.

† Chemical deposition of a nickel phosphide coating by reduction of a nickel salt with hypophosphate (Ed. of Translation).

V. APPLICATION OF ELECTROCHEMICAL METHODS OF SURFACE TREATMENT IN PHYSICOCHEMICAL RESEARCH AND IN SEMICONDUCTOR TECHNOLOGY

No practical device based on a semiconductor–electrolyte system has yet been developed. The Bell Telephone Laboratories have described an internally powered transistor [178], based on the cell

$$Ge|KOH|Ag_2O, Ag,$$

and a field triode [179], in which the properties of the ZnO–electrolyte interface are utilised, but neither device has yet been put to practical use‡. Nevertheless, electrochemical methods have found wide application in semiconductor device technology.

Electrochemical (as well as chemical) etching techniques are used to remove mechanically damaged layers from semiconductor surfaces. For silicon and silicon carbide the electrolyte is a solution of hydrofluoric acid [181,182]; for germanium, solutions of sodium or potassium hydroxide have been used [183], and other compounds [184–187]. Germanium can be electropolished in aqueous alkali or in non-aqueous solutions [188–190]. Mixed melts of alkali metal halides have also been used for electropolishing germanium [191]. Silicon is electropolished in solutions of hydrofluoric acid [192–194], gallium arsenide and indium antimonide in a mixture of perchloric acid and acetic anhydride [195]. Current densities are usually between a few hundredths of an ampere and a few amperes per cm^2 of specimen surface. A very smooth surface, with a roughness of less than 50 Å, can be obtained by stirring the electrolyte [196,197].

Electrolytic polishing of germanium in KOH solutions, and also in solutions of SbOCl, produces surfaces of extremely low surface recombination velocity (of the order of 100–200 cm sec^{-1}) [198–200].

The jet-etching method [201] has been developed for the production of shallow depressions a few tens of microns in diameter on germanium wafers in the manufacture of surface-barrier transistors. A thin jet of electrolyte is directed from a glass nozzle on to the sample, which is biased anodically. The cathode is sealed in the wall of the nozzle. Under factory conditions two jets are used, one on each side of the wafer. The electrolyte consists of potassium hydroxide [202–204] or a metallic salt [173–179,182–196,198–208]. The electrolyte should have a much higher resistivity than the germanium. Etching is carried out at a current density of about 1 A cm^{-2}, and the operation is stopped when the remaining thickness of germanium (which is to form the base of the transistor) is no more than a few microns. The method is also suitable for gallium arsenide [209], but a solution of $Cd(CN)_2$ must be used as the electrolyte.

Germanium can also be jet-etched cathodically (formation of GeH_4), but very high current densities are needed (up to 160 A cm^{-2}). [210–212]

Depressions of any desired shape can be etched into germanium by the use of microcathodes situated very close to the surface [213,214]. Sharp points, with a radius of curvature of 1 μ and suitable for field emission experiments, can be prepared by etching germanium in NaOH. [215] Lastly, an electrolytic saw for germanium has been made [216] in which the cathode is a moving, fine tungsten wire.

‡ A recent communication [180] claims that the $Si-H_2SO_4$ system can form the basis of a radiation detector.

Thick, non-porous oxide films have been grown on germanium and silicon devices, to protect them from the effect of their ambient surroundings, by anodising the semiconductors in a solution of nitrates in methylacetamide [217].

By taking advantage of the rectifying properties of p-n junctions and of the dependence of the rate of dissolution of germanium on the type and magnitude of its conductivity, selective etching of the various parts of a transistor (emitter, base, collector) can be achieved [218–221]. Various techniques for revealing the presence of p-n junctions in germanium single crystals are based on the same principle [222,223]. If, for example, a reverse-biased p-n junction (n region connected to the positive terminal of the battery, p region connected to the negative terminal) is immersed in a dilute solution of alkali, most of the applied potential is dropped across the junction itself and the two regions are at a very different potential. The n region, being anodic, will dissolve, whereas the p region will act as a cathode. If, on the other hand, both sides of the junction are at the same (anodic) potential, and an auxiliary cathode is provided, the p region will dissolve preferentially because at a given overpotential p-type germanium anodes dissolve faster than n-type. The method can also be used to reveal boundaries between regions of the same conductivity type, but of widely different donor (or acceptor) concentration: the so-called l-h junctions [224–226].

It is also possible to delineate p-n junctions in germanium by electrodeposition of copper or gold. A reverse-biased p-n junction immersed in a solution of a copper or gold salt will be electroplated on the p side, since this region is at a cathodic potential [227–231]. If a solution of the dye Methylene Blue is used instead of the salt solution, the dye is reduced (and decolorised) on the p side of the junction [232]. Silicon junctions are not usually polarised from an external battery, but are flooded with light instead [233]: the injected hole–electron pairs are separated by the p-n junction (which behaves in this case as a photodiode), charging the n region negatively and ensuring that metal (gold, copper, or silver) is electrodeposited only on this region [234–237].

Electrodeposition is also used to prepare rectifying and ohmic contacts on silicon and germanium [238–242]. Germanium coatings on other metals can be electrodeposited from non-aqueous electrolytes [243–246]; electrolysis of molten salts gives germanium dendrites suitable for use in semiconductor devices [247].

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FLUORIDES OF XENON AND RADON

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Until recently it was universally considered that the so-called inert, or noble gases — helium, neon, argon, krypton, xenon, and radon — differ sharply from all the other elements in that they do not react chemically, either with one another, or with any other substance. By virtue of this peculiarity they occupy a special place in the Periodic System — Group 0.

Experiments to disprove the hypothesis of the inertness of the Group 0 elements have been undertaken more than once. Thus, there have been papers on the existence of "compounds" of helium with certain metals (mercury, tungsten, platinum, palladium, bismuth, iron, etc.), but it is improbable that chemical reaction occurred in these cases.

Clathrate compounds of argon, krypton, and xenon with β-hydroquinone, phenol, and water have been obtained[1-4]. It is known that in such compounds there is no chemical reaction between the crystal lattice of the clathrate-forming compound and the gas molecules occluded in the lattice vacancies[5].

Claims concerning the preparation of compounds of the inert gases with molecules having strong electron-acceptor properties, such as BF_3 or $B(CH_3)_3$, have not been confirmed subsequently[6].

Band spectra observed in an electric discharge were ascribed to XeO and KrO molecules but corresponding stable compounds were not isolated[7].

Very recently it has been claimed that at least two inert gases — xenon and radon — are able to form chemical compounds.

Bartlett[8] first published an account of the preparation of a complex which contained xenon, $XePtF_6$. This complex, obtained by direct reaction of xenon and platinum hexafluoride in the gas phase, is an orange-yellow solid, insoluble in carbon tetrachloride and having a negligibly small vapour pressure at room temperature. The compound sublimes on heating in a vacuum; on exposure of the sublimate to water vapour it is rapidly hydrolysed with liberation of xenon and oxygen (the composition of the liberated gas was established by mass spectroscopy) and precipitation of hydrated platinum dioxide:

$$2XePtF_6 + 6H_2O \longrightarrow 2Xe + O_2 + 2PtO_2 + 12HF.$$

By analogy with the complex $O_2^+[PtF_6]^-$ obtained earlier by Bartlett and Lohmann[9] the xenon compound was given the structure $Xe^+[PtF_6]^-$. The basis for such an analogy was provided, firstly, by the identical method of making both compounds and the similarity in their formulae, and secondly by the closeness of the ionisation potentials of the oxygen (12.2 eV)[10] and xenon (12.13 eV)[10] molecules, which makes it plausible that xenon is oxidised by the platinum hexafluoride to form the positive ion Xe^+.

Calculation of the lattice energy of $Xe^+[PtF_6]^-$ by Kapustinskii's equation[11] gave the value of ~100 kcal mole^{-1}, *i.e.* in all, ~10 kcal mole^{-1} less than for $O_2^+[PtF_6]^-$. Hence, assuming the compound to be ionic, a minimum value of 170 kcal mole^{-1} was found for the electron affinity of the hexafluoroplatinum, more than twice the corresponding value for the fluorine atom (~83 kcal g-atom^{-1})[12].

Somewhat later, Bartlett's experiments were reproduced, and furthermore it was shown that xenon reacts at room temperature with RuF_6 and PuF_6, but not with the hexafluorides of uranium, neptunium, or iridium[13].

Recently Claassen *et al.*[14] reported the production of xenon tetrafluoride XeF_4, a stable solid at room temperature, and gave preliminary results of the investigation of certain chemical and physical properties of this compound. Somewhat more detailed information concerning the physicochemical properties of XeF_4 and the possibility of existence of other fluorides of xenon was published soon afterwards by a group of investigators which include the authors mentioned.

To prepare xenon tetrafluoride, one part of xenon and about five parts of fluorine were mixed under pressure in a nickel vessel, the mixture of gases was heated to 400° for an hour and then rapidly cooled on the water-bath to room temperature. The atomic ratio of fluorine to xenon in the product was determined by weighing the nickel vessel before and after admitting the xenon and on finishing the reaction, and also by evacuating, freezing, and weighing the unreacted fluorine (with excess of fluorine all the xenon took part in the reaction). The F : Xe ratio in four experiments was 4.05, 3.92, 3.91, and 3.97, which closely corresponds to the formula XeF_4. Another method of finding the composition of the compound, leading to the same formula, was to reduce a weighed specimen of the substance with hydrogen at 400°. The reduction was found to take place by the reaction:

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF,$$

with formation of xenon and hydrogen fluoride.

Xenon tetrafluoride is a colourless solid with a vapour pressure negligibly small at -78° and equal to ~3 mm Hg at room temperature; it readily sublimes at ordinary temperatures. Specimens sealed under vacuum in a glass tube form coarse colourless crystals after a few hours.

Xenon tetrafluoride is stable at room temperature and can be stored for quite a long time in nickel or glass containers. No decomposition of the XeF_4 or reaction with the glass was observed during storage in a Pyrex vessel for more than six weeks. In a thin-walled capillary of Pyrex glass XeF_4 did not melt below 100°.

Dilute solutions of NaOH or water hydrolyse xenon tetrafluoride to form a yellow product, which slowly dissolves to form a transparent pale-yellow solution. Analyses for total fluorine support the following equation for the hydrolysis:

$$XeF_4 + 2H_2O \longrightarrow Xe + O_2 + 4HF,$$

but the quantity of gas evolved and the xenon : oxygen ratio did not agree with this equation.

The yellow alkaline solution can be evaporated to dryness without loss of xenon by use of a heater lamp. If the solution is previously acidified, then xenon is liberated during the evaporation. These results show that hydrolysis of XeF_4 proceeds by a complex mechanism and that in the aqueous solution there are xenon compounds, possibly in ionic form.

Xenon tetrafluoride does not dissolve in perfluoroheptane and does not react with it, but it dissolves with reaction in benzene. It dissolves readily in anhydrous hydrogen fluoride without reaction; at -78° the solubility is <1 mg ml^{-1} and at 60° exceeds 100 mg ml^{-1}. Such solutions do not decompose when stored for two weeks in poly(chlorotrifluoroethylene) vessels. The electrical conductivity of solutions of XeF_4 in HF is small. Since hydrogen fluoride is a good ionising solvent, the low conductivity of solutions of XeF_4 in it shows that there is little probability of ionic reactions occurring and excludes the possibility of an ionic mechanism for the fluorination reaction.

The absorption spectrum in the region from 50 000 to 400 cm^{-1} of a dilute (0.2 M) solution of XeF_4 in HF does not differ appreciably from the spectrum of pure hydrogen fluoride with the exception of the absorption in the ultraviolet region, which increases with decreasing wavelength.

A solution of XeF_4 in hydrogen fluoride is a moderately powerful fluorinating agent, in comparison with uranium hexafluoride. The action of such a solution on bright platinum forms PtF_4 and quantitatively releases xenon. Neither dry XeF_4 nor its solution in HF react with AgCl.

A preliminary investigation of the infrared absorption spectrum of xenon tetrafluoride vapour showed the presence of an intense band at 586 cm^{-1} (*i.e.* in the region in which the frequencies of the stretching vibrations of the fluorine–metal bonds usually lie), a weaker one at 290 cm^{-1} and very weak bands at 1100 and 1130 cm^{-1}. The Raman spectrum of solid XeF_4 contains two very intense bands at 502 and 543 cm^{-1} and probably one weak band at 235 cm^{-1}. These results agree with a square planar structure for xenon tetrafluoride and the previous results of X-ray structural analysis do not contradict this.

Direct determination of the molecular weight, confirming the correctness of the formula XeF_4 was accomplished by analysis of specimens of xenon tetrafluoride using a time-of-flight mass spectrometer; the results showed that other compounds of xenon and fluorine exist. Specimens for the mass spectrometric investigation were obtained by various methods. In one case xenon tetrafluoride was made using especially pure fluorine. The mass-spectrum of the vapour of the specimen taken at room temperature showed that in addition to XeF_4 there are XeF, XeF_2, and XeF_3. On slowly heating a specimen frozen at -78°, peaks appeared corresponding to XeF and XeF_2. It was concluded that XeF_2 exists as a stable compound, more volatile than XeF_4, whereas XeF and XeF_3 are probably fragments of XeF_2 and XeF_4 respectively.

Another specimen was made using ordinary fluorine containing a few tenths of one per cent of oxygen. Specimens were taken from the residue after removing almost all the xenon tetrafluoride. The spectrum, more complex than in the previous case, showed masses corresponding to the compounds XeF, XeF_2, XeF_3, XeF_4, XeO, XeOF, $XeOF_2$, $XeOF_3$, and $XeOF_4$. The authors consider that the compounds containing the group XeO are fragments of the oxide fluorides $XeOF_3$ and $XeOF_4$, whereas the latter exist as stable compounds comparable in volatility with xenon tetrafluoride.

The formation of xenon tetrafluoride during the reaction of gaseous xenon and fluorine was confirmed by Holloway and Peacock[15], who proposed a simple method of obtaining XeF_4 with a yield of 30–50% in a circulating system.

The reaction of xenon with fluorine (in molar ratio 1 : 2) also takes place when a mixture of these gases is illuminated at room temperature by a high-pressure quartz mercury lamp[13].

A colourless crystalline condensate with a composition near to XeF_4 is formed by the action of an electric discharge on a mixture of xenon and fluorine (in volumetric ratio 1 : 2) at room temperature in a quartz vessel[16].

Smith[17] succeeded in obtaining XeF_2 by reaction of xenon (partial pressure 60 mm Hg) and fluorine (240 mm Hg) in a circulating system (8 h circulation) at 400° and above. The compound was identified by its mass-spectrum.

Xenon difluoride is a colourless solid substance with a vapour pressure of ~3 mm Hg at room temperature, which readily sublimes under ordinary conditions with the formation of rhombohedral crystals. The infrared spectrum of XeF_2 has two branches: the *R*-branch with a maximum at 566 cm^{-1} and a *P*-branch with a maximum at 550 cm^{-1}. On the basis of the spectroscopic results conclusions were drawn concerning the linearity and symmetry of the XeF_2 molecule; the Xe–F distance was calculated as 1.7 Å.

This was soon followed by a report on the preparation of xenon hexafluoride[18,19] by reaction of the gaseous components at 300°–450° in nickel[18] and stainless steel[19] apparatus. The formula XeF_6 was established by chemical analysis. Mass-spectrometric investigation[18] showed the existence of XeF_6 and of certain of its fragments.

Xenon hexafluoride is a colourless solid stable at room temperature with a vapour pressure of 6–7.5 mm Hg at 0° and 27–30 mm Hg at 20°–25°. It reacts vigorously with water and hydrogen at room temperature, but dissolves without reaction in anhydrous hydrogen fluoride.

Its infrared spectrum contains an intense band at 610–612 cm^{-1}. It was concluded from the spectroscopic data that the XeF_6 molecule is symmetrical[19].

Following the reports on xenon compounds Fields *et al.*[20] described the reaction of traces of radon with fluorine. These authors found that radon forms a stable fluoride which is less volatile than XeF_4.

Gaseous radon (^{222}Rn) collected from an aqueous solution of radium chloride, was passed through a drying tube of magnesium perchlorate and a metallic vacuum line and frozen in a trap at -195°. On heating this trap to -78° the radon passed under vacuum into another part of the vacuum line, cooled to -195°. The position of the radon was determined by the 1.8 MeV gamma activity of the daughter ^{214}Bi isotope ($T_{\frac{1}{2}}$ = 19.7 min).

In the first experiments on the production of the fluoride, 5.1 μc of radon were condensed in a nickel vessel of capacity 5 cm^3, fluorine at a pressure of 300 mm Hg was introduced, and the mixture was heated at 400° for 30 min. Then the vessel was cooled to -78°, the excess of fluorine evacuated and cooled at -195°. During this operation it was noted that the volatility of the product was appreciably less than that of the initial radon: at 2×10^{-6} mm Hg and gradual heating to 150° radon was not released, but at 230°–250° part of the radon was removed from the vessel and condensed in the exit trap at ~100°.

To check whether the behaviour of radon in the presence of macroscopic amounts of a carrier is different, a mixture of xenon and radon was fluorinated: 87 μc radon were put in a 7 cm^3 nickel vessel, xenon (partial pressure 100 mm Hg) and fluorine (partial pressure 1200 mm Hg) were added,

and it was heated at 400° for 25 min. After cooling the vessel to -78° the excess of fluorine was evacuated and the vessel heated to 50° when xenon fluoride sublimed in the vacuum and passed into a trap at -195°. Less volatile radon fluoride remained in the vessel and was only removed on heating to 250°. It was shown by control experiments that pure radon does not react with the walls of the nickel vessel on heating to 400°.

The authors did not succeed in establishing the composition of the radon fluoride formed. As for its chemical properties, it is known only that it is quantitatively reduced by hydrogen to elemental radon. The reaction with hydrogen does not take place at 200°, but at 500° and a hydrogen pressure of 800 mm Hg reduction is complete after 15 min.

The experimental results described are of considerable interest but the available material unfortunately is insufficient to attempt to draw any definite conclusions concerning the structure of these compounds. To decide these questions it will be necessary to study further the physicochemical properties of the fluorides of xenon and radon, especially the magnetic properties and structure.

Reports on the preparation of compounds of the inert gases and fluorine show that there is evidently interest in even an approximate comparison of the inert gases and halogens according to their electronegativity, *i.e.* according to Mulliken[21], by the sum of the ionisation potentials and electron affinity.

The Table gives the appropriate data[12]. For the atoms of the inert gases the electron affinity has been taken as approximately zero; published results for helium, neon, and argon (respectively -0.53, -0.8, and -1.0 eV)[12] show that no substantial error is involved.

The Table shows that on passing from neon to argon there is a sharp change in ionisation potential and consequently in the electronegativity; starting with argon the inert gas is less electronegative than fluorine, chlorine, and bromine, and xenon and radon less even than iodine.

On the other hand it is known that starting from argon the atoms of the inert gases have incomplete *nd* electron shells (where $n = 3$ for argon, 4 for krypton, etc.) Both these circumstances favour the formation of chemical compounds of the inert gases under suitable conditions.

As noted above, in view of the lack of sufficient experimental evidence it is difficult to express any judgement concerning the nature of the fluorides of xenon and radon. Nevertheless the very fact of the appearance of reports on the preparation of these compounds cannot but favour the emergence of different hypotheses attempting to explain the formation of chemical bonds by atoms of the inert gases.

TABLE.

Element	Ionisation potential, eV	Electron affinity, eV	Electronegativity, eV
F	17.418	3.62	21.038
Cl	13.01	3.82	16.83
Br	11.84	3.54	15.38
I	10.44	3.23	13.67
He	24.58	~0	~24—25
Ne	21.559	~0	~21—22
Ar	15.755	~0	~15—16
Kr	13.996	~0	~13—14
Xe	12.127	~0	~12
Rn	10.745	~0	~10—11

Allen[22] took the first step in this direction, qualitatively considering the effect of correlation in pairs of electrons with antiparallel spins (α and β) on the geometric distribution of electron density in the xenon atom. Allen considered that correlation necessitates a certain spatial distribution of the clouds of the three p_α electrons and three p_β electrons with disturbance of spherical symmetry; through this there is a tendency to form an approximately octahedral relative distribution of the p electrons with alternation of the spins of four electrons about the equator and with antiparallel spins of two electrons on the polar axis (the two s electrons form an ellipse and are nearer to p electrons on the polar axis).

Four electrons (two with spin α and two with spin β) situated on the equator can, according to Allen, form bonds with halogen atoms. In the case of formation of xenon tetrafluoride two electrons of the fluorine atoms must have spin α and two spin β; as a result, the XeF molecule should be diamagnetic.

From Allen's ideas there results a square planar configuration for the XeF_4 molecule, which is consistent with the results of spectroscopic investigations on XeF_4.[13] Allen also briefly considered the possibility of the formation of XeF_2 and xenon oxide fluorides.

In another paper Allen and Horrocks[23] qualitatively described the fluorides and oxide fluorides of xenon using ideas expressed in electron pair terminology. For XeF_4 they considered a system of 12 electrons (the mechanism of formation of such a system is not discussed) which forms six pairs. From electrostatic concepts the authors propose the following model for the XeF_4 molecule: the molecule consists of a right octahedron at the centre of which is the Xe atom, with 4 F atoms at the corners of a square and two unshared electron pairs at the two other vertices. Such a structure corresponds to d^2sp^3 hybridisation. The Xe – F distance in XeF_4 was calculated to be 1.97 Å.

An analogous treatment for XeF_2 leads to a trigonal bipyramidal structure (dsp^3 or d^3sp hybridisation) with the Xe atom in the centre, three unshared pairs at the vertices of the triangle in the plane and two F atoms at the vertices above and below the plane of the triangle.

The formation of the oxide fluorides XeF_4O and XeF_4O_2 (in the case of XeF_4) and of XeF_2O, XeF_2O_2, and XeF_2O_3 (in the case of XeF_2) can be, according to Allen, accomplished as a result of completion of the electron clouds of the oxygen atoms by unshared electron pairs of the fluorides.

According to a recent paper of Rundle[24], which considered qualitatively the bond in the xenon fluorides from the aspect of molecular orbitals, a three-centred four-electron bond in which the d electrons would not take part is proposed for these compounds. By comparing XeF_4 and IF_5 Rundle calculated certain thermodynamic quantities for XeF_4 and found the Xe – F distance in XeF_4 to be ~1.96 Å.

With insufficient experimental data available it is difficult to say to what extent these hypotheses correspond with actuality. However, the intense development of the investigation of the compounds of the inert gases provides a basis for hoping that in the near future we will obtain sufficient data for a more detailed discussion of the structure of these interesting substances.

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POLYYNES

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I. INTRODUCTION

Polyacetylenes or polyynes are compounds of general formula $R-[C\equiv C]_n-R'$, the molecules of which are made up of carbon atoms linked together by alternating single and triple bonds.

This class of compounds attracted the attention of research workers long ago. As early as 1885 Baeyer [1] tried to obtain compounds containing a large number of acetylenic bonds and consisting solely of carbon atoms. He suggested that these compounds would possess characteristic properties, being "explosive diamonds".

From propiolic acid, Baeyer was able to obtain, *via* butadiynedicarboxylic acid, butadiyne itself, which shows a great tendency to polymerise. When he tried to prepare octatetrayne, he was unable to isolate even the corresponding dicarboxylic acid, since it is immediately converted into an insoluble black mass. The instability of such compounds led Baeyer to formulate his strain theory.

Baeyer's work on the synthesis of polyacetylenic compounds was followed by a considerable break, with only isolated papers appearing. Comparatively recently, interest in this class of compounds has been rearoused; the active development of the chemistry of acetylene created the preconditions for the synthesis of polyacetylenic compounds; thus butynediol and hexynediol, the starting materials for the preparation of diynes and triynes have become readily available.

An important stimulus to the resumption of work in this field was the discovery of representatives of this group of compounds in Nature. In 1935 Vil'yams *et al.* [2] isolated from the essential oil of *Lachnophyllum gossypinum* a crystalline substance having the structure

$$CH_3-CH_2-CH_2-C\equiv C-C\equiv C-CH=CH-COOCH_3 .$$

This discovery resulted in a systematic study of polyacetylenic compounds by the schools of Jones in England and of Bohlmann in Germany.

At the present time polyynes containing up to 10 conjugated triple bonds in the molecule have been synthesised. Great effort has been required to investigate the properties of such compounds, the lifetimes of most of which are measured in seconds under ordinary conditions. During recent years interesting electrical and magnetic properties have been discovered in the polyynes.

The present survey covers work on the synthesis of polyynes from the simplest members of the polyynes series to polymers, and including macrocyclic compounds containing triple bonds. Work on the synthesis of natural polyacetylenic compounds is not considered in the review, since this would make it too long. Readers can obtain a detailed idea of these papers from the exhaustive reviews of Bohlmann[3], Jones[4], and Sörensen[5].

II. SYNTHESIS OF POLYYNES

Let us consider briefly the main methods for synthesising polyynes, which paved the way for broad investigations in this field.

In 1870 Glaser[6] observed that the copper derivative of phenylacetylene is smoothly oxidised by atmospheric oxygen to diphenylbutadiyne:

$$2C_6H_5C{\equiv}C{-}Cu \xrightarrow{O_2} C_6H_5C{\equiv}C{-}C{\equiv}C{-}C_6H_5.$$

Oxidative dehydrocondensation is still, in various versions, the main reaction of polyacetylenic synthesis.

Another important reaction was discovered by Cadiot and Chodkiewicz[7], who showed that monosubstituted acetylenes react with 1-bromoacetylenes in the presence of catalytic quantities of cuprous salts to give high yields of diacetylenic compounds:

$$RC{-}C{\equiv}CH + Br{-}C{\equiv}C{-}R \xrightarrow{Cu^+} R{-}C{\equiv}C{-}C{\equiv}C{-}R.$$

A classic method for obtaining a triple bond is the dehydrohalogenation of 1,1- or 1,2-dihalogenated compounds with strong bases[8]. Jones employed this method to synthesise polyynes, for example[9]:

$$CH_3CHCl{-}[C{\equiv}C]_4{-}CHClCH_3 \xrightarrow{NaNH_2} CH_3{-}[C{\equiv}C]_5{-}CH_3.$$

Variation and combination of these fundamental methods have made it possible to synthesise many polyacetylenic hydrocarbons.

1. Buta-1,3-diyne (Diacetylene)

The simplest member of the polyyne series is butadiyne, which was first obtained by Baeyer[1] in low yield by the decarboxylation of its dicarboxylic acid. A more convenient route for the synthesis of butadiyne is the oxidation of metal derivatives of acetylene. Straus and Kollek[10] oxidised cuprous acetylide with cupric chloride. Since both hydrogen atoms of acetylene can be replaced by copper, oxidation can result in the repeated doubling of the carbon chain of acetylene right up to the formation of macromolecular products. Butadiyne is an intermediate product in this reaction; polymeric compounds are the main products.

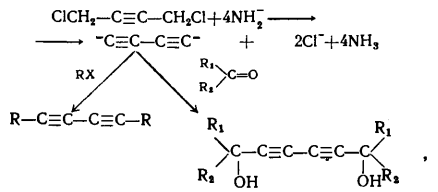
Schlubach and Wolf[11] obtained a 5% yield of butadiyne by oxidising sodium acetylide with air in liquid ammonia (in the presence of ferric oxide as catalyst).

Since this procedure does not give satisfactorily yields (owing to the fact that the butadiyne which is formed immediately reacts with sodamide), these workers attempted to effect oxidation with other agents, of which potassium permanganate proved to be the best, giving yields of 35% of butadiyne. In addition, 17.6% of a polymer was formed, representing more far reaching oxidative condensation of the sodium derivative of butadiyne formed in the reaction. The polymer is a black product, similar in appearance to coal, which does not burn in the flame of a burner.

A more convenient method for synthesising butadiyne was discovered by Keyssner[12] and developed by Johnson[13]. It consists in the dehydrochlorination of 1,4-dichlorobut-2--yne, which is readily obtainable from the corresponding diol. The nature of the alkaline reagent was found to play an important part. Use of aqueous solutions of caustic alkalis $Ca(OH)_2$ and K_2CO_3 makes possible a 60% yield of butadiyne.

Butadiyne decomposes rapidly close to its boiling point, and therefore it can be stored only at temperatures below -25°.

If dehydrohalogenation is carried out with sodamide in liquid ammonia, the disodium derivative of butadiyne is formed, and this can then react with alkyl halides to yield symmetrical conjugated butadiyne hydrocarbons and with ketones to give glycols



where R = C_2H_5, C_4H_9, $CH_2{=}CHCH_2$; $R_1 = C_6H_5CH{=}CH$; $R_2 = CH_3$.

Attempts to make disodiobutadiyne react with ethylene oxide, propylene oxide, and epichlorohydrin were unsuccessful. There is obviously no analogy here between the behaviour of sodium acetylide and the corresponding derivatives of butadiyne.

Such a difference may be assumed to be due to the greater acidity of butadiyne, which on the one hand diminishes the reactivity of its anion as a nucleophilic reagent towards carbonyl compounds, and on the other diminishes the possibility of reaction with ketones in the enolic form, which are acids.

It is interesting that Mansfield and Whiting[14], in an investigation of the relative strength of several unsaturated acids, in particular of acetylenic acids, established that the latter are stronger than their ethylenic and saturated analogues. The dissociation constants ($10^5 K$) these acids[15] are compared in Table 1.

Introduction of a second acetylenic bond into the acid molecule increases the dissociation constant, but the further increase in acidity of a polyacetylenic acid is insignificant.

Before Jones's work, only four monosubstituted butadiynes had been obtained.

$$\underset{(I)}{HOCR_1R_2C{\equiv}C{-}C{\equiv}CH};\quad \underset{(II)}{R_1{-}C{\equiv}C{-}C{\equiv}C{-}R_2}$$

$$\underset{(III)}{RC{\equiv}C{-}C{\equiv}CH}$$

TABLE 1.

R	RC≡C–COOH	RCH=CH–COOH	RCH_2CH_2COOH
CH_3	246	5.6	1.5
$CH_3(CH_2)_3$	140	1.5	1.4
Ph	590	8.6	2.3
H	1400	5.5	1.2

2-Methylhexa-3,5-diyn-2-ol (I: $R_1 = R_2 = CH_3$) was prepared by Zal'kind and Aizikovich[16] by heating the glycol (II: $R_1 = R_2 = CH_3CHOH$) with alkaline reagents.

Penta-1,3-diyne (III: $R = CH_3$) was prepared by Schlubach and Wolf from sodium acetylide and methylene iodide or prop-2-ynyl bromide[17]. They also synthesised phenylbutadiyne[18].

Jones[19] synthesised monosubstituted butadiynes by dehydrohalogenation of 1,4-dichlorobut-2-yne with sodamide in liquid ammonia. With three moles of the sodamide the main product is the monosodium derivative of butadiyne; addition of a halide yields the corresponding substituted butadiyne. Thus methyl iodide gave the extremely unstable penta-1,3-diyne (III: $R = CH_3$).

Hexa-1,3-diyne and octa-1,3-diyne (III: $R = C_2H_5$ and C_4H_9) were prepared from the corresponding bromides in 45% yield.

Allyl bromide probably forms hept-1-ene-4,6-diyne (III: $R = CH_2{=}CHCH_2$), which was not identified owing to its ease of decomposition.

Carbonyl compounds also react with the monosodium derivative of butadiyne. Thus acetone gave 2-methylhexa-3,5-diyn-2-ol (I: $R_1 = R_2 = CH_3$); with benzophenone, butyraldehyde, and formaldehyde the corresponding alcohols were obtained.

It was found that in all these reactions an appreciable quantity of the corresponding diacetylenic glycols was formed. These are of considerable interest, since they enable us to pass to triacetylenic compounds.

But a more convenient and simpler method of obtaining diacetylenic glycols is the oxidative condensation of acetylenic alcohols, a reaction used by Zal'kind and Aizikovich[20,21]. They employed air as oxidising agent, and carried out the dimerisation in the presence of cuprous chloride

$$2HO{-}CMe_2C{\equiv}CH + O_2 \xrightarrow{CuCl,\ NH_4Cl} HO{-}CMe_2C{\equiv}C{-}C{\equiv}C{-}CMe_2OH.$$

Jones and Boden[22] improved this method by carrying out the reaction at a higher temperature (~55°). However, rise in temperature results in resinification of the compounds obtained.

Zal'kind[20] made a fundamental improvement in this method by using pure oxygen for the oxidation, which increased the rate of condensation, since oxygen acts as an acceptor for the hydrogen evolved in the reaction. In the case of 2-methylbut-3-yn-2-ol it was shown that the rate of dimerisation is increased approximately sixfold compared with oxidation by air.

The early work on the oxidative dimerisation of acetylenic alcohols[23] was carried out in a solution of the complex of NH_4Cl and cuprous chloride at pH 3 before addition of the acetylenic compound. The pH can be varied by adding hydrochloric acid or ammonia; at pH > 5 copper derivatives of the acetylenes are usually precipitated, but the oxidative dimerisation takes place smoothly.

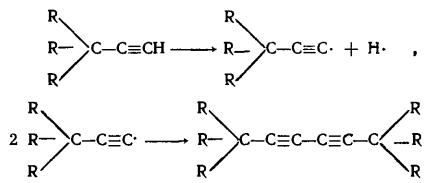
Zal'kind[20] found that reaction occurs also in concentrated ammoniacal solution, but an alkaline solution (cuprammonium, a strong base) in several cases breaks down the reaction products, which affects the yield.

The reaction can also be carried out at higher acidities without appreciable diminution in the reaction velocity or the yield. Acidity does not prevent oxidative dimerisation, but different products can be formed depending on the medium[24]. Thus the following products can be formed, depending on the pH, by the oxidative dehydrocondensation of hex-2-en-5-yn-4-ol:

$$CH_3CH{=}CH{-}CH(OH){-}C{\equiv}CH \xrightarrow{pH\ 6.5;\ 93\%} [CH_3CH{=}CHCH(OH)C{\equiv}C]_2$$
$$\downarrow\ pH1;\ 81\%$$
$$[CH_3CH(OH)CH{=}CH{-}C{\equiv}C]_2.$$

Several investigations have been made of the mechanism of oxidative dehydrocondensation.

Zal'kind and his collaborators[25] consider that the process starts with the breakdown of the acetylenic compound into radicals, which then recombine to form a diacetylenic derivative:



They assume that the formation of diacetylenic compounds takes place more readily the stronger the positive inductive effect of the groups or atoms in the vicinity of the triple bond. The hydrogen evolved in the reaction is either used up in hydrogenating part of the initial acetylene or else is oxidised by atmospheric oxygen to water. The role of copper salts and of atmospheric oxygen remains obscure in this mechanism.

In the case of the conversion of propyne into hexadiyne in the presence of cuprous chloride and atmospheric oxygen Mkryan and Papazyan[26] showed that formation of the diacetylenic compound is a result of interaction of the monosubstituted acetylenic derivative with the partly oxidised catalyst.

Klebanskii *et al.*[27] consider that the formation of diacetylenic compounds in aqueous solution takes place by an ionic–radical mechanism. First of all, acetylide ions are formed. If the reaction is carried out in acid medium, as in the oxidation of acetylenic compounds in the presence of cuprous chloride and atmospheric oxygen, for example, the acetylide ion may result from secondary dissociation of the complex anion $[R{-}C{\equiv}C(CuCl.NH_4Cl)]^-$ which is formed. The acetylide ions are then oxidised by cupric ions to radicals, which recombine to yield a molecule of the diacetylenic derivative. The whole process can be represented by the following equations:

$$2Cu^+ + {}^1/_2O_2 + H_2O \longrightarrow 2Cu^{2+} + 2OH^-,$$
$$R{-}C{\equiv}CH \rightleftharpoons R{-}C{\equiv}C^- + H^+,$$
$$R{-}C{\equiv}C^- + 2Cu^{2+} \longrightarrow R{-}C{\equiv}C\cdot + Cu^+,$$
$$R{-}C{\equiv}C\cdot + \cdot C{\equiv}C{-}R \longrightarrow R{-}C{\equiv}C{-}C{\equiv}C{-}R.$$

Clearly, formation of a diacetylenic compound in the presence of cuprous salts cannot take place in the absence of oxygen. The use of cuprous salts and also of atmospheric oxygen is not essential, as has been confirmed experimentally in the case of the reaction of monosubstituted derivatives of acetylene with cupric salts. In this case ammonia or an amine (pyridine, triethylamine) must be added to combine with the protons liberated in the reaction:

$$2Cu^{2+} + 2R{-}C{\equiv}CH \longrightarrow 2Cu^{+} + R{-}C{\equiv}C{-}C{\equiv}C{-}R + 2H^{+}.$$

This is unnecessary with cuprous salts, since hydroxide ions are formed as a result of the oxidation of univalent copper to the bivalent state.

2. Hexa-1,3,5-triyne (Triacetylene)

Grignard *et al.*[28] reported, without going into details, the synthesis of 1-iodo- and 1-phenyl-hexa-1,3,5-triyne.

Hunsmann[29] observed the formation of hexatriyne as a side-product in the electrical cracking of methane. The hexatriyne was isolated in the form of its addition product with acetone, 2,9-dimethyldeca-3,5,7-triyne-2,9-diol:

$$HO(CH_3)_2C{-}(C{\equiv}C)_3{-}C(CH_3)_2OH\ .$$

This same worker described the synthesis of hexatriyne from dichlorohexadiyne[29].

Schlubach and Franzen[30] found that reaction of the Grignard reagent from phenylacetylene with 1-iodo-2-phenylacetylene in the presence of cobaltous chloride yields diphenylbutadiyne. If, however, the starting materials are two moles of the Grignard reagent and diiodoacetylene, diphenylhexatriyne is formed, but another reaction also takes place:

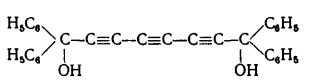
$$2C_6H_5C{\equiv}C{-}MgBr + IC{\equiv}CI \rightleftarrows C_6H_5C{\equiv}CI + BrMgC{\equiv}CMgBr\ .$$

Boden[31] obtained 1,6-diphenylhexa-2,4-diyne-1,6-diol, from which, after preliminary treatment of the diol with thionyl chloride and subsequent elimination of hydrogen halide with alcoholic alkali, he obtained diphenylhexatriyne:

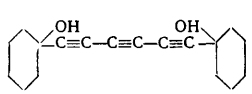
$$C_6H_5CHCl{-}C{\equiv}C{-}C{\equiv}C{-}CHCl{-}C_6H_5 \rightarrow C_6H_5{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C_6H_5.$$

In comparison with the extremely unstable hexatriyne, the diphenyl derivative is quite stable, remaining unchanged in air and in the light, and melting at 95°.

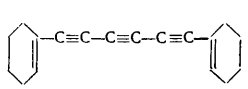
Kuhn and Zahn[32] described the tetraphenyloctatriynediol



Bohlmann[33] obtained diphenyl- and dicyclohexenyl-hexatriynes, using 1,6-dichlorohexa-2,4-diyne as starting material for the synthesis of hexatriyne, and sodamide for the dehydrochlorination. At the instant of formation hexatriyne condenses with ketones and aldehydes. Thus cyclohexanone yields bis-(1-hydroxycyclohexyl)hexatriyne



Elimination of water from this diol gives dicyclohex-1-enylhexatriyne:



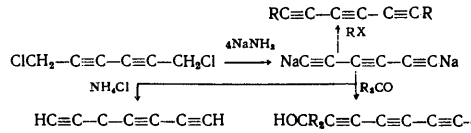
With benzophenone a good yield of 1,1,8,8-tetraphenylocta-2,4,6-triyne-1,8-diol was obtained, which was also prepared by Kuhn[32].

Diphenylhexa-2,4-diyne-1,6-diol was converted into diphenylhexatriyne by the series of reactions

$$C_6H_5CH(OH){-}C{\equiv}C{-}C{\equiv}C{-}CH(OH)C_6H_5 \rightarrow$$
$$\rightarrow C_6H_5CHCl{-}C{\equiv}C{-}C{\equiv}C{-}CHClC_6H_5 \rightarrow$$
$$\rightarrow C_6H_5{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C_6H_5.$$

All these compounds are relatively stable.

Jones *et al.*[34] applied to the synthesis of triacetylenic compounds the method previously worked out for obtaining butadiyne:



When an excess of sodamide is used, a disodium derivative is obtained, which can be converted into a disubstituted hexatriyne or a triacetylenic alcohol. The isolation of hexatriyne is considerably more complicated than its synthesis, since this substance is very unstable, and polymerises even at -50°.

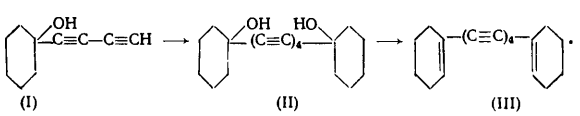
Diphenylhexatriynes are far more stable than the aliphatic hexatriynes[35,36].

3. Octa-1,3,5,7-tetrayne (Tetraacetylene)

Until 1951 the sole tetraacetylenic derivative was the very unstable dicarboxylic acid described by Baeyer and Landsberg[1].

Dimethyl- and diphenyl-octatetrayne were synthesised by Schlubach and Franzen[37]. A 78% yield of the former was obtained by the reaction of pentadiynylmagnesium bromide with cuprous chloride. The instability of the decatetrayne and the impossibility of studying its properties compelled these workers to synthesise diphenyloctatetrayne, which proved to be a quite stable compound melting at 113°.

Substituted tetraynes were also synthesised by Bohlmann[38] by the oxidative dimerisation of diacetylenic compounds. Thus bis-(1-hydroxycyclohexyl)octatetrayne was prepared by condensing butadiynylsodium with cyclohexane to form 1-butadiynylcyclohexanol (I), which on oxidation in air in the presence of cuprous chloride yielded the tetraacetylenic alcohol (II), elimination of water from which gave dicyclohex-1-enyloctatetrayne (III):



The diol (II) is a relatively stable compound melting at 151° without decomposition. The hydrocarbon (III) obtained from it is also stable, and is yellow, with m.p. 127°.

Condensation of butadiyne with formaldehyde yields penta-2,4-diynol (IV), a very unstable product with a tendency to polymerise. Dimerisation converts (IV) into the

extraordinarily reactive deca-2,4,6,8-tetrayne-1,10-diol (V), which in the light is instantly transformed into an insoluble dark blue substance:

$$\underset{\text{(IV)}}{HOCH_2-C\equiv C-C\equiv CH} \longrightarrow \underset{\text{(V)}}{HOCH_2-(C\equiv C)_4-CH_2OH}.$$

Jones *et al.*[34] prepared substituted tetraynes (VI) by oxidative dimerisation with atmospheric oxygen in the presence of cuprous chloride and ammonium chloride:

$$\underset{\text{(VI)}}{R-C\equiv C-C\equiv C-C\equiv C-C\equiv C-R}.$$

In this way a good yield of deca-2,4,6,8-tetrayne (VI: R = CH_3) was obtained from penta-1,3-diyne.

These workers[34] synthesised tetraacetylenic glycols. It is interesting that they were able to obtain from 2-methylhexa-3,5-diyn-2-ol a quantitative yield of the corresponding diol [VI: R = $(CH_3)_2COH$] only on replacing air by oxygen in the oxidative dimerisation. In a similar manner a low yield of the diol (VI: R = CH_3CH_2CHOH) was obtained from the secondary alcohol. Unsubstituted octatetrayne was obtained by Jones[39] as a solution in heptane by synthesising it as follows:

$$HOCH_2(C\equiv C)_3CH_2OH \longrightarrow ClCH_2(C\equiv C)_3CH_2Cl \rightarrow H(C\equiv C)_4H.$$

Examination of the ultraviolet spectrum of the heptane solution confirms the formation of octatetrayne by this method.

4. Deca-1,3,5,7,9-pentayne (Pentaacetylene)

A solution of decapentayne was obtained by Jones[39] by the series of reactions

$$HOCH_2-(C\equiv C)_4CH_2OH \xrightarrow[C_5H_5N]{SOCl_2} ClCH_2-(C\equiv C)_4-CH_2Cl \xrightarrow{NaNH_2} H-(C\equiv C)_5-H.$$

This method cannot be used to add on further ethynyl groups, since the yield of the hydrocarbons falls rapidly with increasing number of acetylenic bonds, in the sequence: butadiyne (60%), hexatriyne (50%), octatetrayne (12%), decapentayne (3%). Moreover, the latter hydrocarbons were not isolated in the pure form because of their great instability.

It was noted above that the diphenyl derivatives of octatetrayne are more stable than the dimethyl derivatives. An attempt was made to prepare a phenylated decapentayne.

Schlubach and Franzen[40] synthesised 1,10-diphenyldeca-1,4,6,9-tetrayne-3,8-diol from phenylpropiolaldehyde and butadiynylenedimagnesium dibromide:

$$C_6H_5-C\equiv C-CH(OH)-C\equiv C-C\equiv C-CH(OH)-C\equiv C-C_6H_5.$$

The diol was converted into the dichloride, and the latter treated with alcoholic alkali. Chromatographic purification resulted in the isolation of diphenyldecapentayne, a dark yellow compound which is comparatively stable to light and heating.

Bohlmann[41] found that a still more stable pentayne could be obtained by introducing a t-butyl group as substituent:

$$\underset{\text{(I)}}{(CH_3)_3C-C\equiv C-CHO} + BrMgC\equiv C-C\equiv C-MgBr \longrightarrow$$

$$\longrightarrow \underset{\text{(II)}}{(CH_3)_3C-C\equiv C-CH(OH)-C\equiv C-C\equiv C-CH(OH)-C\equiv C-C(CH_3)_3} \longrightarrow$$

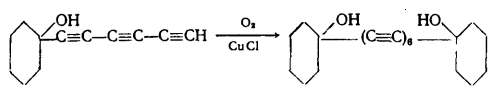
$$\longrightarrow \underset{\text{(III)}}{(CH_3)_3C-C\equiv C-CHCl-C\equiv C-C\equiv C-CHCl-C\equiv C-C(CH_3)_3} \longrightarrow$$

$$\longrightarrow \underset{\text{(IV)}}{(CH_3)_3C-(C\equiv C)_5-C(CH_3)_3}.$$

A good yield of the decapentayne (IV) was obtained. It melts without decomposition at 129°–130°.

5. Dodeca-1,3,5,7,9,11-hexayne (Hexaacetylene)

Bohlmann[33] obtained 1,12-bis-(1-hydroxycyclohexyl)-dodecahexayne by condensing hexatriyne with cyclohexanone and then dimerising the 1-hexatriynylcyclohexanol thus formed:



Unfortunately, this diol could not be obtained in the pure form, since it is converted into an insoluble black polymer even in the dark at 0°. Bohlmann considers[33] that the synthesis of compounds having a larger number of conjugated triple bonds is impossible, since, owing to the increasing energy content of such substances, they tend to pass into compounds containing less energy. This view was held also by Jones, who remarked that, as new members of the polyyne series are obtained, it becomes more and more difficult to isolate them owing to their poor solubility and increasing instability. But a little later this barrier was surmounted: these same workers obtained higher polyyne homologues containing stabilising substituents in the molecule.

Being now convinced of the extreme instability of tetradecahexayne, obtained by the oxidative dimerisation of heptatriyne[39], Jones worked out a synthesis of diphenyldodecahexayne[42] starting from phenylhexatriyne:

$$PhC\equiv C-C\equiv C-C\equiv CH \xrightarrow[O_2]{CuCl} Ph(C\equiv C)_6Ph.$$

Diphenyldodecahexayne proved to be very stable in comparison with the dimethyl analogue.

Bohlmann[41] obtained the di-t-butylhexayne by the following reactions:

$$(CH_3)_3C-C\equiv C-CHO + BrMgC\equiv CCH_2OMgBr \rightarrow (CH_3)_3C-C\equiv C-CHOHC\equiv C-CH_2OH \xrightarrow{SOCl_2}$$

$$\longrightarrow (CH_3)_3C-C\equiv C-CHCl-C\equiv C-CH_2Cl \xrightarrow{NaNH_2} (CH_3)_3C-(C\equiv C)_2-C\equiv CH \xrightarrow[CuCl,\ NH_4Cl]{O_2}$$

$$\longrightarrow (CH_3)_3C-(C\equiv C)_6-C(CH_3)_3.$$

The resulting 2,2,15,15-tetramethylhexadecahexayne was very stable, fusing at 140° and being converted into a black mass.

6. Tetradeca-1,3,5,7,9,11,13-heptayne (Heptaacetylene)

2,2,17,17-Tetramethyloctadeca-3,5,7,9,11,13,15-heptayne was obtained by Bohlmann[41] as follows:

$$(CH_3)_3C-(C\equiv C)_2-CHO + BrMgC\equiv C-C\equiv CMgBr \rightarrow (CH_3)_3C-(C\equiv C)_2CH(OH)-(C\equiv C)_2-$$

$$-CH(OH)\cdot(C\equiv C)_2-C(CH_3)_3 \xrightarrow{SOCl_2}$$

$$\longrightarrow (CH_3)_3C-(C\equiv C)_2CHCl-(C\equiv C)_2-CHCl-(C\equiv C)_2-C(CH_3)_3 \xrightarrow{NaHCO_3}$$

$$\longrightarrow (CH_3)_3C-(C\equiv C)_7-C(CH_3)_3.$$

This compound is remarkably stable to light and heat, being converted into an insoluble black mass only on being heated above 150°.

7. Hexadeca-1,3,5,7,9,11,13,15-octayne (Octaacetylene)

Diphenylhexadecaoctayne $C_6H_5-(C\equiv C)_8-C_6H_5$ was obtained by Jones[42] in ~0.5% yield from phenyloctatetrayne. It is extremely unstable and sensitive to light, a black product resembling coal being precipitated even from dilute solutions. The fact that the substance was the diphenyloctayne was confirmed by elemental analysis and the ultraviolet spectrum.

A more stable product was the di-t-butyl derivative, which was synthesised by Jones[42] as follows:

$$(CH_3)_3C-C\equiv C-CHO + BrMgC\equiv C-CH(OMgBr)C\equiv CH \longrightarrow$$
$$\longrightarrow (CH_3)_3C-C\equiv C-CH(OH)-C\equiv C-CH(OH)-C\equiv CH \xrightarrow[C_5H_5N]{SOCl_2}$$
$$\longrightarrow (CH_3)_3C-C\equiv C-CHCl-C\equiv C-CHCl-C\equiv CH \xrightarrow{NaNH_2}$$
$$\longrightarrow (CH_3)_3C-(C\equiv C)_3-C\equiv CH \xrightarrow[C_5H_5N]{Cu(CH_3COO)_2} (CH_3)_3C-(C\equiv C)_8-C(CH_3)_3.$$

The most difficult stage in the synthesis was oxidation of the tetrayne to the octayne. Attempts to carry out oxidative condensation under ordinary conditions were unsuccessful because of the extremely low solubility of its copper derivatives.

By using Eglinton's method[43] (oxidation with a pyridine solution of copper acetate), Jones obtained an octayne which was, like its lower homologues, a stable compound.

8. Eicosa-1,3,5,7,9,11,13,15,17,19-decayne (Decaacetylene)

The introduction of t-butyl substitutents as end-groups in polyynes made it possible to synthesise higher members of this series. However, they are difficult to prepare and the yields are low primarily because of the instability of the intermediate products.

The t-butyldecayne was synthesised by Jones[44] by the following scheme:

$$(CH_3)_3C-CHCl-C\equiv CCH_2Cl \rightarrow (CH_3)_3C-CCl=CH-C\equiv CH + (CH_3)_3C-(C\equiv C)_2H,$$
$$(CH_3)_3-C(C\equiv C)_2H \xrightarrow[Me_2NHCO]{EtMgBr} (CH_3)_3C-(C\equiv C)_2CHO \xrightarrow{BrMgC\equiv C-CH(OMgBr)C\equiv CH}$$
(I)
$$\longrightarrow (CH_3)_3C-(C\equiv C)_2CH(OH)-C\equiv C-CH(OH)C\equiv CH,$$
(II)
$$\xrightarrow[C_5H_5N]{SOCl_2} (CH_3)_3C-(C\equiv C)_2CHCl-C\equiv CCHClC\equiv CH \xrightarrow{KOH+Al_2O_3}$$
(III)
$$\longrightarrow (CH_3)_3C-(C\equiv C)_2H \xrightarrow[C_5H_5N]{(CH_3COO)_2Cu} (CH_3)_3C-(C\equiv C)_{10}-C(CH_3)_3.$$
(IV) (V)

The main difficulties were met in synthesising 6,6-dimethylhepta-2,4-diynal (I), the stage involving conversion of the glycol (II) into the dichloride also taking place with difficulty; the pentayne (IV) was obtained in 17% yield. It is noteworthy that the use of copper acetate enables the dichloride (III) to be directly converted into the decayne (V) in 24% yield.

The decayne was isolated as pinkish yellow crystals stable for several days in air and in light at room temperature. When heated it is converted into a coal-like substance.

III. PROPERTIES OF POLYYNES

1. Stability of Polyynes

It follows from the above data that the stability of polyynes drops sharply as the number of acetylenic links in the chain increases. Thus hexatriyne is considerably less stable than butadiyne, while octatetrayne cannot be isolated at all as a pure compound.

Polyynes are usually sensitive to light in the solid state, but are more stable in solution. This probably depends on the density of packing of the polyyne molecules in the crystal lattice. X-Ray structure data have shown that the linear molecules in decatetrayne or butadiynedicarboxylic acid are distant 3.8–4 Å from one another in the crystals. Interaction between the chains, resulting in the formation of insoluble network structures, is then possible.

The stability of polyynes is greatly increased by replacing the terminal hydrogen atoms by alkyl or aryl radicals. The volume and the configuration of the substituents also affect the stability. Thus unsubstituted hexatriyne decomposes explosively at -10°, decatetrayne is stable up to 50°, and bis-(1-hydroxycyclohexyl)octatetrayne fuses without decomposition at 151°. The greatest stabilising effect is shown by t-butyl end-groups. This has been explained[44] by the ability of bulky end-groups having cylindrical symmetry to keep the rodlike polyyne chains a sufficient distance apart.

At the same time, the possibility of attack on a terminal hydrogen atom, for example by free radicals, is eliminated in the disubstituted acetylenes.

From a comparison of Stuart models of the molecules of dimethyldodecahexayne (tetradecahexayne) and of the di-t-butyl derivative (see Fig. 1), Bohlmann[41] concluded that, in the former case, the straightened parallel polyyne chains can approach one another, whereas in the latter case the presence of the bulky t-butyl substituents prevents the parallel chains from coming closer than to within 3 Å. It is only at high temperatures that closer approach of the chains is possible, and that polymerisation of the polyyne can occur.

It is interesting to compare the melting points (or decomposition points) of the methyl- and t-butyl-polyynes (see Table 2).

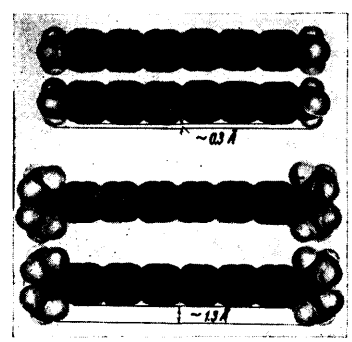


Fig. 1.

TABLE 2.

n	Methyl, m.p., °C	t-Butyl, m.p., °C
2	64°	130°–132°
3	128°	70°
4	decomposes at 80°	99°–100°
5	decomposes at – 5°	129°–130°
6	decomposes at – 5°	140°
7	–	decomposes at 150°
8	–	decomposes at 130°
10	–	decomposes at 100°

The stability of the di-t-butyldecayne and the high yield (40%) at the last stage make one confident that higher members of the series can be obtained.

2. Absorption Spectra of Polyynes

On comparing the infrared absorption spectra of a series of phenylated polyynes $C_6H_5-(C\equiv C)_n-C_6H_5$, (I), we note[42] that the hydrocarbons (I: n = 2–4, 6) absorb in the range characteristic of the phenyl group (3070, 1660, 1490, 1445, 920, and 680 cm^{-1}). Furthermore, the characteristic frequency of the C≡C bond (2200 cm^{-1}) is observed in all the hydrocarbons, its intensity increasing with increase in n.

Variation in frequency (cm^{-1}) with n

(I: $n = 2$)	(I: $n = 3$)	(I: $n = 4$)	(I: $n = 6$)
2200	2200	2205	2180, 2166

The positions of the absorption maxima of the bands due to the diphenyl polyynes are listed in Table 3.

Bands of medium intensity (A–D) increase in intensity from ϵ = 200 to ϵ = 500–20 000 with retention of the fine structure. The bands due to the diphenylpolyynes are somewhat less intense than those of the aliphatic polyynes. As in the aliphatic series, the intensity of the bands increases with n, although not to such a great extent, since the mean intensity of the bands is less.

The absorption spectra show the same pattern in the t-butylpolyynes. Fig. 2 shows the comparative absorption spectra of the di-t-butylpolyynes[45].

Bands of medium intensity occur in the visible range, and coincide in intensity with the lower homologues of the polyyne series. These results support the assumption that the intensity of absorption in this region is independent of the length of the polyyne chain[44]. High-intensity bands are more intense, as was to be expected, in the higher homologues.

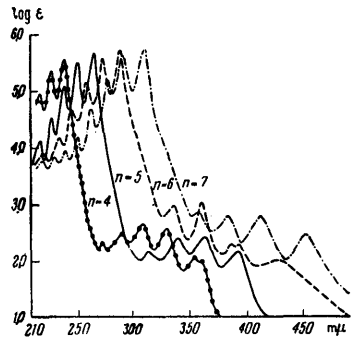


Fig. 2.

Compared with the dimethylpolyynes, the simple di-t-butylpolyynes exhibit a more complicated fine structure in the long-wave region than is observed with polyynes containing one or more ethynyl groups.

It is interesting to compare the absorption spectra of the polyynes $[Bu^t(C\equiv C)_nBu^t]$ with those of the polyenes, as was done by Bohlmann[41]. The former show a considerable shift in the maxima towards shorter wavelengths compared with the corresponding polyenes. Table 4 collates the chief absorption maxima of the two series of hydrocarbons.

The reason for the different positions of the maxima must be sought in the different bond lengths and in differences in the π-electron layers. The doubling of the number of π electrons in the polyynes compared with the polyenes increases the probability of a transition, and hence the intensity of absorption is doubled.

The spectra are also influenced by differences in structure. According to Kuhn[46], the zigzag configuration of the *trans*-polyenes should lower the theoretical absorption intensity by about 25%. This does not occur with the completely straight polyyne chains. Finally, the sharpness of the bands in the polyynes is due to the rigidity of the molecule: the more inflexible the molecule, the more distinct the fine structure and the sharper the maxima[47]. The spectra of the diphenylpolyynes differ still more from those of the diphenylpolyenes[48].

The widely held view in the literature that acetylenic compounds absorb at shorter wavelengths than the corresponding ethylenic compounds applies here to the lower

TABLE 3.

n	A		B		C		D	
	λ_{max}, Å	$10^{-3}\cdot\varepsilon$	λ_{max}, Å	$10^{-3}\cdot\varepsilon$	λ_{max}, Å	$10^{-3}\cdot\varepsilon$	λ_{max}, Å	$10^{-3}\cdot\varepsilon$
2	3270	27.8	3060	31.0	2880	22.0	—	—
3	3580	20.2	3300	30.3	3120	23.0	—	—
4	3970	21.2	3670	34.0	2415	33.8	3180	27.3
6	4600	8.75	4240	17.7	3920	17.4	3610	25
8	5090	4.45	4660	9.6	4300	12.3	3950	33

TABLE 4.

n	Polyyne		Polyene	
	λ_{max}, Å	ε	λ_{max}, Å	ε
2	< 2000	—	2260	22 500
3	2170	119 000	2630	51 500
4	2430	276 000	2960	64 000
5	2650	442 000	3260	72 500
6	2900	500 000	3600	82 200*

* In benzene.

members of the series. The absorption coefficient of the first few bands of the diphenylpolyynes is surprisingly low, and falls still more with increase in conjugation, which is contrary to what would be expected.

3. Reactions of Polyynes

The present section compares the chemical properties of acetylene and its higher polyyne homologues due to the presence and number of conjugated triple bonds. The peculiar position occupied by acetylenic hydrocarbons among organic compounds is due to their specific reactivity.

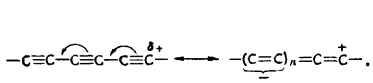
The anomalous reactivity of acetylenic compounds can be explained as follows. The electronic structure of the acetylenic bond differs from that of the ethylenic bond in that the σ bond is formed from two *sp* hybrid orbitals. The reactivity of an unsaturated system is determined solely by the π electrons, which are readily displaced, with the formation of reactive polar forms. It would appear that the C≡C bond, formation of which involves two pairs of π electrons, should exhibit a tendency to electrophilic reactions.

Physicochemical data have shown that the π electrons of a triple bond are less mobile than those of a double bond. This is evident, for example, from the ultraviolet spectra[50]. It is obvious that the energy of the π bond forms part of the total energy of the C≡C bond. Estimation of this quantity[49] taking into account the coulombic repulsion showed that the energy of an acetylenic π bond is 15–20% greater than that of an ethylenic π bond. Here the steric factor must also be taken into account: the formation of π complexes, which occurs in the electrophilic reactions of a double bond, is hardly possible with the triple bond, since the electrons are diffused throughout the molecule.

The nucleophilic reactivity of an acetylenic bond and the acidity of the acetylenic hydrogen are explained by the lack of symmetry of the electron distribution.

Formation of each electronic link involves a shift in electron density towards the middle of the bond. The magnitude of this shift is greater for each σ bond than for a π bond. Whereas with the olefines the displacement is roughly symmetrical, the acetylenes show an unsymmetrical effect. The C≡C grouping contains electrophilic carbon atoms even in the ground state.

In the polyynes this effect becomes stronger as the number of triple bonds increases, since each conjugated bond influences the neighbouring bond. There results a tendency for the π electrons to be displaced towards the centre of the molecule, which can be represented by a cumulene type of mesomeric structure:

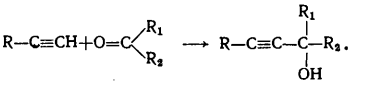


This makes clear the ease of occurrence of nucleophilic reactions in polyynes. Any electron donor would weaken this effect.

(a) Hydrogen replacement reactions. Owing to the electron-acceptor character of the triple bond, the elimination of hydrogen as a hydride anion is probably excluded. Rupture of a ≡C—H bond with the formation of free radicals was postulated by Zal'kind[25] purely hypothetically to explain the formation of diynes from monoacetylenic hydrocarbons.

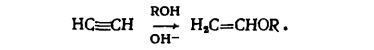
A very characteristic reaction of unsubstituted acetylenic hydrocarbons is the splitting off of hydrogen as a proton. Acetylene itself is a weak C-acid of strength comparable with that of N-acids of the phthalimide type. No work has been done on the comparative acidity of acetylene and the polyynes; it may be supposed that an increase in the number of C≡C groups will strengthen the acid properties. This follows from Mansfield's observation[14] that introduction of a second C≡C group into the molecule of propiolic acid results in an appreciable increase in the dissociation constant. Introduction of a larger number of triple bonds only slightly increases the acidity.

Acetylides from polyynes are considerably less soluble than copper acetylide from acetylene[42]. Replacement of hydrogen by alkali metals (Li, Na) takes place more readily with butadiyne than with acetylene. Whereas acetylene can be condensed with ketones in the presence of KOH in anhydrous medium, with butadiyne this reaction takes place in aqueous solution, which is undoubtedly associated with the increased acidity of the hydrogen atom in the polyyne[49]:

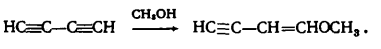


(b) Nucleophilic addition reactions. Olefines react with nucleophilic reagents only if they are polarised by an electron-acceptor substituent; such polarisation is not required with an acetylenic bond.

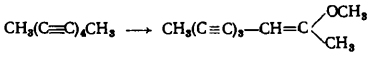
A typical example is the formation of vinyl ethers[51]:



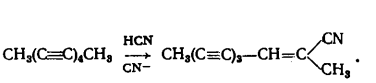
Addition takes place still more readily to butadiyne; methanol forms 1-methoxybut-1-en-3-yne[50], which is of interest for preparative purposes:



Triynes and tetraynes undergo nucleophilic addition still more rapidly[52]. Owing to the great difference in rates of addition in this case, ethers of monoenols can be isolated. Decatetrayne, for example, yields a mixture of *cis*- and *trans*-isomers of the enol ether:

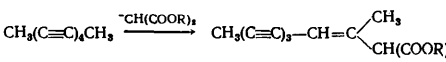


Like alcohols, amines react particularly readily with polyynes[53]. Hydrocyanic acid adds on readily to polyynes in the presence of cyanide ions[54]:



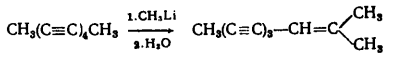
Complex catalysts are required for acetylene to undergo this reaction.

With polyynes the Michael type of addition is possible. Thus sodiomalonic ester adds on to polyynes[54]:

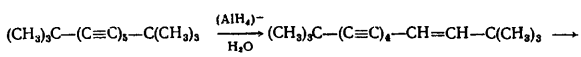


Lithium alkyls have not been observed to add on either to acetylene or to butadiyne, at least three conjugated

acetylenic bonds being required; thus decatetrayne instantly adds on methyllithium, yielding after hydrolysis substituted polyenynes[49]:

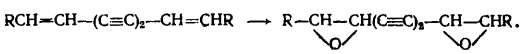


Lithium aluminium hydride reacts similarly. Addition of this reagent is possible only with polyynes[49]. The tetrayne reacts very rapidly, whereas the triyne reacts very slowly. Since the reaction involves ultimately partial hydrogenation of one triple bond, this route can be utilised for the synthesis of polyenynes:



This example shows especially clearly that the rate of nucleophilic addition is higher with polyynes.

(c) Electrophilic addition reactions. Typical electrophilic addition reactions take place more slowly with acetylenes than with olefines (by a factor of about 10). This is especially noticeable with oxidative reactions. Even a polyenyne reacts slowly with peracids, forming a partly epoxidised derivative[52]:



The triple bond reacts only with the peracid present in a large excess.

Acetylenes are ozonised far more slowly than are olefines.

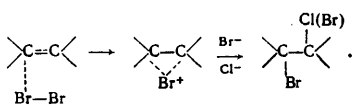
Reaction with hydrogen halides is very slow, this appearing especially clearly on passing from acetylene to polyynes, when the rate of nucleophilic addition reactions increases tenfold, while electrophilic addition shows the reverse order[53]. Thus acetylene reacts very slowly with hydrogen halides, while octatetrayne does not react at all[55].

The addition of water (in the presence of acids) takes place in a similar manner. Although butadiyne is converted comparatively rapidly into a ketone, hexatriyne reacts slowly. Tetraynes do not react at all[56]. The stable di-t-butylpentayne can be heated with concentrated H_2SO_4 at 50° for 1 h without apparent reaction.

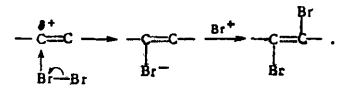
From these examples it is clear that the reactivity in electrophilic addition drops rapidly with increasing number of conjugated triple bonds.

Halogens react with olefines by electrophilic addition. Bromination is very rapid even in the dark. Acetylene reacts with bromine in the dark extremely slowly, butadiyne somewhat more rapidly. Bromine adds on still more rapidly to triynes and tetraynes[56].

An electrophilic mechanism for the halogenation of olefines is confirmed by the fact that bromination in the presence of chlorine results in the formation of compounds containing both chlorine and bromine:

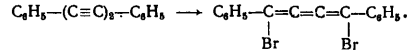


The reaction with decatetrayne under the same conditions yields only bromides, which supports a mechanism of nucleophilic addition:

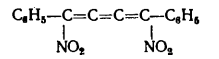


(d) Radical reactions. The addition of bromide to the polyyne series under the influence of light obeys different laws. Decyne reacts with bromine 40 times as rapidly in the light as in the dark[49]. Diynes and tetraynes react with bromine more rapidly solely on account of the greater number of triple bonds[55].

Schlubach[40] showed that in the diphenylpolyynes the addition of bromine takes place at the ends of the chain:



Schlubach and Rott[57] found that nitrogen dioxide in ethereal solution reacts similarly, and with diphenylacetylenes it was possible to isolate dinitro-derivatives having a cumulene structure:

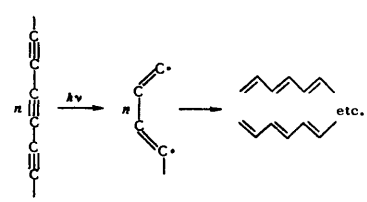


(e) Catalytic hydrogenation. A triple bond is hydrogenated to a double bond more readily than olefines are hydrogenated to alkanes. A comparison of the rates of hydrogenation of mono-, di-, and tetra-acetylenic compounds showed[55] that the reaction velocity increases linearly in proportion to the number of conjugated triple bonds. The mechanism of the catalytic hydrogenation of acetylenes probably consists in the preliminary dissociation of the hydrogen molecules into free radicals (atoms) on the surface of the catalyst. Atomic hydrogen adds on rapidly at a triple bond.

(f) Polymerisation of polyynes. Acetylene is converted by ultraviolet irradiation into a macromolecular product[58], butadiyne and benzene being formed as by-products.

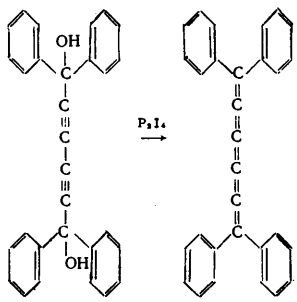
Polyynes undergo polymerisation especially readily. The tetrayne is converted after a few seconds into an insoluble black polymer. Diynes and triynes polymerise more slowly, the products being brown to red in colour.

Bohlmann[49] has put forward a hypothetical mechanism for this reaction. Under the influence of light the electron pairs are parted, and the resulting radicals recombine to form large rings of aromatic character:



(g) Formation of cumulenes from polyynes. Reduction of polyacetylenic alcohols can yield compounds with conjugated double bonds of allene type, cumulenes.

For example, the action of phosphorus diodide on 1,1,6,6--tetraphenylhexa-2,4-diyne-1,6-diol, prepared from benzophenone and butadiynylenedimagnesium dibromide, yields tetraphenylhexapentaene[59]:



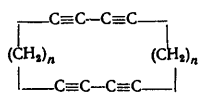
Cumulenes are also extremely unstable, and the same methods are used for their stabilisation as in the synthesis of polyynes, namely the introduction of phenyl and t-butyl substituents[60]. A heptaene and a nonaene have been synthesised[60] by introducing the latter substituents at the ends of the cumulene chain.

According to Kuhn[59], the mechanism of the formation of cumulenes from acetylenic glycols in the presence of phosphorus diiodide consists in replacement of hydroxyl by iodine with subsequent spontaneous elimination of the iodine and rearrangement to a cumulene structure. Replacement of the hydroxyls by chlorine atoms (by the action of HCl) in the presence of reducing agents (of the type of vanadous or chromous chloride) enabled the yield of cumulenes to be sharply increased[59].

Cumulenes (like polyynes) consist of rigid, immobile "rods" of carbon atoms[59].

IV. MACROCYCLIC COMPOUNDS CONTAINING CONJUGATED ACETYLENIC BONDS

Eglinton[61] and independently Sondheimer[62] found that the oxidative dimerisation of the alkadiynes $HC\equiv C-(CH_2)_n-C\equiv CH$ yields, in addition to linear products $H[C\equiv C-(CH_2)_n-C\equiv C]_mH$, cyclic compounds:



Eglinton[63] showed that the cupric ion is an oxidant for acetylenic hydrocarbons. The reaction is carried out in aqueous medium at pH 6, monoacetylenes giving a 50% yield of $\alpha\gamma$-diynes. Half of the ethynyl compound is converted into insoluble copper(I) acetylide:

$$4R-C\equiv CH + 2Cu^{2+} \longrightarrow R-C\equiv C-C\equiv C-R + 2RC\equiv C-Cu + 4H^+.$$

The acetylide can be converted into the $\alpha\gamma$-diyne with an excess of cupric ions, or by oxidation with oxygen and other oxidising agents.

In order to prepare cyclic compounds from diynes, the reaction must be effected in homogeneous solution and at great dilution, in order to avoid formation of the linear polymer:

$$HC\equiv C-(CH_2)_n-C\equiv C-[C\equiv C-C-(CH_2)_n-C\equiv C]_m-C\equiv C-(CH_2)_nC\equiv CH\ .$$

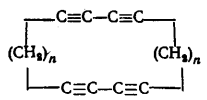
The formation of cyclic compounds is favoured by the rigidity of the tetratomic system $C-C\equiv C-H$.[64]

The most suitable medium for the reaction is a mixture of pyridine and methanol, in which all the components are soluble. At the same time the pyridine combines with the acid evolved in the reaction. For preparative purposes it is more convenient to use an excess of copper acetate. Sometimes the formation of an insoluble reddish brown acetylide is observed during the reaction.

When atmospheric oxygen in the presence of cuprous chloride was used as oxidant, the diynes (I)

$$HC\equiv C-(CH_2)_n-C\equiv CH$$
(I)

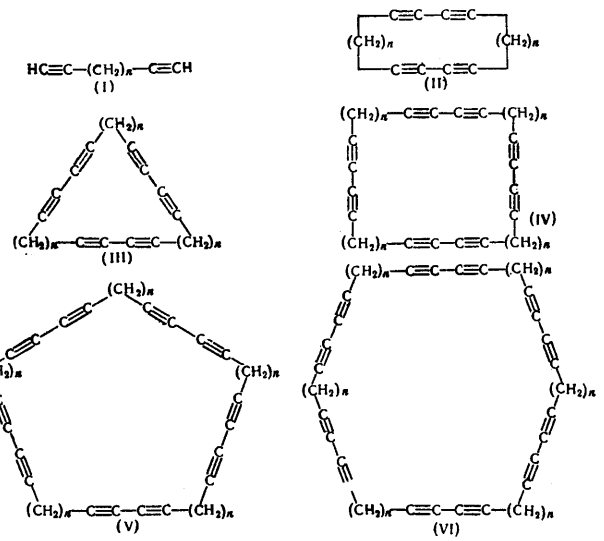
with n = 2 and 6 did not yield cyclic products, whereas with copper acetate mainly cyclic products were formed:



where n = 4 and 5.

This fact indicates that cyclisation is favoured by a homogeneous medium.

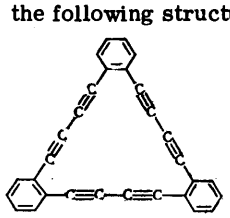
When Sondheimer also employed this oxidant[65], the diyne (I) gave not only cyclic dimers (II) but also cyclic trimers (III), tetramers (IV), pentamers (V), hexamers (VI), and still higher cyclic polyynes (see Scheme 1).



Scheme 1

Here n = 2–5. When n = 2, a linear product is formed at the same time.

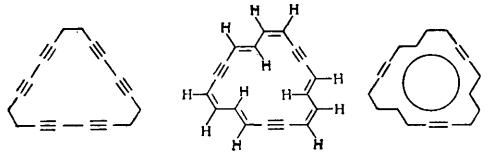
By the oxidative polymerisation of o-diethynylbenzene, Eglinton[66] obtained a 30% yield of a crystalline substance to which, on the basis of an elemental analysis and infrared spectroscopic data, the following structure is assigned†:



† See, however, Chem. and Ind., 699 (1959); Proc. Chem. Soc., 231 (1959) (Ed. of Translation).

At -5° this substance is stable for several months, but it decomposes explosively on being heated or on standing at room temperature.

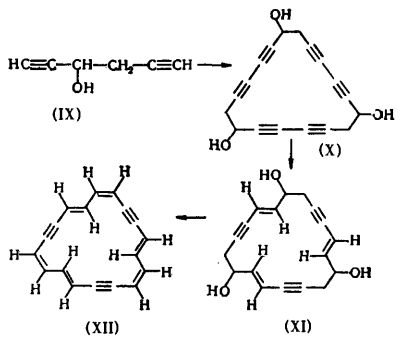
It is noteworthy that, in the presence of potassium t-butoxide, cyclic acetylenes rearrange into fully conjugated cycloalkenynes[67]. Thus cyclooctadeca-1,3,7,9,13,15-hexayne (VII) is converted into cyclooctadeca-*cis*-1,7,13,*trans*--3,9,15-hexaene-5,11,17-triyne:



(VII) (VIII) (VIIIa)

The hydrocarbon (VIII) contains 18 conjugated π electrons. In this compound the conditions of Hückel's rule are satisfied [the presence of $(4n + 2)$ conjugated π electrons][68], although, of course, not all the carbon–carbon bonds are equivalent here, as is required for maximum stability of aromatic compounds. As was to be expected, compound (VIII) is quite stable, remaining unchanged for several days under normal conditions.

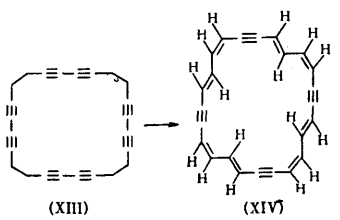
The conjugated hexaenetriyne (XII) was also obtained by a different route[67]:



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

The cyclic polyol (X) was obtained by oxidation of compound (IX) (with copper acetate in pyridine), and from it was obtained, after dehydration with potassium bisulphate in a boiling mixture of acetic anhydride and acetic acid, the required hexaenetriyne (XII).

Similarly, cyclotetracosa-1,3,7,9,13,15,19,21-octayne on treatment with a t-butoxide gave a cyclic product with a conjugated 24-membered ring, cyclotetracosa-1,3,7,9,13,-15,19,21-octaene-5,11,17,23-tetrayne[67]:



(XIII) (XIV)

The octaenetetrayne molecule cannot be planar because of the presence of four double bonds having a *cis*-configuration.

Partial hydrogenation of the octaenetetrayne on a palladium catalyst resulted in a compound which decomposed on being heated. On the basis of analytical and infrared spectroscopic data, this compound is assigned the structure cyclotetracosa-1,3,5,7,9,11,13,15,17,19,21,23-dodecaene. The infrared spectrum and the colour indicate that all twelve double bonds form part of one chromophoric system, and as a result *trans*-addition of hydrogen takes place.

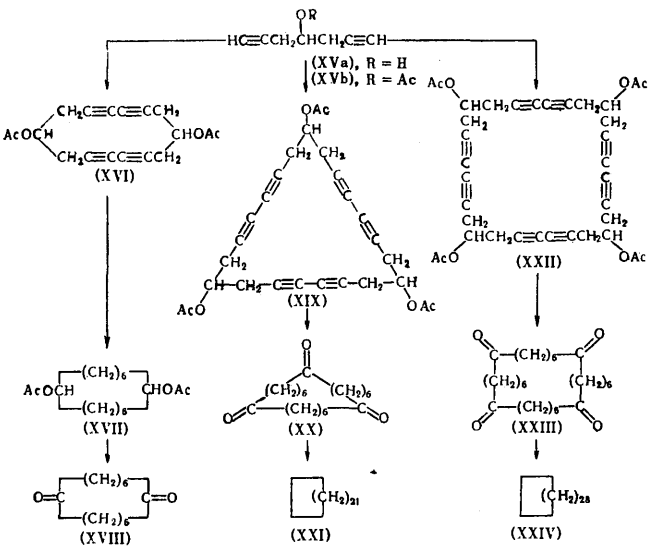
Cyclotetracosadodecaene is a 24-π-electron system which, in contrast to the cyclooctadecanonaene synthesised earlier[69], does not satisfy Hückel's rule. Therefore the cyclotetracosadodecaene is far less stable than the latter compound.

Later Sondheimer[70] and his collaborators prepared oxygen-containing cyclic polyynes. The starting material chosen was hepta-1,6-diyn-4-ol (XVa). Oxidation was effected with oxygen in the presence of cuprous chloride in aqueous alcohol acidified with hydrochloric acid. An insoluble crystalline product was isolated (exploding on being heated to 235°), which from its elemental analysis and infrared spectrum (the presence of α-diacetylene and the absence of terminal ethynyl groups) was one of the two possible stereoisomers of diacetyl cyclotetradeca-3,5,10,12-tetrayne-1,8-diol (XVI).

Chromatography on aluminium oxide of the reaction mixture after removal of (XV) yielded three different crystalline products: triacetyl cycloheneicosa-3,5,10,12,17,19--hexayne-1,8,15-triol (XIX) (probably a mixture of two possible stereoisomers) and tetraacetyl cyclooctacosa-3,5,10,12,17,19,24,26-octayne-1,8,15,22-tetraol (XXII).

In addition to these, an acyclic product was obtained, which was not investigated; its infrared spectrum showed its molecule to be linear and to contain acetylenic bonds.

The structure of the cyclic compounds obtained was demonstrated by hydrogenating them to the corresponding cyclic hydrocarbons (see Scheme 2).



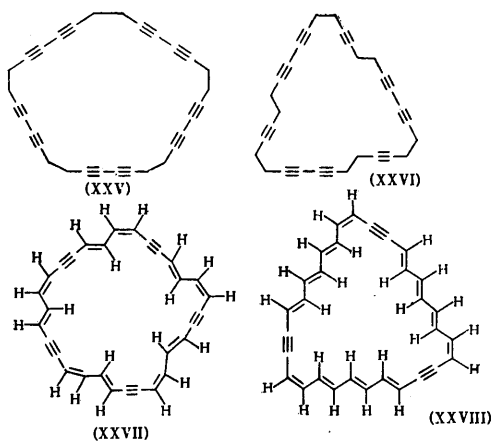
Scheme 2

Hepta-1,6-diyn-4-ol (XVa) is the principal diyne from which, under conditions of oxidative dehydrocondensation (oxygen, cuprous chloride, ammonium chloride, aqueous ethanol), are obtained the more complicated compounds (XIX) and (XXII) as well as the cyclic dimers (XVI). This result indicates that no substantial difference exists between the two methods of obtaining cyclic polyynes. The

solubility is of fundamental importance. The carbinol (XVa) is more soluble in aqueous ethanol than are the hydrocarbons described earlier. If the carbinol (XVa) is replaced by its acetate (XVb) in the oxidative dehydrocondensation (atmospheric oxygen in the presence of CuCl + + NH_4Cl), the main product is the cyclic dimer (XVI). This is obviously due to the acetate being less soluble than the carbinol (XVa) in aqueous ethanol. If, however, (XVb) is oxidised with copper acetate, the main product is the cyclic trimer (XIX).

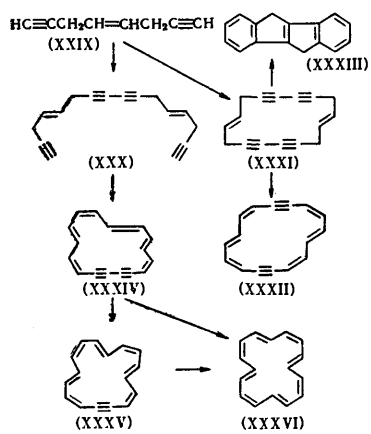
Recent papers by Sondheimer and his coworkers[71,72] describe syntheses of conjugated cyclic systems.

The formation may be noted of cyclotriaconta-1,3,7,9,-13,15,19,21,25,27-decaene-5,11,17,23,29-pentayne (XXVII) from the 1,3,7,9,13,15,19,21,25,27-decayne (XXV) by treatment with a t-butoxide (see Scheme 3).



Scheme 3

Here (XXVII) represents a monocyclic system containing thirty π electrons, which obeys Hückel's rule and is extremely stable.



Scheme 4

Oxidative condensation of oct-*trans*-4-ene-1,7-diyne (XXIX) with atmospheric oxygen in the presence of cuprous chloride, ammonium chloride, and ethyl alcohol containing dilute hydrochloric acid yielded the linear hexadeca-*trans*-4,*trans*--12-diene-1,7,9,15-tetrayne (XXX) and the cyclic dimer cyclohexadeca-*trans*-1,*trans*-9-diene-4,6,12,14-tetrayne (XXXI). Treatment of the cyclic dimer (XXXI) with potassium ethoxide in benzene results in a mixture of isomers, to which the structure (XXXII) is attributed. In addition, an appreciable yield of the indenoindene (XXXIII) is formed.

Oxidative condensation of the linear dimer (XXX) with copper acetate leads to the formation of a new cyclic compound (XXXIV), partial hydrogenation of which gives compounds to which the structures (XXXV) and (XXXVI) are attributed.

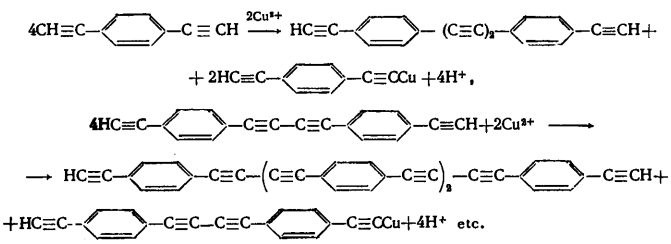
In concluding this survey of work on the synthesis of macrocyclic polyynes, we may note that, in the oxidation of diynes of the type $HC{\equiv}C-(CH_2)_n-C{\equiv}CH$, linear polymeric products are obtained as well as the interesting and theoretically important products. The yield of linear polymers drops sharply with increase in n and in the dilution of the reactants (in the case of oxidation with copper acetate). At high dilutions the yield of linear products is practically zero (see Scheme 4).

V. SYNTHESIS OF POLYYNES BY THE OXIDATIVE DEHYDROPOLYCONDENSATION OF DIYNES

In 1960 Hay[73] extended oxidative dehydrocondensation to *m*- and *p*-diethynylbenzenes. He used atmospheric oxygen as oxidant, in the presence of catalytic quantities of cuprous chloride in pyridine.

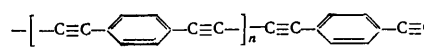
m-Diethynylbenzene yielded a polymer which was soluble in chlorobenzene and in nitrobenzene. Its infrared spectrum showed the presence of ≡CH end-groups (3290 cm^{-1}), their number indicating a molecular weight of 7000. The polymer was stable at room temperature, but decomposed at 180° with the evolution of hydrogen and methane.

Oxidation of *p*-diethynylbenzene gave a yellow product insoluble in organic solvents. At the same time[74-76] a polymer of *p*-diethynylbenzene was obtained by oxidative dehydropolycondensation with bivalent copper. It is obvious that oxidation of *p*-diethynylbenzene produces a mixture of polyynes and copper(I) acetylides:



Further oxidation of the reaction mixture (for example with aqueous potassium ferricyanide) results in the formation of polyynes having the structure $[-C{\equiv}C-C_6H_4-C{\equiv}C-]_n$. The main reaction product is a powder insoluble in organic solvents; a soluble product of low molecular weight, bis--*p*-ethynylphenylbutadiyne, was also isolated[74]. The infrared spectrum of the latter compound is identical with that of the insoluble portion[75] of the product of oxidative dehydropolycondensation of *p*-diethynylbenzene. A similar polymer was obtained by Kotlyarevskii *et al.*[77], who used as oxidant air in the presence of cuprous chloride and ammonium

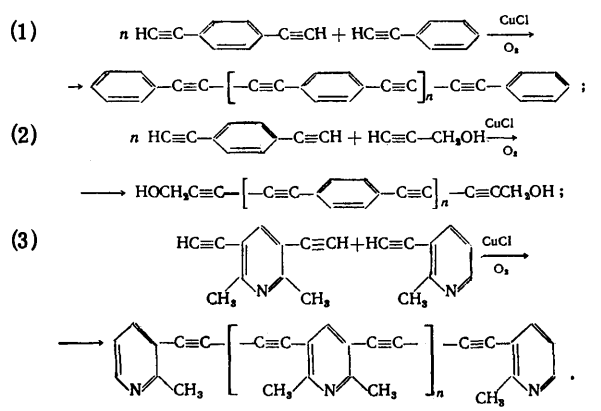
chloride. The sample contained 4.2% of chlorine, which was explained by the presence of the terminal group



Interesting results were obtained[75] in the oxidation of acetylene. When acetylene is passed into an ammoniacal solution of copper nitrate, an insoluble black powder is formed which is clearly a mixture of polyynes and copper acetylides. Further oxidation with potassium ferricyanide yielded a substance having a higher carbon content (up to 98%). The sample contained a small amount of copper. The X-ray diffraction pattern of polyacetylene contains a relatively strong interference band corresponding to a period of 3.85 Å, which can be attributed to the intermolecular distance in an ordered set of parallel linear $[C{\equiv}C]_n$ molecules. On heat treatment, no carbonisation or graphitisation is observed. It is only on heat treatment at 2300° that graphite is formed. But a graphitic structure can be obtained on prolonged boiling of ignited samples of polyacetylene in concentrated hydrochloric acid.

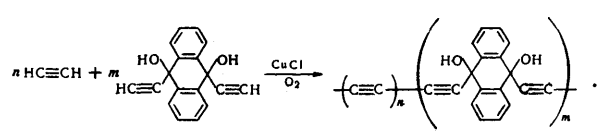
The use of stronger oxidising agents (hydrogen peroxide) and also oxidation by Eglinton's method[61] give cross-linked structures.

In order to obtain soluble polymers containing conjugated triple bonds, experiments were made on the oxidative dehydrocopolycondensation of (1) *p*-diethynylbenzene with phenylacetylene, (2) *p*-diethynylbenzene with propargyl alcohol, and (3) 3,5-diethynyl-2,6-dimethylpyridine with 3-ethynyl-2-methylpyridine[76]. Formation of the following products was to be expected:



By varying the amounts of the reactants it was possible to isolate soluble (in addition to insoluble) products of oxidative dehydrocopolycondensation, whose structures were confirmed by the infrared spectra and X-ray examination.

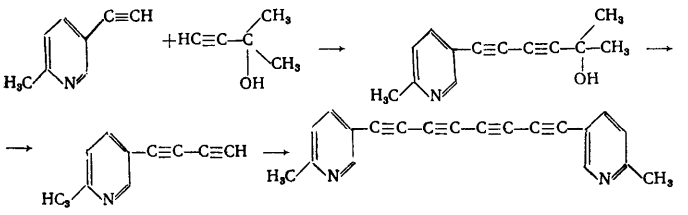
The oxidative dehydrocopolycondensation of acetylene and 9,10-diethynyl-9,10-dihydroanthrahydroquinone also yielded a soluble product[80]:



It is obvious that the introduction of bulky substituents forces apart the rigid linear polyacetylene molecules, facilitating penetration of solvent molecules.

Kotlyarevskii *et al.*[78,79] obtained a product of the oxidative dehydropolycondensation of 9,10-diethynyl-9,10-dihydroanthrahydroquinone together with other diynes. They also effected the synthesis of pyridylpolyynes by building up the acetylenic chain by the oxidative condensation of pyridylacetylenes with 2-methylbut-3-yn-2-ol and decomposing the resulting alcohols into monopyridyldiacetylenes and acetone[80].

Dipyridylpolyacetylenes are obtained by the oxidative dimerisation of monopyridylacetylenes:



Properties of the Polyacetylenes Obtained

The insoluble products of the oxidative dehydropolycondensation of acetylenes (acetylene, *p*-diethynylbenzene, diethynylpyridine, etc.) are characterised by a narrow electron paramagnetic resonance (EPR) signal, typical of conjugated systems, with 10^{16}–10^{19} unpaired electrons per gramme of the substance. Soluble products of the oxidative cocondensation of acetylenes give no EPR signals, which is consistent with the assumption that the concentration of unpaired electrons increases as the chain becomes longer[81–83]. An exception is provided by the polymer obtained by the simultaneous oxidation of acetylene and 9,10-diethynyl-9,10-dihydroanthrahydroquinone[76]. The soluble reaction product in this case contains 2.2×10^{17} unpaired electrons per gramme.

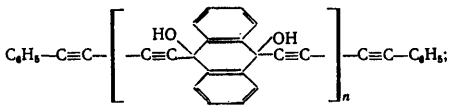
Preliminary data on the heat treatment of the resulting polyacetylenes showed that a rapid rate of heating produces explosive decomposition of the specimens. Such decomposition can be avoided by heating more slowly. The electrical properties of the products are usually improved. For example, the magnetic susceptibility of the polymer of *p*-diethynylbenzene ($10^6\chi = 0.2$) is increased tenfold when a specimen is heated to 200°.[77]

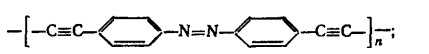
The electrical resistivity of a sample of polyacetylene obtained by oxidising acetylene with potassium ferricyanide is $\rho \simeq 10^6\ \Omega\ cm^{-1}$. With rise in temperature ρ falls, which may be explained by the accumulation of crystalline copper as a result of thermal dissociation and the separation of terminal copper atoms from the polyacetylene. However, the resistivity continues to decrease even at higher temperatures (above 2000°), when the copper has vaporised from the specimen, and this can be explained by the increase in length of the polyacetylene chains during pyrogenic synthesis due to thermal dissociation and separation of copper with subsequent recombination of the resulting free radicals[74].

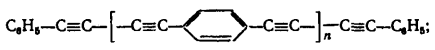
The thermo-e.m.f. of the initial polyacetylene specimen has a negative sign and a value of 1.38×10^4 mV deg^{-1}. At 1300° and 1500° α has a positive sign, and varies with temperature according to a characteristic curve having a maximum at 2300°, which corresponds to the temperature at which polyacetylene changes into graphite.

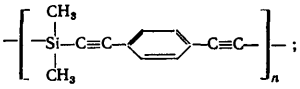
The measurements of ρ and α for the polyacetylene indicate that the sample was an n-type semiconductor in which copper atoms acted as donors. The observed change in sign of the thermo-e.m.f. corresponds to the transition of the polyacetylene to a p-type semiconductor, in which positive holes act as current carriers. Such a transition is linked with thermal dissociation involving the elimination of copper and hydrogen atoms from the carbon chain and is probably due to the acceptor properties of the terminal carbon atoms.

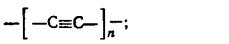
Some of the polyacetylenes which have recently been synthesised[84] display a high photoelectric sensitivity in modulated light, among them being the polymers

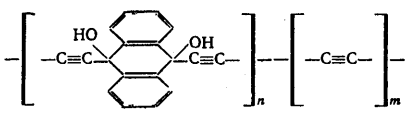












The considerable photosemiconductor sensitivity detected in these polymers suggests possible ways of synthesising photosensitive polymers.

In his interesting work on the synthesis of polydimethyleneacetylene, Bailey[85] chose as starting material 1-bromo-4-chlorobut-2-yne. With an excess of magnesium a Grignard reagent is readily formed, which on standing yields a mixture of soluble and insoluble polydimethyleneacetylenes:

$$Cl{-}CH_2{-}C{\equiv}C{-}CH_2{-}Br \longrightarrow Cl{-}CH_2{-}C{\equiv}C{-}CH_2MgBr,$$
$$ClCH_2C{\equiv}CCH(CH_2C{\equiv}CCH_2)_xCH_2C{\equiv}CCH_3 .$$

The molecular weight of the soluble part was 1500. Hydrogenation of polydimethyleneacetylene yielded a linear polymethylene. It is interesting that the softening point of the polydimethyleneacetylene was 550°, that of polymethylene being 65°–90°.

Papers have recently appeared on the synthesis of polyynes by the oxidative dehydropolycondensation of 4,4′-diethynylbiphenyl[86] and of bis-p-butadiynylphenyl ether[87].

It is evident from this review that the polyacetylenes represent a very interesting class of organic compounds.

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INORGANIC CYCLIC SILICON-CONTAINING COMPOUNDS AND THEIR ORGANIC DERIVATIVES

K. A. Andrianov, I. Haiduc,
and L. M. Khananashvili

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INTRODUCTION

The growth of the chemistry of macromolecular organic derivatives of inorganic elements has been due to their valuable technical properties, which have ensured their wide use in various fields of technology and life. Of particular interest are polymers consisting of inorganic main chains substituted by organic groups; these are structurally intermediate between organic and inorganic compounds. The production of polymers containing inorganic chains has been little studied. It is difficult, and in most cases actually impossible, to adapt or use for the production of polymers containing inorganic chains the usual methods for the production of organic polymers.

The widely used polymerisation of unsaturated organic compounds cannot be used for the production of polymers containing inorganic chains, because there are no corresponding reactive unsaturated monomers. No attempts to polymerise monomers containing the P=O bond have yet been successful.

Polycondensation reactions, which are widely used for the preparation of organic polymers, are of limited application to polymers with inorganic chains, since in most cases they are accompanied by side reactions producing low-molecular-weight cyclic compounds.

The formation of inorganic rings and their conversion to macromolecular compounds are of great significance in the chemistry of organic–inorganic polymers containing inorganic chains[1,2]. The ring-opening polymerisation of octamethylcyclotetrasiloxane has given linear polymers of molecular weight of the order of 10^6. The study of the formation of inorganic silicon-containing rings and their conversion to macromolecular compounds is of exceptional theoretical and practical interest. There have been no general reviews of the production and reactions of inorganic cyclic silicon compounds.

This review deals with various aspects of the chemistry of inorganic silicon rings and includes the most important material published in the first half of 1962. For convenience in dealing with the large volume of experimental material, all inorganic silicon-containing rings have been divided into the following classes[3,4,5]: (1) homocyclic silicon compounds $[R_2Si]_n$; (2) symmetrical heterocyclic silicon compounds $[R_2SiX]_n$, where X = O, N, S, or Se; (3) heterocyclic compounds of mixed type $[R_2SiO]_n$–Q–Y, where Q = Al, B, Ti, P, As, or Sb, and Y = O or N; and (4) polycyclic silicon compounds.

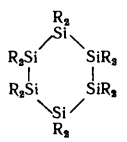
I. HOMOCYCLIC SILICON COMPOUNDS

These homocyclic compounds contain rings formed only from silicon atoms. Derivatives of the following rings have been described:



(I)

Cyclotetrasilanes



(II)

Cyclohexasilanes

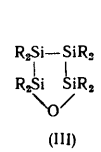
CYCLOTETRASILANES

Only the aryl-substituted cyclotetrasilanes $[R_2Si]_4$, where R = C_6H_5 [6–15] or $CH_3C_6H_4$ [10] have been described. These were obtained by the action of metallic sodium on diaryldichlorosilanes:

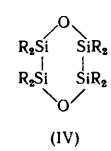
$$4R_2SiCl_2 + 8Na \longrightarrow [R_2Si]_4 + 8NaCl.$$

Two compounds of composition $[(C_6H_5)_2Si]_4$ have been characterised[6–13]. One, the so-called product A, is a chemically unsaturated reactive compound which was therefore originally assigned a linear structure with two "tervalent" silicon atoms. The second compound, product B, was less reactive; Kipping assigned to it structure (I) with R = C_6H_5. However, recent studies have shown that product A is the cyclic tetramer (I) (R = C_6H_5) [14,15], and that product B, to which structure (I) had been incorrectly assigned, is in fact the hexamer (II) (R = C_6H_5).[15–17]

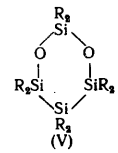
Octaphenylcyclotetrasilane reacts with iodine[6], dichloroethane[6], and mercuric chloride[18], the ring opening to form the diiodo- and dichloro-derivatives of octaphenyltetrasilane respectively, with the structures $Cl[(C_6H_5)_2Si]_4Cl$ and $I[(C_6H_5)_2Si]_4I$; hydrolysis of these gives a compound $(C_6H_5)_8Si_4O$, which has been assigned the cyclic structure (III) (R = C_6H_5).[6,19] Oxidation of octaphenylcyclotetrasilane or compound (III) with nitric acid or moist iodine[6,19] produces a compound of composition $(C_6H_5)Si_4O_2$, which is also formed by dehydration of tetraphenyldisilanediol $HO[(C_6H_5)_2Si]_2OH$,[19] which proves structure (IV) (R = = C_6H_5). Oxidation of octaphenylcyclotetrasilane with nitrobenzene produces another isomeric form of $(C_6H_5)_8.Si_4O_2$, of structure (V) (R = C_6H_5).[6,19]



(III)



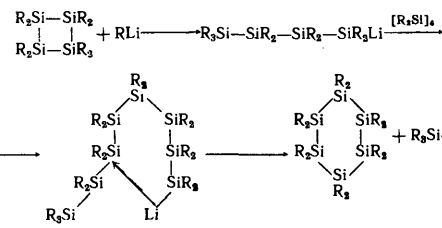
(IV)



(V)

Lithium metal in tetrahydrofuran opens the four-membered ring to form $Li[(C_6H_5)_2Si]_4Li$, in which the lithium can be replaced by methyl groups; this has been used as an indirect proof of the structure of the initial cyclic compound[14,15].

Organometallic compounds also react with $[(C_6H_5)_2Si]_4$; for example phenyllithium gives a mixture of products, from which dodecaphenylcyclohexasilane, a higher cyclosilane, has been isolated[20]:



where R = C_6H_5.

The reaction between octaphenylcyclotetrasilane and triphenylsilyllithium also produces $[(C_6H_5)_2Si]_6$, among other products[20].

Octaphenylcyclotetrasilane is decomposed on heating, giving a very complex mixture of products containing the groups $-(C_6H_5)_2Si-$ and $(C_6H_5)_3Si-$.[21]

Fig. 1 shows the most important reactions of octaphenylcyclotetrasilane.

CYCLOHEXASILANES

Dodecamethyl- [22] and dodecaphenyl-cyclohexasilanes[16,17] have been described.

Dodecamethylcyclohexasilane (II) (R = CH_3) was isolated from the products of the reaction between dimethyldichlorosilane and metallic sodium[22], and its use as an additive for improving the properties of butyl rubber has been patented[23]; it apparently acts as an oxidation inhibitor.

Dodecaphenylcyclohexasilane (II) (R = C_6H_5) was first obtained by Kipping, who erroneously considered it to be the tetramer $[(C_6H_5)_2Si]_4$.[6,8] Gilman and coworkers, who obtained this compound from diphenyldichlorosilane and metallic sodium[16,17], proved that Kipping's product B is not the tetramer, but the cyclic hexamer.

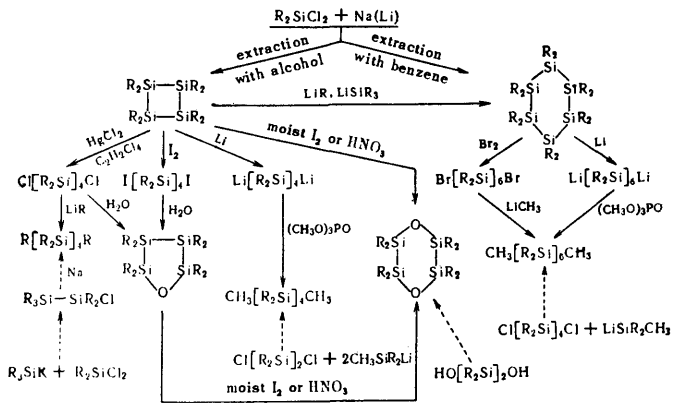


Fig. 1. Reactions of organocyclosilanes (R = C_6H_5).

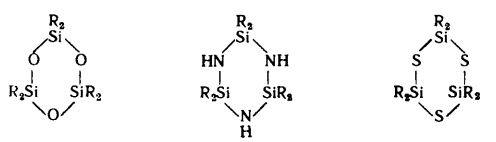
Certain observations have indicated that cyclohexasilanes are more stable than cyclotetrasilanes, since the ring is less strained. Thus unlike the tetramer, the cyclic hexamer does not react with phenyllithium[20] and is not oxidised by nitrobenzene. However, the six-membered ring is opened by lithium in tetrahydrofuran, giving $Li[(C_6H_5)_2Si]_6Li$, and by bromine, giving $Br[(C_6H_5)_2Si]_6Br$.[17]

The reactions and interconversions of cyclosilanes and their derivatives are shown in Fig. 1. The preparation of some of the cyclosilane reaction products by other methods is a proof of their structure.

The production of Si_6H_6 and derivatives thereof has been reported[24], and a cyclic unsaturated structure has been proposed for them, involving conjugated $-Si=Si-$ double bonds in the ring, but this structure requires confirmation, since it is improbable on the basis of existing data.

II. HETEROCYCLIC SILICON COMPOUNDS

Heterocyclic silicon compounds are obtained when some of the silicon atoms in the homocyclic compounds are replaced by other heteroatoms [see formulae (III)–(V)], or when silicon atoms alternate with other elements such as oxygen, nitrogen, sulphur, and selenium around the ring:



These three rings, which are made up of the repeating units SiO, SiN, and SiS, play an important part in the chemistry of inorganic cyclic silicon compounds.

Mixed rings are obtained when some of the silicon atoms in rings made up of identical repeating units are replaced by other elements (for instance phosphorus or boron), or when some of the oxygen in oxygen-containing rings is replaced by nitrogen.

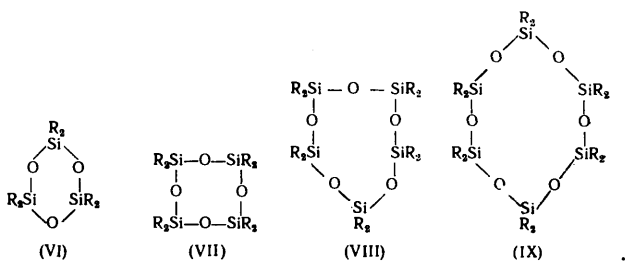
Consequently, three types of inorganic heterocyclic silicon rings are known at present: (a) heterocycles containing the $-Si-Si-$ bond and hetero-atoms; (b) heterocycles with a regular alternation of silicon atoms with atoms of other elements (oxygen, nitrogen, sulphur, or selenium); and (c) mixed heterocycles, containing different structural units.

Heterocyclic compounds of type (a) have been little studied, and what is known of them has been discussed in the preceding section in connection with the reactions of organocyclosilanes. Monomers such as $Cl[R_2Si]_2Cl$ and $Cl[R_2Si]_4Cl$ are known, and it would seem that nitrogen- and sulphur-containing analogues of the oxygen-containing heterocycles already described should be obtainable from these by ammonolysis and thiohydrolysis.

Silicon is an element of low electronegativity, and hence the $-Si-Si-$ bond is sensitive to oxidation, so that rings containing such bonds are relatively unstable. The alternation of silicon atoms with atoms of more electronegative elements in a ring is therefore of great importance, since such rings, containing oxygen, nitrogen, or sulphur in addition to silicon, will be more stable, because the tendency of the silicon towards oxidation will be compensated by the tendency of the electronegative elements towards reduction[5,25]. Another factor is that electronegative elements such as oxygen and nitrogen are electron donors, and their unshared electron pairs may be delocalised in the ring with utilisation of the free *d* orbitals of the silicon atoms, and this will also increase the stability of the ring and will lead to partial aromatic character (see Haiduc's book[5], Chapters XXI and XXII).

1. CYCLOSILOXANES

The structural unit SiO is the basis of a large number of cyclic inorganic and organosilicon compounds, which are known as "cyclosiloxanes". Cyclosiloxanes of the general formula $[R_2SiO]_n$ containing 3–12 SiO groups in the ring have been described:



(VI) (VII) (VIII) (IX)

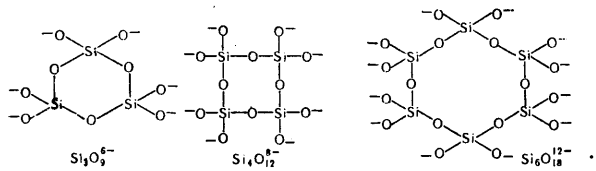
Such rings can contain inorganic groups (R = Cl, Br, OH, or $O^{(-)}$), organic radicals (R = alkyl or aryl), or functional groups (R = alkoxy, aryloxy, alkylamino, arylamino, etc.) as substituents taking up the remaining valencies of the silicon after formation of the ring. Mainly the six- and eight-membered rings have been studied.

Inorganic Derivatives

Several silicates have been shown by X-ray diffraction to contain a cyclic silicate anion; such minerals are usually named cyclosilicates[26]. The six-membered ring Si_3O_3 is contained as the anion $Si_3O_9^{6-}$ in benitoite $BaTi[Si_3O_9]$,[27] wadeite $K_2Zr[Si_3O_9]$,[28] catapleiite $Na_2Zr[Si_3O_9].H_2O$,[29] eudialite $(Na, Ca, Fe)_6Zr[(OH, Cl)(Si_3O_9)_2]$,[30] manganese metasilicate α-$MnSiO_3$,[31] and other minerals[26]. The

eight-membered ring Si_4O_4 is contained as the anion $Si_4O_{12}^{8-}$ in neptunite $Na_2(Fe, Mn)Ti[Si_4O_{12}]$,[32] kainosite $Ca_2(Ce, Y)_2.[(CO_3)(Si_4O_{12})]$,[33] axinite $Ca_2(Fe, Mn)Al_2[(OH)(BO_3)Si_4O_{12}]$,[33] and others. The twelve-membered ring Si_6O_6 is contained as the anion $Si_6O_{18}^{12-}$ in beryl $Be_3Al_2[Si_6O_{18}]$,[34,35] dioptase $Cu_6[Si_6O_{18}].6H_2O$,[35-38] lovozerite $Na_2Zr[Si_6O_{12}(OH)_6]$,[39] and in a number of silicates of the tourmaline group[26].

These cyclic anions have the structures:



The acids corresponding to these anions have not been isolated, because of the great tendency of Si—OH bonds towards condensation, so that polysilicic acids are always obtained as macromolecular compounds. However, the formation of tetrametasilicic acid $Si_4O_4(OH)_8$ (VII) (R = OH) has been observed in the hydrolysis of silicon sulphide[40].

Silicon oxyhalides $[X_2SiO]_n$, where X = Cl or Br and n = 3 or 4, are also cyclic compounds. The oxychloride $Cl_8Si_4O_4$ (octachlorocyclotetrasiloxane) has been obtained by oxidising silicon tetrachloride vapour at an elevated temperature[41-45]. It has recently been shown[46] that this reaction also produces the trimer $Cl_6Si_3O_3$ (VI) (R = Cl) and the pentamer $Cl_{10}Si_5O_5$ (VIII) (R = Cl). The oxidation of silicon tetrabromide at 670°–695° produces the oxybromide $Br_8Si_4O_4$ (octabromocyclotetrasiloxane)[47], together with linear bromosiloxanes of the general formula $Br_{2n+2}Si_nO_{n-1}$.

The hydrocyclosiloxanes $[H_2SiO]_n$, where n = 4, 5, or 6, have been obtained[48]; these (VII, VIII, and IX) (R = H) are the prototypes of the organic derivatives.

Organic Derivatives

This section deals with compounds containing two organic radicals directly attached to each silicon atom, *i.e.* dialkyl-, diaryl-, and alkylaryl-cyclosiloxanes.

In principle, organocyclosiloxanes can be prepared by any reaction in which siloxane bonding is produced. Siloxane bonding is produced by many different types of reaction, which can be classified as follows:

(a) *Reactions of functional derivatives of silicon with substances which can release oxygen.* The oxygen source can be water, metal oxides, ethers, aldehydes, ketones, alcohols, mixtures of alcohols with acids, etc.:

$$2{\equiv}Si{-}X + H_2O \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + 2HX, \quad (1)$$
$$2{\equiv}Si{-}X + MeO \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + MeX_2, \quad (2)$$
$$2{\equiv}Si{-}X + R_2O \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + 2RX, \quad (3)$$
$$2{\equiv}Si{-}X + RCHO \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + RCHX_2, \quad (4)$$
$$2{\equiv}Si{-}X + ROH \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + RX + HX, \quad (5)$$
$$2{\equiv}Si{-}X + ROH + R'COOH \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + R'COOR + 2HX. \quad (6)$$

Of these hydrolysis is the most important reaction.

(b) *Homofunctional condensation reactions.* These usually take place in the presence of catalysts or condensation agents:

$$2{\equiv}Si{-}OH \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + H_2O, \quad (7)$$
$$2{\equiv}Si{-}OR \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + ROR, \quad (8)$$
$$2{\equiv}Si{-}OCOR \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + (RCO)_2O, \quad (9)$$
$$2{\equiv}Si{-}OR + 2R'COOH \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + 2RCOOR' + H_2O. \quad (10)$$

(c) *Heterofunctional condensation reactions.* These normally occur in the presence of catalysts or on heating:

$$\equiv Si{-}X + RO{-}Si{\equiv} \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + RX, \quad (11)$$
$$\equiv Si{-}X + ROCO{-}Si{\equiv} \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + RCOX, \quad (12)$$
$$\equiv Si{-}X + HO{-}Si{\equiv} \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + HX, \quad (13)$$
$$\equiv Si{-}X + MO{-}Si{\equiv} \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + MX\ (M{=}Na, K), \quad (14)$$
$$\equiv Si{-}OR + R'OCO{-}Si{\equiv} \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + ROCOR', \quad (15)$$
$$\equiv Si{-}OR + HO{-}Si{\equiv} \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + ROH, \quad (16)$$
$$\equiv Si{-}NH_2 + HO{-}Si{\equiv} \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + NH_3. \quad (17)$$

(d) *Reactions involving rupture of a siloxane–element bond:*

$$2{\equiv}Si{-}O{-}Q{-} \longrightarrow {\equiv}Si{-}O{-}Si{\equiv} + Q{-}O{-}Q. \quad (18)$$

(e) *Reactions involving rupture of an organo-silicon bond,* under the action of sulphuric acid or other reagents:

$$2{\equiv}Si{-}R \xrightarrow[2.H_2O]{1.H_2SO_4} {\equiv}Si{-}O{-}Si{\equiv} + 2RH. \quad (19)$$

The production of organocyclosiloxanes clearly requires only bifunctional compounds. In addition to cyclic compounds there will also be obtained linear polymers retaining terminal functional groups. Not all of the above reactions have been used in the production of organocyclosiloxanes. Some have simply not yet been sufficiently studied, while others have given only linear polymers. The factors which determine the mode of a reaction and the structure of the products are not yet fully understood, and further study is therefore required.

An interesting case of the production of organocyclosiloxanes is the *depolymerisation of macromolecular linear diorganosiloxanes*, by which the products of any of the above reactions can be converted into organocyclosiloxanes, a feature of the reaction being that the total number and nature of the bonds remain unaltered, the starting materials and products differing only in molecular weight. The reaction involves only the rearrangement or redistribution of the siloxane bonds, the macromolecular polymers being converted into low-molecular-weight cyclic compounds[49-54]:

$$[R_2SiO]_x \longrightarrow y\,[R_2SiO]_n, \quad (20)$$

where $ny = x$. This reaction has been widely used, especially for the preparation of hexaorganocyclotrisiloxanes[55-70].

(a) Reactions of functional derivatives of silicon with substances which can release oxygen. The hydrolysis of functional derivatives of silicon is the most important method for the production of cyclosiloxanes. Organocyclosiloxanes $[R_2SiO]_n$ are formed, together with the linear siloxanes $HO[R_2SiO]_xSiR_2OH$, when bifunctional compounds R_2SiX_2, (where X = halogen, $-OR'$, $-OCOCH_3$, etc.), are hydrolysed [reaction (1)]. Despite the relatively simple structure of the starting materials,

the hydrolysis is a complex process involving two competing reactions:

hydrolysis of Si–X bonds

$$\equiv Si{-}X + H_2O \longrightarrow \equiv Si{-}OH + HX,$$

and condensation

$$\equiv Si{-}OH + HO{-}Si\equiv \longrightarrow \equiv Si{-}O{-}Si\equiv + H_2O,$$
$$\equiv Si{-}OH + X{-}Si\equiv \longrightarrow \equiv Si{-}O{-}Si\equiv + HX.$$

This reaction is more correctly named hydrolytic polycondensation[75].

It should be noted that hydrolysis alone cannot produce cyclic compounds, since the hydrolysis products are dialkyl- (or diaryl-) silanediols. The reaction can be stopped at this stage only if the medium is kept strictly neutral, since traces of acid produce further condensation of the diorganosilanediols with the formation of linear and cyclic organosiloxanes. The formation of rings and linear chains is thus the result of stepwise hydrolytic polycondensation.

The mechanism of formation of organosiloxanes in the hydrolysis reaction has been most studied with diorganodichlorosilanes (and in particular with dimethyldichlorosilane); several intermediates have been isolated. It can be assumed that dialkoxy- and diacetoxy-silanes undergo hydrolysis by an analogous mechanism.

Fig. 2 illustrates the hydrolysis of dialkyldichlorosilanes. Under the influence of protons, the hydrolysis products $R_2SiClOH$ and $R_2Si(OH)_2$ can react with one another and with their reaction products to give various different compounds. Proof of this mechanism is to be found in the hydrolysis of dimethyldichlorosilane under various conditions. Hydrolysis with a deficiency of water (in a homogeneous medium) will produce $\alpha\omega$-dichloroorganosiloxanes (series a_1-a_n); *e.g.* the compounds $Cl[R_2SiO]_{n-1}SiR_2Cl$, where $R = CH_3$ and $n = 1-5$, have been obtained in this way[49,71]. With hydrolysis in a neutral medium (with neutralisation of the hydrogen chloride formed) it is possible to isolate dimethylsilanediol $(CH_3)_2Si(OH)_2$ [72,73] and tetramethyldisiloxanediol $HO(CH_3)_2SiOSi(CH_3)_2OH$.[74] Compounds of series *b*, *i.e.* organochlorosiloxanols, cannot be obtained, because of the impossibility of the simultaneous existence of $\equiv Si-Cl$ and $\equiv Si-OH$ bonds, which immediately condense with the elimination of HCl and the formation of an $\equiv Si-O-Si\equiv$ bond.

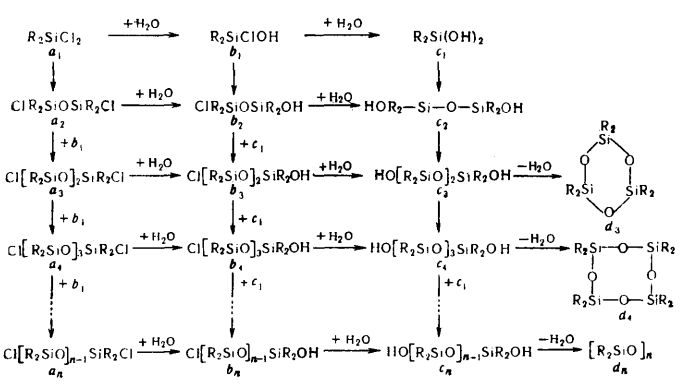


Fig. 2. Hydrolysis of diorganodichlorosilanes.

The chain grows as a result of intermolecular condensation. Cyclisation occurs by intramolecular reactions of this type with chains containing more than three silicon atoms; a proof of this is the condensation of $\alpha\omega$-organosiloxanediols, which gives high yields of cyclic compounds[75]. The monomeric silicone R_2SiO and the cyclic dimer $[R_2SiO]_2$ have not been isolated, although species of mass corresponding to $(CH_3)_2SiO$ and $(C_2H_5)_2SiO$ have been observed by mass spectrometry[76].

The factors which determine the course of hydrolysis have been little studied, but it is known that the composition of the reaction products depends greatly on the nature of the organic radical and the functional groups of the initial monomer, and on the temperature, concentration, and pH of the medium[75].

The organic radicals determine the size of the rings formed: the hydrolysis of dimethyldichlorosilane produces 6-, 8-, 10-, and 12–18-membered rings, the ethyl compound and certain other diorganodichlorosilanes produce 6-, 8-, 10-, and 12-membered rings, while many diorganodichlorosilanes produce only 6- and 8-membered rings. This may be due to the steric effect of the organic radical.

The functional groups of the monomer determine the rate of hydrolysis, since different groups have different reactivities. The following order of reactivity in hydrolysis reactions has been established[75]:

$$-Cl \geqslant -OCOR > -OR,$$

in accordance with the change in electronegativity of these groups.

The composition of the reaction products also depends on the concentration and on the nature of the solvent used. A decrease of concentration increases the formation of cyclic compounds and reduces the yield of linear products. The nature of the solvent also affects the reaction[77]; thus the hydrolysis of diethyldichlorosilane in ether gives 41% of the trimer $[(C_2H_5)_2SiO]_3$ and 31% of the tetramer $[(C_2H_5)_2SiO]_4$,[78] while hydrolysis in methanol produces the cyclic tetramer in 70% yield[70]. In general, water-miscible solvents increase the yield of cyclic compounds.

The acidity of the medium has a large effect on the composition of the hydrolysis products. As already mentioned, diorganosilanediols can be isolated from a netural medium, while an acid medium favours condensation, especially the formation of low-molecular-weight cyclic organosiloxanes. An alkaline medium prevents ring-formation to a considerable extent. It is of interest here that the hydrolysis of diorganodichlorosilanes by aqueous solutions of metal salts also gives large amounts of cyclic siloxanes[80].

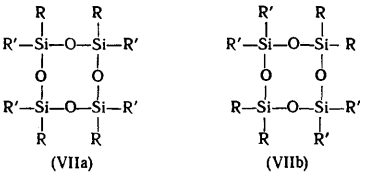
Hydrolysis of the corresponding diorganodichlorosilanes has provided the following cyclosiloxane derivatives of general formula $[R_2SiO]_n$, the substituent radicals being dimethyl ($n = 3-9$)[49,77,81-85], hydrogen and methyl ($n = 4-6$)[86-89], diethyl ($n = 3-5$)[78,90-93], hydrogen and ethyl ($n = 3-5$)[94,95], methyl and ethyl ($n = 3-6$)[96,97], methyl and butyl ($n = 3-5$)[97], methyl and trifluoropropyl ($n = 3$)[98], methyl and trifluorobutyl ($n = 4$)[99], methyl and vinyl ($n = 4$ and 6)[100], ethyl and vinyl ($n = 3$)[101], diphenyl ($n = 3$ and 4)[82,102,103], methyl and phenyl ($n = 3$ and 4)[90,104,105], di-(chlorophenyl) ($n = 3$ and 4)[106], methyl and chlorophenyl ($n = 3$ and 4)[107,108], ethyl and phenyl ($n = 3$ and 4)[82,90], ethyl and benzyl ($n = 3$)[109], spiropentamethylene ($n \leqslant 5$)[110], and others[82,97,111-121].

The hydrolysis of the $\alpha\omega$-dichloroorganosiloxanes $Cl[R_2SiO]_{n-1}SiR_2Cl$ (where R = CH_3 and C_2H_5) has also been studied[122]; this produces cyclic compounds with n, $2n$, $3n$, ... siloxane groups in the ring.

The hydrolysis of dialkyl(or aryl)dialkoxysilanes has also produced cyclosiloxanes: dimethyl (n = 3–12)[123-129], methyl vinyl (n = 4–6)[130-132], methyl chlorophenyl (n = = 3)[133], ethyl vinyl (n = 3)[101], tetramethylbisferrocenyl[134], and others[135]. The hydrolysis of alkoxysilanes even with a deficiency of water yields cyclic compounds in addition to the linear organodialkoxysiloxanes $RO[R_2SiO]_{n-1}SiR_2OR$.[136]

The hydrolysis of methylhexynyldiacetoxysilane with water has given tetra-(methylhexynyl)cyclotetrasiloxane $[CH_3(CH_2)_3C\equiv C-Si(CH_3)O]_4$.[137]

The organocyclosiloxanes so far described have identical repeating units in the ring. The simultaneous hydrolysis of two (or sometimes more) bifunctional monomers gives cyclic compounds containing different units in the ring (*i.e.* differently substituted units). Simultaneous hydrolysis is thus a method for the production of organocyclosiloxane isomers differing in the positions of the organic radicals around the ring, *e.g.*:



(VIIa)

(VIIb)

A compound (VIIa) is produced by the simple hydrolysis of a monomer $RR'SiX_2$, and a compound (VIIb) by the simultaneous hydrolysis of two monomers R_2SiX_2 and R'_2SiX_2. Dimethyldichlorosilane has been cohydrolysed with H_2SiCl_2,[138] CH_3SiHCl_2,[139,140] $CH_3(CH_2=CH)SiCl_2$,[141-143] $C_2H_5(CH_2=CH)SiCl_2$,[142,143] $(C_6H_5)_2SiCl_2$,[144] $C_6H_5(CH_3)$. $.SiCl_2$,[144,145] $ClC_6H_4(CH_3)SiCl_2$,[144,145] and $C_6H_5(CH_3)Si$. $.(OC_2H_5)_2$;[146] other cohydrolysis reactions have also been described[90,135,140,142,143,147,148].

In the reaction of organodichlorosilanes with metal oxides [reaction (2)] the oxide oxygen is used to form the siloxane bond; for example, the reaction between dibenzyldichlorosilane and mercuric oxide produces the trimer $[R_2SiO]_3$.[149] Oxides of copper, zinc, beryllium, magnesium, silver, cadmium, and lead have been used[150-152]. With a deficiency of metal oxide, acyclic organohalogenosiloxanes are formed[153]. The reaction between dimethyldichlorosilane and ferric oxide also does not produce cyclic compounds, and only 1,3-dichlorotetramethyldisiloxane is formed[154,155].

In general, this interesting type of reaction has been insufficiently studied, and it is still not clear why the mode of the reaction varies with the metal used as the oxide.

Metal salts may be used in place of the oxides[152,156]; thus diethyldichlorosilane with $NaHCO_3$ yields the trimer $[(C_2H_5)_2SiO]_3$.[156]

Organohalogenosilanes react with ethers to form cyclosiloxanes [reaction (3)]. Dimethyldibromosilane and ethyl ether give $[(CH_3)_2SiO]_4$ and ethyl bromide[157]. At 200° and under pressure dimethyldichlorosilane reacts with dimethyl ether in the presence of $AlCl_3$ to give a silicone oil which contains the trimer $[(CH_3)_2SiO]_3$.[158]

The reaction between chlorosilanes and aldehydes [reaction (4)] has been used to prepare silicon oxychlorides[159]. Alkylalkoxysilanes react with aldehydes to form organocyclosiloxanes[160]. Acetone reacts with diphenyldichlorosilane to yield cyclosiloxanes; the reaction mechanism is not clear[161,162]. Dimethylformamide also reacts with organochlorosilanes to give linear and cyclic siloxanes[163,164]. In all these cases the organochlorosilane splits off and combines with the carbonyl oxygen.

The reaction of chlorosilanes with alcohols normally produces alkoxysilanes, but siloxanes are formed in a side-reaction [by reaction (5)], particularly with methyl[165,166] and t-butyl alcohols[167,168]. The yield of cyclic organosiloxanes is very low, since the reaction proceeds effectively the whole time with a deficiency of water, which is produced by the reaction of the alcohol with hydrogen chloride.

Reaction (6) is actually a disguised hydrolysis reaction, since it takes place by virtue of the water liberated; it produces mainly linear polymers. The yield of cyclic organosiloxanes when dimethyldichlorosilane is reacted with a mixture of methanol and acetic acid, is less than 10%.[169]

(b) Homofunctional condensation reactions. The condensation of organosilanols [reaction (7)] is one of the competing reactions in the hydrolysis of bifunctional organosilanes, since in some cases organosilanols can be isolated during the hydrolysis. The condensation of diphenylsilanediol in alcohol or acetic anhydride produces the cyclic trimer $[(C_6H_5)_2SiO]_3$, which was the first organocyclosiloxane to be identified[170]. Other reactions of this type have been described[102,106,111,171-179].

Condensation with ring-formation has been especially studied with siloxanediols $HO[R_2SiO]_nH$, which give mainly cyclic compounds containing $2n$, $3n$ ... R_2SiO groups in the ring when $n \geq 2$ or even when $n \geq 3$.[75]

The condensation of organosilanols is favoured by heat and the catalytic action of acids or bases. It is interesting that the condensation of $(C_6H_5)_2Si(OH)_2$ produces the tetramer $[(C_6H_5)_2SiO]_4$ in the presence of alkalis[180,181], but the trimer in the presence of acids or alcohols[181]. The condensation of organosilanediols by the action of ion-exchange resins has been described: diethylsilanediol yields a mixture of the trimer and the tetramer[182].

The homocondensation of alkoxysilanes to form siloxanes [reaction (8)] is carried out by heating under pressure in the presence of catalysts (AlX_3, BX_3). Diethyldiethoxysilane gives linear alkoxysiloxanes and the cyclic trimer[183].

Organic acids and their anhydrides can be used as condensation agents for alkoxysilanes[184-186] [reaction (10)]: thus dimethyldiethoxysilane reacts readily with acetic anhydride or acetic acid to give linear and cyclic organosiloxanes. The mechanism here is more complex, and includes heterofunctional condensation reactions between alkoxysilanes and acetoxysilanes[187].

The homocondensation of acyloxysilanes, *e.g.* diacetoxydiorganosilanes [reaction (9)], is carried out by heating above 200°, and gives liquid organosiloxanes[188]; the reaction products were not fully investigated.

(c) Heterofunctional condensation reactions. These are reactions between two monomers having different functional groups attached to silicon atoms;

a siloxane bond is formed, with elimination of a secondary reaction product [reactions (11)–(17)].

Organohalogenosilanes react with alkoxysilanes [reaction (11)] on heating in the presence of a Friedel–Crafts catalyst; generally the products are linear organosiloxanes containing the functional groups. With an exactly equimolar mixture of R_2SiCl_2 and $R_2Si(OR)_2$ (R = C_2H_5) and in the presence of $AlCl_3$, the main products are organocyclosiloxanes[183]. Excess of chloro- or alkoxy-silane produces the linear $\alpha\omega$-dichloro- or $\alpha\omega$-dialkoxy-siloxane. When R = CH_3, a polymer is formed[189]. Heating $(CH_3)_2.Si(OCH_3)_2$ at 80° in the presence of $FeCl_3$ yields a mixture of linear and cyclic siloxanes[190].

The reaction of organohalogenosilanes with acyloxysilanes, in particular with acetoxysilanes [reaction (12)] leads predominantly to the formation of linear siloxanes[191].

The reaction between organohalogenosilanes and organosilanols [reaction (13)] is one of the steps in hydrolytic polycondensation, and produces cyclic and linear polymers. The reaction of dimethyldichlorosilane with tetramethyldisiloxane-1,3-diol gives a polydimethylsiloxane[192].

Reaction (14) has been used for the preparation of organocyclosiloxanes containing functional groups, and is dealt with below.

Alkoxysilanes react with acyloxysilanes [reaction (15)] on heating in the presence of alkaline or acid catalysts. The reaction is not of great interest for the production of cyclic compounds, since it gives mainly linear polymers[191,193].

The reaction of alkoxysilanes with organosilanediols [reaction (16)] takes place in the presence of alkaline or acidic catalysts, *e.g.* sodium silanolates, and can be used for the preparation of cyclic compounds. The reaction of $(CH_3)_2.Si(OC_2H_5)_2$ with $(t\text{-}C_4H_9)_2Si(OH)_2$ in the presence of H_2SO_4 produces the cyclotetrasiloxane $(t\text{-}C_4H_9)_4(CH_3)_4Si_4O_4$.[194] The following reactions have also been carried out[194]:

$$(C_6H_5)_2Si(OH)_2+C_2H_5O(CH_3)_2SiOSi(CH_3)_2OC_2H_5 \xrightarrow{-C_2H_5OH} (C_6H_5)_2(CH_3)_4Si_3O_3,$$

$$2(C_6H_5)_2Si(OH)_2+2(CH_3)_2Si(OC_2H_5)_2 \xrightarrow{-C_2H_5OH} (CH_3)_4(C_6H_5)_4Si_4O_4.$$

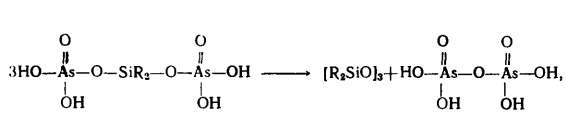
Aminosilanes also react with organosilanols to form the siloxane bond [reaction (17)]. The formation of linear and cyclic organosiloxanes[195] has been demonstrated in the reaction of $(CH_3)_2Si[N(C_2H_5)_2]_2$ with hexamethyltrisiloxane-1,5-diol.

(d) Reactions involving rupture of a siloxane – element bond [reaction (18)] can occur hydrolytically or by disproportionation on heating, and can also produce cyclosiloxanes, *e.g.*[196,197]:

$$(R_2SiClO)_3B \xrightarrow{160°} [R_2SiO]_3+R_2SiCl_2+B_2O_3,$$

where R = CH_3.

The formation of cyclosiloxanes has also been observed in the disproportionation of arsenatosiloxanes[198]:



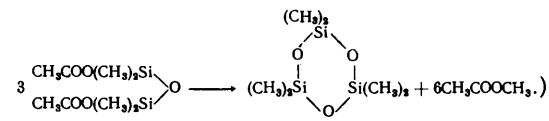
where R = C_6H_5.

The Si–O–Pb, Si–O–Mg, Si–O–Cu, and Si–O–Hg bonds are also readily broken, with the formation of cyclosiloxanes[199].

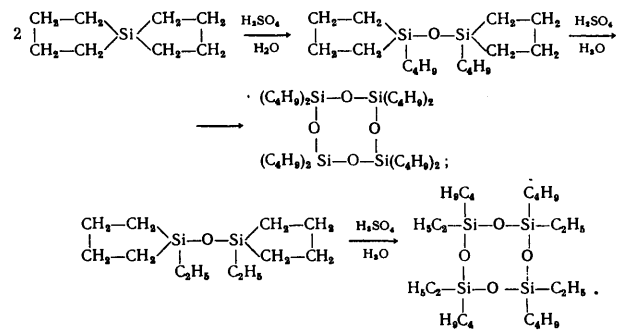
(e) Reactions involving rupture of an organo-silicon bond generally proceed under the action of concentrated sulphuric acid and water, forming the hydrocarbon and a siloxane bond. The first stage of the reaction is the formation of silyl sulphates, which are then hydrolysed by the water. The trimethylsilyl group may thus be converted into the dimethylsiloxane group[200]:

$$(CH_3)_3Si- \xrightarrow[2.H_2O]{1.H_2SO_4} \frac{1}{n}[-(CH_3)_2Si-O-]_n+CH_4.$$

(These elimination reactions are typical of a series of compounds containing functional groups in the organic radical, *e.g.* [201]:



An interesting use of this reaction is the conversion of cyclic silicon-containing hydrocarbons into cyclosiloxanes[202]:



Phenyl groups are more easily removed from silicon atoms than alkyl groups. Di-(cyclohexyl)phenylsilanol gives a cyclic trimer on heating with HCl or HNO_3 in acetic acid[111]:

$$3C_6H_5(C_6H_{11})_2SiOH \longrightarrow [(C_6H_{11})_2SiO]_3+3C_6H_6.$$

Bromine in acetic acid produces a mixture of the same trimer together with the tetramer[111].

Physical Properties of Organocyclosiloxanes

In addition to such physical properties as melting and boiling point, density and refractive index, other physical properties of certain organocyclosiloxanes, in particular the dimethyl derivatives, have been determined. Thus data have been given on viscosity[203–209], compressibility[209–211], surface tension[212], and molecular volume[203]. Thermodynamic characteristics have been evaluated: heats of formation[213–217], equation of state[218], thermal expansion[203], vapour pressure[204,218–220], heats of evaporation[203,218,220], heats of fusion and sublimation and entropy[218,219,221], and cryoscopic constants[218,221–223]. Dielectric constants[224–226], dipole moments[224,227,228], and magnetic properties[229] have been determined. Organocyclosiloxanes have been quite widely studied spectroscopically. Infrared spectra have

been recorded for dimethylcyclosiloxanes[90,230,231], diethylcyclosiloxanes[90], diphenylcyclosiloxanes[90,232,233], other cyclosiloxanes containing organic radicals[90,234-236], and cyclic silicates[237,238]. It has been shown that the absorption band at 1020 cm^{-1} corresponds to the six-membered ring, and the band at 1060–1080 cm^{-1} to the eight-membered ring. The Raman spectra of dimethyl-[230,231,239-241], diethyl-[242], and other cyclo-siloxanes[233,242,243], have been investigated. The ultraviolet[244] and nuclear magnetic resonance spectra[245-248] of certain organocyclosiloxanes have been described.

Structure of the Organocyclosiloxanes

The structure of the dimethylcyclosiloxanes has been investigated by electron diffraction[249-253] and X-ray diffraction[254-258] methods.

The six-membered Si_3O_3 rings in the trimer $[(CH_3)_2SiO]_3$ is planar. The Si–O bond distance of 1.614 Å is considerably less than the sum of the covalent radii of oxygen and silicon, demonstrating delocalisation of the oxygen π electrons because of the 3*d* orbitals of the silicon, with partial aromatisation[5]. The bond angles[256] $\angle$ OSiO = 104° and $\angle$ SiOSi = 136° in the planar ring indicate that the ring is somewhat strained, which is shown in the greater reactivity of the cyclotrisiloxanes as compared with their cyclosiloxane homologues.

The eight-membered Si_4O_4 ring in the tetramer $[(CH_3)_2.SiO]_4$ is not planar, and has the "chair" configuration. The Si–O distance of 1.65 Å [257] also indicates delocalisation of π electrons with $d_\pi - p_\pi$ conjugation[5,259]. The bond angles are $\angle$ SiOSi = 142.5° and $\angle$ OSiO = 109°.

Chemical Properties of Organocyclosiloxanes

The cyclosiloxane derivatives are very reactive. They can react with retention of the ring (substitution reactions), breakdown of the ring (production of monomers), or opening of the ring (production of oligomers, telomers, and polymers). Cyclosiloxanes are not very reactive in homolytic reactions, and are very stable from this point of view, but, because of the polarity of the Si–O bonds in the rings, they can undergo many diverse heterolytic reactions, and their reactions with electrophilic and nucleophilic reagents are very widely used for the preparation of various types of silicon compounds.

The composition of the reaction products of cyclosiloxanes with various reagents depends on the relative proportions of reactants used. The same reagent, *e.g.* NaOH, can produce monomers or oligomers or can lead to polymerisation of the cyclosiloxane. The reaction mechanism is the same, but the products will differ, depending on the relative quantities of NaOH and cyclosiloxane used and on the reaction conditions.

Reactions involving breakdown of the ring. If sufficient reactant is taken to react with all the Si–O bonds of the cyclosiloxane, the products will be monomers, *i.e.* compounds containing only one silicon atom per molecule. Thus the reaction between NaOH and a cyclosiloxane taken in the molar ratio NaOH : $[R_2SiO]_n$ = = 2*n* : 1 (where *n* is the number of SiO groups in the ring) produces the monomers $R_2Si(ONa)_2$. Acids, for instance HCl and HF, also decompose the siloxane ring; thus HF converts $[(C_2H_5)_2SiO]_3$ into $(C_2H_5)_2SiF_2$.[260] Lithium aluminium hydride reduces organocyclosiloxanes to diorganosilanes[261]:

$$2\,[R_2SiO]_n + n\,LiAlH_4 \longrightarrow 2n\,R_2SiH_2 + n\,LiAlO_2,$$

where R = CH_3.

Organomagnesium compounds produce triorganosilanols after hydrolysis of the intermediates[262,263]:

$$1/n\,[R_2SiO]_n + RMgI \longrightarrow R_2SiOMgI \xrightarrow{H_2O} R_2SiOH + MgIOH.$$

Boron halides react with organocyclosiloxanes to form compounds containing the Si–O–B bond; these disproportionate to the diorganodihalogenosilane and B_2O_3.[196,197] The stereochemical influence of the organic radicals and the size of the ring have been studied: the larger the organic radical and the greater the number of SiO units in the ring, the more hindered is the reaction, because of the difficulty of approach of the reactant to the ring oxygen atoms.

Aluminium halides also break down the ring, but only half the silicon appears as a chloro-derivative; the remainder forms aluminosiloxanes[264]; $[(C_6H_5)_2SiO]_3$ produces $SiCl_4$.[265]

Organocyclosiloxanes are also converted into dialkyldichlorosilanes by the action of $SiCl_4$ at 250° under pressure; *e.g.* with sufficient $SiCl_4$ $[(CH_3)_2SiO]_4$ gives $(CH_3)_2.SiCl_2$.[266]

Under certain conditions alkylhalogenosilanes also decompose cyclosiloxanes in the presence of ferric chloride; *e.g.* alkylbromo- and alkyliodo-silanes react at the boiling point[267]:

$$[(CH_3)_2SiO]_4 + 8\,(C_2H_5)_3SiBr \xrightarrow{FeCl_3} 4\,(CH_3)_2SiBr_2 + 4\,(C_2H_5)_3SiOSi(C_2H_5)_3.$$

Alkylchlorosilanes decompose cyclosiloxanes only under pressure.

An interesting reaction is the decomposition of organocyclosiloxanes by alcohols or phenols in the presence of 1–10 mole % of sodium hydroxide, alkoxide, or silanolate[268-273]:

$$1/n\,[R_2SiO]_n + 2R'OH \overset{\text{catalyst}}{\rightleftharpoons} R_2Si(OR')_2 + H_2O,$$

where *n* = 3, 4, or 5, and R = alkyl or aryl. The water formed must be removed by azeotropic distillation, or, preferably, by using a dehydrating agent such as $Si(OC_2H_5)_4$.

A special case of this reaction is the decomposition of cyclosiloxanes by alkoxysilanes[269,270,271] in the presence of KOH:

$$2\,[R_2SiO]_n + n\,Si(OC_2H_5)_4 \xrightarrow{KOH} 2n\,R_2Si(OC_2H_5)_2 + n\,SiO_2 \quad (n \geqslant 3),$$

$$1/n\,[R_2SiO]_n + 2R''_3SiOR' \xrightarrow{KOH} R_2Si(OR')_2 + R''_3SiOSiR''_3.$$

The ease of catalytic decomposition of organocyclosiloxanes by alkoxysilanes decreases in the series[272]:

$$[R_2SiO]_3 > [R_2SiO]_4 > [R_2SiO]_{n+3} > R_3Si[OSiR_2]_nR \quad (n \geqslant 2).$$

A similar reaction is the disproportionation of alkoxycyclosiloxanes in the presence of KOH:[269,270,272]

$$2\,[(RO)_2SiO]_n \xrightarrow{KOH} n\,Si(OR)_4 + n\,SiO_2.$$

Organocyclosiloxanes react with butyl titanate[274] to form dialkoxysilanes and a polymer containing the Si–O–Ti linkage:

$$[R_2SiO]_4 + Ti(OC_4H_9)_4 \xrightarrow{180°} R_2Si(OC_2H_5)_2 + C_4H_9OSiR_2OSiOSiR_2OC_4H_9 + \text{polymer}.$$

Ring opening with the formation of oligomers. Particular interest attaches to the cleavage of only one siloxane bond of cyclosiloxanes, which produces linear oligomers; thus the action of sodium or potassium hydroxide on organocyclosiloxanes converts them into oligomers containing the same number of silicon atoms[275]:

$$[(C_6H_5)_2SiO]_{3,4} \xrightarrow{+NaOH,3\%} NaO[(C_6H_5)_2SiO]_{3,4}Na \xrightarrow{CH_3COOH} HO[(C_6H_5)_2SiO]_{3,4}H.$$

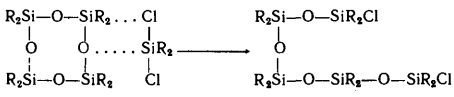
Certain organometallic compounds react similarly[276]:

$$[R_2SiO]_4 + AlR'_3 \longrightarrow R'[R_2SiO]_4AlR'_2.$$

At a high temperature and under pressure diorganodihalogenosilanes also give oligomers[277]:

$$[R_2SiO]_n + R_2SiCl_2 \xrightarrow{380^\circ-400^\circ} Cl[R_2SiO]_nSiR_2Cl \quad (n = 3-6).$$

Ring opening with the formation of telomers. An interesting case of siloxane ring opening with increase of the siloxane chain length is telomerisation; thus at a high temperature (250°–300°) and under pressure organocyclosiloxanes react with dialkyldichlorosilanes to give a series of $\alpha\omega$-dichlorosiloxanes containing $an + 1$ silicon atoms, where n is the number of silicon atoms in the initial ring, and $a = 1, 2, 3 \ldots$. The reaction can be considered to proceed as follows. The first stage is the opening of the ring with the formation of an $\alpha\omega$-dichlorosiloxane containing $n + 1$ silicon atoms[278]:



Under the reaction conditions the $\alpha\omega$-dichlorosiloxane reacts with a second cyclosiloxane molecule, and the chain increases in length by n SiO units. This method has been used to obtain $\alpha\omega$-dichlorosiloxanes $Cl[R_2SiO]_nSiR_2Cl$ with $n = 3$, 6, and 9, and R = CH_3 and C_2H_5 by ring opening of $[R_2SiO]_3$,[279] and $Cl[R_2SiO]_nSiR_2Cl$ with $n = 4$, 8, 12 ... and R = CH_3, C_2H_5, etc. by ring opening of $[R_2SiO]_4$.[278,280] Ring opening of cyclosiloxanes with trialkylchlorosilanes yields oligomers containing the R_3Si group at one end of the chain[281].

A similar telomerisation reaction is that between titanium tetrachloride and organocyclosiloxanes[282], to produce compounds $Cl[R_2SiO]_nTiCl_3$, where $n = 4$, 8, etc.

According to patent data, dimethylsiloxane-$\alpha\omega$-diols $HO[(CH_3)_2SiO]_nH$ (where n has average values of 5.5, 10.4, and 18.1) are produced by the action of water under pressure on hexamethylcyclotrisiloxane[283].

Rearrangement reactions. Mixtures of organocyclosiloxanes with organodisiloxanes react in the presence of alkali metal hydroxides, acids, silanolates, or other compounds (quaternary ammonium and phosphonium bases, etc.) as catalysts, with rearrangement of the siloxane bonds and formation of linear organosiloxanes with terminal R_3SiO groups[49,284-291]:

$$n[R_2SiO]_4 + R_3SiOSiR_3 \xrightarrow{catalyst} R_3SiO[SiR_2O]_{4n}SiR_3.$$

The reaction of an organocyclosiloxane with an organodisiloxane produces linear polymers $R_3SiO[R_2SiO]_{an}SiR_3$, where n is the number of SiO groups in the initial ring, and a is 1, 2, or 3.[285] This reaction is widely used for the production of liquid organosiloxanes. Many examples of this catalytic rearrangement have been described, *e.g.* the reaction of $[(CH_3)_2SiO]_4$ with $(CH_3)_3SiOSi(CH_3)_3$,[49,284-291] $[(C_6H_5)_2(CH_2=CH)Si]_2O$,[292] $[(C_6H_5)(CH_3)_2Si]_2O$,[293] and $[(CH_3)_2SiO]_2SO_4$,[294] the reaction of $[(CH_3)_2SiO]_3$ with $[ClCH_2(CH_3)_2Si]_2O$,[295,296] of $[(CH_3)_2SiO]_4$ with $[(C_2H_5)_3Si]_2O$,[297] and others[138,298].

Kinetic studies have shown[286] that the ability of organosiloxanes to rearrange in the presence of acid catalysts decreases in the series:

$$[R_2SiO]_3 > R_3SiOSiR_3 > R_3Si[OSiR_2]OSiR_3 > R_3Si[OSiR_2]_2OSiR_3 > [R_2SiO]_4.$$

With alkaline catalysts the order changes:

$$[R_2SiO]_3 > [R_2SiO]_4 > R_3Si[OSiR_2]_2OSiR_3 > R_3Si[OSiR_2]OSiR_3 > R_3SiOSiR_3.$$

The rearrangement reaction is of particular interest for the production of linear siloxane oligomers containing substituted hydrocarbon end-groups: organocyclosiloxanes and a symmetrical disiloxane are used:

$$a[R_2SiO]_n + ZR_2SiOSiR_2Z \xrightarrow{catalyst} \Phi R_2Si[OSiR_2]_{an}OSiR_2Z,$$

where Z is a substituted hydrocarbon group, $a = 1$, 2, 3 ..., and n is the number of SiO groups in the initial ring. This method has given siloxane oligomers having the following terminal groups:

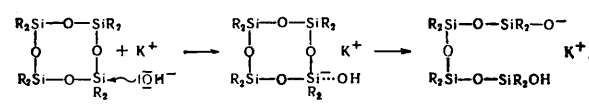
$C_2H_5OCOCH_2CH_2(CH_3)_2SiO$,[299,300]
$HOOC(CH_2)_4OCOCH_2(CH_3)_2SiO$,[301]
$2\text{-}C_5H_4NCH_2CH_2(CH_3)_2SiO$,[302]
$2\text{-}C_5H_5NCH_2CH_2(CH_3)_2SiO$,[303]
$Cl_2C_6H_3OCOCH_2(CH_3)_2SiO$,[304]
$Cl_5C_6OCH_2(CH_3)_2SiO$,[305]
$Cl_5C_6SCH_2(CH_3)_2SiO$,[306]
$Cl_2C_6H_3OCH_2OCOCH_2(CH_3)_2SiO$,[307]
$HOC_6H_4OCOCH_2(CH_3)_2SiO$,[308]
$CH_3OCO(CH_2)_3(CH_3)_2SiO$,[309]
$CH_3OCO(CH_2)_4(CH_3)_2SiO$,[309,310]

and others[311-315].

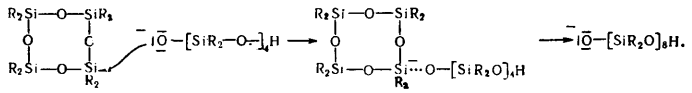
Ring opening with the formation of polymers. Attention is directed to the following features of some of the reactions described above: (*a*) agents such as alkalis and acids can open the siloxane ring; and (*b*) the initial products of ring opening can themselves open further siloxane rings, with growth of the chain. The mechanism of polymerisation of organocyclosiloxanes under the catalytic action of alkalis, acids, or other agents can thus be understood. The mechanism is general for a number of types of reaction, but the nature of the final product depends on the amount of ring-opening agent used. Catalytic amounts cause polymerisation by continuous chain growth as the result of reaction between the active end-groups and cyclic molecules before equilibrium is reached.

Organocyclosiloxanes can be polymerised by nucleophilic reagents (alkalis, alkoxides, etc.) or by electrophilic reagents (acids, boron halides, aluminium halides, etc.).

The mechanism of polymerisation by alkaline catalysts can be represented as follows. In the first step a hydroxy-group coordinates with a silicon atom by virtue of its free 3*d* orbital, and this produces a redistribution of electron density and opening of the ring:



The anionic end of the linear organosiloxane chain then attaches itself to a silicon atom of another cyclic molecule, and this produces redistribution of electron density and ring opening as before, with growth of the chain[316-321]:

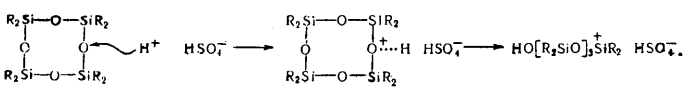


The process continues in this way until equilibrium is reached. The equilibrium mixture obtained in the polymerisation of $[(CH_3)_2SiO]_4$ by the action of potassium hydroxide contains ~ 94% of macromolecular polymer and 6% of unreacted cyclosiloxane[317]. This reaction is the basis of the production of dimethylsilicone rubbers, and many examples of the reaction have been investigated[361].

Kinetic studies have shown[316] that the catalytic activity of aqueous alkali metal hydroxides falls in the series CsOH > KOH > NaOH > LiOH, and of alcoholic hydroxides in the series RbOH > CsOH > $(CH_3)_4NOCH_3$ > KOH. In addition to alkali metal hydroxides[141,316-335], sodium or potassium silanolates[143,323,325,330,336-339], quaternary ammonium or phosphonium bases[330,337,340-344], potassamide[345], or alkali metal alcoholates[346] can be used as catalysts.

The ability of organocyclosiloxanes to undergo polymerisation depends on the number of siloxane groups in the ring and on the organic radicals present. Six-membered rings are the most easily polymerised; the tendency towards polymerisation decreases with increase of the number of SiO groups in the ring[75,347] and with increase in the size of the organic radical.

Electrophilic reagents react differently from nucleophilic reagents, *e.g.*[145]:



There is thus stepwise polymerisation. It has been considered[49,348,349] that a later step is the heterofunctional condensation between ≡Si—OH and ≡Si—OSO_3H groups under the action of protons. It is easy to see that polycondensation can hardly produce polymers of molecular weight as high as 10^6 in short reaction times. The reactivity of the rings depends on the number of SiO groups present: six-membered rings polymerise more readily than eight-membered rings. Increase in the size of the organic radical and the presence of electronegative groups also decrease the ability of the compound to polymerise[141,145,335].

The polymerisation of $[(CH_3)_2SiO]_4$ under the action of H_2SO_4 is a second-order reaction with respect to the cyclosiloxane[348]; the velocity constant is proportional to the acid concentration, and the energy of activation is 12.7 kcal mole^{-1}.

Various acids have been used for the polymerisation: sulphuric[49,326,327,334,348,350,351], nitric[348], hydrochloric[348], phosphoric[348,351], pyrophosphoric[348,352], and redox systems[353-357]. Acid-activated clays also show catalytic activity[358-360]. Organic acids, even those as strong as oxalic, trichloroacetic, and perfluorobutyric, do not polymerise $[(CH_3)_2SiO]_4$.[348] Since the first step in the opening of the cyclosiloxane ring is the coordination of the acceptor (a proton in the case of protic acids) at the siloxane oxygen, other electron acceptors (Lewis acids) can be used as catalysts: $SnCl_4$,[362] $FeCl_3$,[351,363] $AlCl_3$ + Fe_2O_3,[364] BF_3,[365] $ZnCl_2$,[365] and $Al_2(SO_4)_3.2H_2O$.[351,366-368]

Patents[369-371] have shown the possibility of thermal polymerisation of organocyclosiloxanes under pressure at elevated temperatures (250°–300°); however, octamethylcyclotetrasiloxane does not polymerise at a pressure of 6000 atm in quartz ampoules (in the absence of catalysts)[348]. The simultaneous use of pressure and alkaline or acid catalysts decreases the time required for polymerisation[372,373].

Other methods of polymerisation are the elimination of organic radicals from the silicon atoms, *e.g.* the polymerisation of $[(C_2H_5)(C_6H_5)SiO]_3$ under the action of acids with elimination of C_6H_6 and formation of a polycyclic linear monomer[374-376], or the thermal oxidation of the organic radicals, *e.g.* the polymerisation of $[(C_2H_5)(C_6H_5).SiO]_3$[377] or $[(CH_3)_2SiO]_3$[82] by treatment with a stream of oxygen at elevated temperatures.

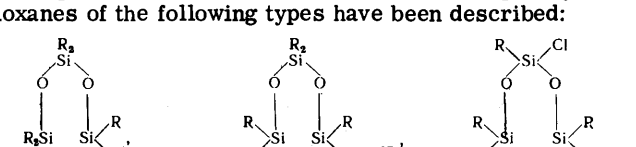
Irradiation also causes polymerisation of organocyclosiloxanes, apparently with retention of the ring and formation of $-CH_2CH_2-$ or $-CH_2-$ bridges between the silicon atoms of different rings[378-383].

Attention is directed to the very much more rapid polymerisation of $[(CH_3)_2SiO]_3$ near its melting point than at higher or lower temperatures[384-386].

Copolymerisation of rings in the presence of electrophilic or nucleophilic catalysts is used to improve the properties of siloxane polymers by the introduction of different radicals. $[(CH_3)_2SiO]_4$ has been copolymerised with the cyclosiloxanes $[H_2SiO]_5$,[48] $[(C_6H_5)_2SiO]_4$,[330,387-389] $[CH_3(CH_2=CH)SiO]_{4.5}$,[130,132,330,390] $[RR'SiO]_n$ (where $n \geq 3$ and R and R′ = CH_3, C_2H_5, or C_6H_5)[341], $[(C_2H_5)_2SiO]_3$,[391] $[(C_2H_5)_2SiO]_4$,[392] $(CH_2=CH)_2(C_2H_5)_4Si_3O_3$,[143] $(CH_2=CH).(C_2H_5)(CH_3)_6Si_4O_4$,[143] $(CH_2=CH)_2(C_6H_5)_2(CH_3)_4Si_4O_4$,[147] $(C_6H_5)(CH_2=CH)(CH_3)_6Si_4O_4$,[393] $[(C_2H_5)(CH_2=CH)SiO]_3$,[394] etc.[322,334,395-400]

Organocyclosiloxanes with functional groups on the silicon atoms. The preceding section has described the preparation of compounds in which all the silicon valencies (other than those forming the ring) are occupied by alkyl or aryl radicals. There have recently been a number of reports on the preparation and properties of organocyclosiloxanes containing functional groups (Cl, OH, OR, NHR, etc.) on silicon atoms, in addition to the organic radicals. We shall now consider the preparation of such organocyclosiloxane derivatives.

Halogen-substituted tri- and tetra-meric organocyclosiloxanes of the following types have been described:



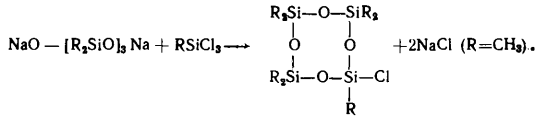
The tetramers have analogous structures.

An interesting method for the preparation of organochlorocyclosiloxanes is the chlorination of hydrogen-containing organocyclosiloxanes[75,87,95,139]:

$$[RHSiO]_n + n\,Cl_2 \longrightarrow [RClSiO]_n + n\,HCl \quad (R=CH_3, C_2H_5;\ n=3-7).$$

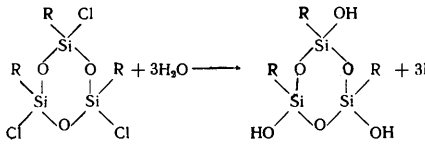
Another method is based on the exchange reaction between sodium silanolates and halogenosilanes; in particular,

this method has been used to prepare monochlorocyclotetrasiloxanes[401,402]:



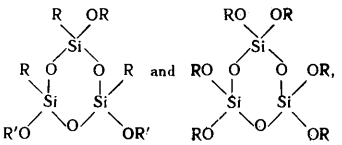
Since the chlorine atom attached to the silicon is readily replaced by other groups, these compounds are of evident interest for the production of other derivatives of organocyclosiloxanes and linear and cyclolinear oligomers and polymers.

Organohydroxycyclosiloxanes are obtained by hydrolysis of the chlorine atoms[75,95]:



Such compounds are weak alkyl(aryl)cyclosilicic acids, as is shown by the recent isolation of the sodium triphenylcyclosilanolate $(C_6H_5)_3Si_3O_3(ONa)_3.10H_2O$ (prepared by the action of 6 *N* NaOH on the phenylsiloxane polymer[403]).

Partially and fully substituted alkoxycyclosiloxanes have been described:



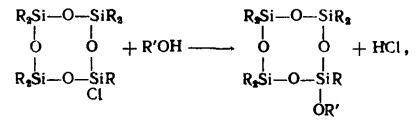
and also the corresponding cyclotetrasiloxanes. Alkylalkoxycyclosiloxanes are obtained by partial hydrolysis of alkyltrialkoxysilanes[404,405]:

$$n\,RSi(OR')_3 + n\,H_2O \longrightarrow [R(R'O)SiO]_n + 2n\,R'OH.$$

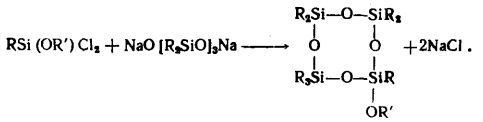
Thus partial hydrolysis of methyltrimethoxysilane has produced the methylmethoxycyclosiloxanes $[CH_3(CH_3O)SiO]_n$, where n = 3, 5, and 6. Hydrolysis of an alkylalkoxydichlorosilane in pyridine gives alkoxy-substituted alkylcyclo-tri- and -tetra-siloxanes[406-408]:

$$n\,RSi(OR')Cl_2 + H_2O \xrightarrow{C_5H_5N} [RSi(OR')O]_n,$$

where R = CH_3, C_2H_5; R′ = CH_3, C_2H_5, iso-C_3H_7; n = 3 or 4. Compounds of similar type can also be obtained by reacting chlorocyclosiloxanes with alcohols or phenols, *e.g.*[401]:



where R = CH_3 and R′ = C_2H_5 or C_4H_9; and by the exchange reaction between alkylalkoxydichlorosilanes and the disodium salts of organosiloxanes[402,409]:



This last method has been used to prepare alkoxyalkylcyclotetrasiloxanes with R = CH_3 and R′ = C_2H_5 or n-C_4H_9; these are transparent liquids.

Dialkoxycyclosiloxanes are obtained either by replacing the chlorine atoms in inorganic chlorocyclosiloxanes by alkoxy-groups[410]:

$$Cl_8Si_4O_4 + 8C_2H_5OH \longrightarrow [(C_2H_5O)_2SiO]_4 + 8HCl,$$

or by partial hydrolysis of tetraalkoxysilanes[411-414]:

$$4Si(OR)_4 + 4H_2O \longrightarrow [(RO)_2SiO]_4 + 8ROH,$$

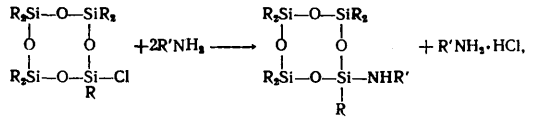
or by hydrolysis of dialkoxydichlorosilanes[415-418] or $[(RO)_3Si]_2O$:[419]

$$n\,(RO)_2SiCl_2 + n\,H_2O \longrightarrow [(RO)_2SiO]_n + 2n\,HCl.$$

The reaction between silicon tetrachloride and isopropyl or isobutyl alcohol in the presence of small amounts of water also gives dialkoxycyclotetrasiloxanes[420]:

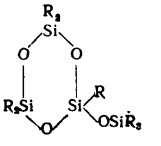
$$4SiCl_4 + 8ROH + 4H_2O \longrightarrow [(RO)_2SiO]_4 + 16HCl.$$

Organoaminocyclosiloxanes have been obtained by replacing the chlorine in organochlorocyclosiloxanes by reaction with ammonia or amines[401]:



where R = CH_3 and R′ = H or C_6H_5.

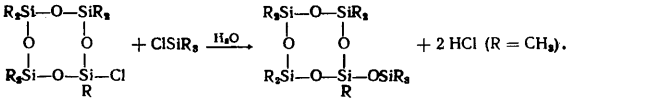
Trialkylsiloxy-substituted organocyclosiloxanes are of interest from the point of view of isomerism of the inorganic rings: thus alkyl(trialkylsiloxy)cyclotrisiloxanes (VII) and dialkylcyclotetrasiloxanes (X):



(X)

are isomers, having the same composition but different ring sizes.

Compounds of type (X) were first prepared by the simultaneous hydrolysis of heptamethylchlorocyclotetrasiloxane and trimethylchlorosilane[75]:



The resulting trimethylsiloxyheptamethylcyclotetrasiloxane is an isomer of the previously known decamethylcyclopentasiloxane. Triethylsiloxy-substituted cyclotri- and cyclotetra-siloxanes have also been described[421].

Organocyclosiloxanes containing functional groups in the organic radical have been described; these are of theoretical and practical interest because of the possibility of their polymerisation. The substituents may be chloroalkyl or chloroaryl RCl, cyano CN, ester COOR, hydroxyl OH, amino NH_2, thiol SH, etc.

The chemistry of silicon derivatives, including organocyclosiloxanes, containing substituted hydrocarbon groups

has been reviewed by George *et al.*[422] and discussed in the book by Petrov and coauthors[423].

The methods for the production of silicon derivatives containing substituted hydrocarbon groups fall into two classes: (1) methods involving formation of a siloxane ring, and (2) methods involving conversion of organic radicals present as substituents in cyclosiloxanes.

The normal methods of hydrolysis and cohydrolysis used for unsubstituted organocyclosiloxanes can be employed for organocyclosiloxanes containing substituted organic radicals, provided that the substituents themselves are not hydrolysed. Thus chloroalkyl- and chloroaryl--cyclosiloxanes are obtained by hydrolysis of the corresponding di-(chloroalkyl)- and di-(chloroaryl)dichlorosilanes, *e.g.*[106]:

$$n(ClC_6H_4)_2SiCl_2 + H_2O \rightarrow [(ClC_6H_4)_2SiO]_n + 2HCl \quad (n = 3, 4).$$

The cyanoalkyl derivatives may also be hydrolysed[424-426]. The simultaneous hydrolysis of dimethyldichlorosilane with α- or β-cyanoethyl(methyl)dichlorosilane produces heptamethyl-α- or heptamethyl-β-cyanoethylcyclotetrasiloxane[427]:

$$3\,R_2SiCl_2 + RR'SiCl_2 + 4\,H_2O \rightarrow \begin{array}{l} R_2Si{-}O{-}SiR_2 \\ \quad\;\; |\qquad\;\; | \\ R_2Si{-}O{-}\underset{\displaystyle R}{\underset{|}{Si}}{-}R' \end{array} + 8\,HCl,$$

where R = CH_3 and R′ = $CH(CN)CH_3$ or CH_2CH_2CN.

Since functional groups are very often reactive, the production of cyclosiloxanes with hydrocarbon radicals containing such groups is difficult by ordinary methods, and they are generally prepared by various substitution reactions occurring in the organic radical attached to a ring silicon atom.

Chemical reactions in the organic radical. An interesting reaction is the chlorination with elemental chlorine of methyl groups attached to silicon in organocyclosiloxanes, to produce the chloromethyl derivatives; thus photochlorination of octamethylcyclotetrasiloxane gives heptamethyl(chloromethyl)cyclotetrasiloxane in 70% yield[428-430]:

$$[R_2SiO]_4 \xrightarrow{Cl_2,\,h\nu} \begin{array}{l} R_2Si{-}O{-}SiR_2 \\ \quad\;\; |\qquad\;\; | \\ R_2Si{-}O{-}\underset{\displaystyle R}{\underset{|}{Si}}{-}CH_2Cl \end{array} \quad (R = CH_3).$$

The pentamer is chlorinated analogously[431].

The importance of the chlorinated methylcyclosiloxanes is that they can be polymerised to chlorinated oils, rubbers, and solid polymers having high low-temperature resistivity, good thermal stability, and good adhesion and low swelling capacity in solvents[430]. A feature of the chloromethyl groups is their ability to undergo substitution reactions without attack on the siloxane ring. They react with metallic magnesium to form Grignard reagents which can then be converted into carboxymethylcyclotetrasiloxanes[432,433], hydroxyalkylcyclotetrasiloxanes[434,435], or cyanoalkylcyclotetrasiloxanes[436]. The chloromethyl groups of cyclosiloxanes react fairly readily with potassium iodide[437,438], salts of organic acids[301,439,400], compounds containing *N*-alkyl or *N*-aryl groups[441-443], and metal mercaptides[444,445]. An interesting fact is that aminoalkyl--substituted organocyclosiloxanes polymerise readily at room temperature[441].

Chloromethylcyclosiloxanes undergo the Arbuzov rearrangement[446]:

$$\begin{array}{l} R_2Si{-}O{-}SiR_2 \\ \quad\;\; |\qquad\;\; | \\ R_2Si{-}O{-}SiR \\ \qquad\;\; | \\ \qquad CH_2Cl \end{array} + P(OC_2H_5)_3 \rightarrow \begin{array}{l} R_2Si{-}O{-}SiR_2 \\ \quad\;\; |\qquad\;\; | \\ R_2Si{-}O{-}Si{-}CH_3 \\ \qquad\;\; | \\ \qquad CH_2{-}PO(OC_2H_5)_2 \end{array} + C_2H_5Cl\,(R = CH_3).$$

The reaction between sulphuryl chloride and $[(CH_3)_2SiO]_4$ produces $(CH_3)_7(CH_2SO_3Cl)Si_4O_4$.[447,448]

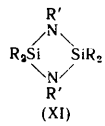
With benzoyl peroxide octamethylcyclotetrasiloxane yields bis-(heptamethylcyclotetrasiloxanyl)ethane[337,449]:

$$2\,[R_2SiO]_4 + (C_6H_5CO)_2O_2 \rightarrow \begin{array}{l} R_2Si{-}O{-}SiR_2 \qquad R_2Si{-}O{-}SiR_2 \\ \quad\;\; |\qquad\;\; | \qquad\qquad\;\; |\qquad\;\; | \\ R_2Si{-}O{-}\underset{\displaystyle R}{\underset{|}{Si}}{-}CH_2{-}CH_2{-}\underset{\displaystyle R}{\underset{|}{Si}}{-}O{-}SiR_2 \end{array}$$

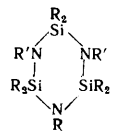
The same reaction occurs on irradiation. These reactions are models for the vulcanisation of polydimethylsiloxane rubber. The two-ring compounds polymerise with ring opening; they are used as partial cross-linking agents in the polymerisation of cyclosiloxanes.

2. CYCLOSILAZANES

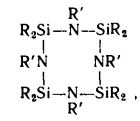
Compounds containing Si–N bonds in a ring are known as cyclosilazanes. Rings containing two, three, and four SiN groups are known:



(XI)



(XII)



(XIII)

In known compounds R is alkyl, aryl, alkoxy, or amino, and R′ is hydrogen, a hydrocarbon group, or an alkylsilyl radical. The first inorganic compounds containing the Si–N bond were obtained by ammonolysis of chlorosilanes. Monocyclic compounds are produced from bifunctional monomers; thus ammonolysis of dichlorosilane gives solid products or oils, depending on the reaction conditions, of general formula $[H_2SiNH]_n$, where $n = 7-8$.[451,452] The cryoscopic determination of the degree of polymerisation in this case gave approximate results only.

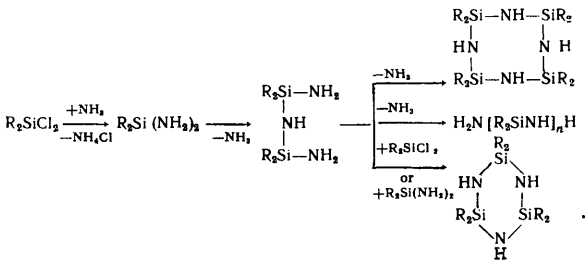
The reaction between gaseous silicon tetrachloride and ammonia at a high temperature (825°)[453] produces the low--molecular-weight linear compound $Cl_3SiNHSiCl_3$ and the cyclic tetramer $Si_8N_4Cl_{20}$ of structure (XIII) (R = Cl, R′ = = $SiCl_3$). The reaction of silicon tetrachloride with nitrogen in a glow discharge produces a range of products[454,455], including the cyclic trimer (XII) (R = Cl, R′ = $SiCl_3$) and tetramer (XIII) (R = Cl, R′ = $SiCl_3$).

The first organocyclosilazanes were obtained in 1948 by ammonolysis of dimethyldichlorosilane[91,457,458]:

$$(CH_3)_2SiCl_2 + 3NH_3 \longrightarrow 1/n\,[(CH_3)_2SiNH]_n + 2NH_4Cl \quad (n = 3, 4).$$

The liquid trimer $[(CH_3)_2SiNH]_3$ and crystalline tetramer $[(CH_3)_2SiNH]_4$ are readily separated from the reaction mixture. Ammonolysis has since been used to prepare the organocyclosilazanes $[(C_2H_5)_2SiNH]_n$ (n = 3 or 4)[91], $[CH_3(C_2H_5)SiNH]_3$,[459] $[CH_3(C_6H_5)SiNH]_3$,[459] $[(n\text{-}C_4H_9)_2$. $SiNH]_3$,[461] $[CH_3SiHNH]_4$,[462] and $[C_2H_5SiHNH]_n$ (n = 3 or 4)[462].

The mechanism of ammonolysis of organodichlorosilanes is not fully clear. The isolation of certain organosilane diamines $R_2Si(NH_2)_2$ when the organic radical is a cause of steric hindrance to further condensation, *e.g.* $(t\text{-}C_4H_9)_2Si(NH_2)_2$, and the production of linear organodiaminodisilazanes $H_2N-SiR_2-NH-SiR_2-NH_2$,[460,463] would suggest that the formation of organocyclosilazanes proceeds simultaneously with the formation of linear organosilazanes as follows:



The conditions which determine the mode of the reaction have been little studied; the particular organic radical, the solvent used, the reaction temperature, the concentration of reactants, etc., affect the mode of the reaction.

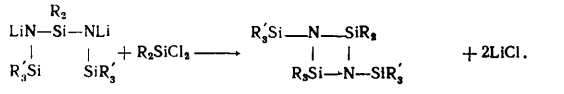
Organocyclosilazanes with functional groups on the silicon can be obtained by analogous reactions; thus ammonolysis of the corresponding dialkoxy- or diaryloxy-dichlorosilanes has given $[(CH_3O)_2SiNH]_n$,[464] $[(C_2H_5O)_2SiNH]_n$,[464] $[(iso\text{-}C_3H_7O)_2SiNH]_{3,4}$,[465,466] $[(t\text{-}C_4H_9O)_2SiNH]_3$,[467] and $[(C_6H_5O)_2SiNH_3]$.[465] As with alkylhalogenosilanes, the ammonolysis of higher alkoxy- and aryloxy-halogenosilanes to produce cyclic products is difficult, apparently because of steric hindrance. The main products are dialkoxysilanediamines $(RO)_2Si(NH_2)_2$ and tetraalkoxydisilazanediamines $(RO)_2(NH_2)SiNHSi(NH_2)(OR)_2$, which are converted into cyclosilazanes only on prolonged heating[465].

Dialkyl- and diaryl-dichlorosilanes react with primary amines, usually forming dialkyldi-(alkylamino)silanes $R_2Si(NHR')_2$,[450] but cyclosilazanes can also be obtained; thus the reaction between dimethyldichlorosilane and aniline produces the *N*-phenylcyclotrisilazane $[(CH_3)_2SiNC_6H_5]_3$ as well as $(CH_3)_2Si(NHC_6H_5)_2$.[456]

Alkylamino-substituted organocyclosilazanes obtained by the thermal decomposition of alkyl(trialkylamino)silanes $RSi(NHR')_3$ have recently been described[468]:

$$3RSi(NHR')_3 \xrightarrow{-R'NH_2} [RSi(NHR')NR']_3.$$

The methods so far discussed have given only cyclic trimers and tetramers. The dimers (XI) are obtained by ammonolysis of bis-(trialkylsiloxy)dichlorosilanes $(R_3SiO)_2.SiCl_2$,[469] by the thermal decomposition of *N*-trialkylsilylcyclosilazanes $[R_2SiNSiR'_3]_n$,[470] or by the exchange reaction[470]:



All organic derivatives of cyclosilazanes are colourless liquids or crystalline solids readily soluble in organic solvents. The physical properties and structure of various organocyclosilazanes have been studied, by infrared spectroscopy[471-473], Raman spectroscopy[472], and nuclear magnetic resonance spectroscopy[474]. Spectroscopic data have shown[472,475] that the unshared pair of electrons from the nitrogen are partially delocalised through the 3*d* silicon orbitals, so that the Si–NH–Si bond has partial double-bond character (the bond order is 1.18) and cyclosilazanes have partial aromatic character[5]. The Si–NH–Si bonds in cyclosilazanes are characterised by absorption bands at 928–932 cm^{-1} and 1169 cm^{-1} in the trimer and 939 cm^{-1} and 1183 cm^{-1} in the tetramer[473].

The following bond lengths and valence angles have been determined in dimethylcyclosilazanes by electron diffraction[251,252]: Si–N 1.78 ± 0.03 Å, ∠ NSiN = 111° ± 5°, ∠ SiNSi = 117° ± 4° (in the trimer) and 123° ± 4° (in the tetramer). Further study is necessary to establish the true structure of organocyclosilazanes, since spectroscopic data indicate that the six-membered ring Si_3N_3 is planar (of symmetry D_{3h})[472], and electron diffraction indicates it to be non-planar[251]. The eight-membered ring Si_4N_4 is non-planar.

Organocyclosilazanes withstand heating to high temperatures. They are less stable towards hydrolysis, and are decomposed by water to ammonia and the diorganosilanediol or organosiloxane. The pH of the medium has a large effect on the hydrolysis: in acid medium organocyclosilazanes are readily hydrolysed, producing the ammonium salt, but they are completely stable to hydrolysis in alkaline medium[476]. Hydrogen chloride decomposes organocyclosilazanes to form the corresponding diorganodichlorosilane and ammonium chloride[471]:

$$[R_2SiNH]_3 + 9\,HCl \rightarrow 3\,R_2SiCl_2 + 3\,NH_4Cl \quad (R = C_6H_5).$$

Interesting data have recently appeared on the transamination of organocyclosilazanes by amines: primary amines in excess open silazane rings, forming diorganodi-(alkylamino)silanes[460]:

$$[R_2SiNH]_3 + 6\,R'NH_2 = 3\,R_2Si(NHR')_2 + 3NH_3.$$

The use of an equivalent quantity of aniline, however, has given the *N*-substituted cyclosilazane[477]:

$$[R_2SiNH]_3 + 3\,R'NH_2 \rightarrow [R_2SiNR']_3 + 3\,NH_3$$

($R = CH_3$, $R' = C_6H_5$). This reaction always produces *N*-substituted cyclotrisilazanes, whether the starting compound is a cyclotrisilazane or a cyclotetrasilazane[477].

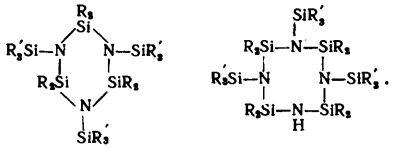
Another interesting reaction is the replacement of the hydrogen of the NH groups in organocyclosilazanes by lithium; the reaction of the cyclosilazanes with butyllithium in n-hexane produces the *N*-lithioorganocyclosilazanes as crystalline solids stable in an atmosphere of nitrogen[478]:

$$[R_2SiNH]_3 + 3\,LiC_4H_9 \rightarrow [R_2SiNLi]_3 + 3\,C_4H_{10}.$$

The hydrogen atoms of 1, 2, or 3 NH groups of the cyclosilazanes can be replaced by lithium by reaction with butyllithium. The *N*-lithio-derivatives of cyclosilazanes react readily with organochlorosilanes to form *N*-silylcyclosilazanes[478]:

$$[R_2SiNLi]_3 + 3\,R'_3SiCl \rightarrow [R_2SiNSiR'_3]_3 + 3\,LiCl.$$

Trimers and a tetramer of analogous structure have been obtained:



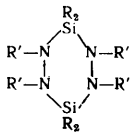
When hexamethyldisilazane was heated with hexamethylcyclotrisilazane at 300°–325° and 350°–410°, the linear

octamethyltrisilazane was isolated from the reaction mixture, indicating rupture of the ring[91].

Cyclosilazanes are starting materials for the production of polymers. The polymerisation of hexaphenylcyclotrisilazane has been described[479], and silazane–siloxane copolymers have been prepared[480]. Polymers with the Si–N bond are considered to have great potential as heat-resistant materials[481]. The use of cyclosilazanes as water-repellents[457,482-484], corrosion inhibitors[466,480,485], modifiers for melamine–formaldehyde resins[479], and hardening agents for epoxy-resins[486], has also been described.

3. DISILATETRAZINES

An interesting class of cyclic compounds are the organocyclodisilatetrazines:



(XIV)

These are obtained by reacting diorganodichlorosilanes with hydrazine[487,488]:

$$2\,R_2SiCl_2 + 6\,H_2N{-}NH_2 \rightarrow [R_2Si{-}NH{-}NH]_2 + 4\,N_2H_5Cl.$$

The methyl compound produces only macromolecular linear polyhydrazinosilanes $[(CH_3)_2SiNHNH]_n$ which are oily or vitreous[488,489], but the phenyl compound gives the cyclic compound (XIV) (R = C_6H_5, R′ = H). Phenylhydrazine also gives cyclic products[488]:

$$2\,R_2SiCl_2 + 6\,C_6H_5NHNH_2 \rightarrow [R_2SiN(C_6H_5)NH]_2 + 4\,C_6H_5NHN_2\cdot HCl$$

(R = CH_3 or C_6H_5).

Cyclic disilatetrazines can be obtained from diorganodichlorosilanes and the lithium derivative of phenylhydrazine[488]:

$$2\,R_2SiCl_2 + 2\,C_6H_5NLiNLiH \rightarrow [R_2SiN(C_6H_5)NH]_2 + 4\,LiCl\ (R = C_6H_5).$$

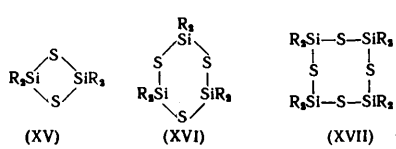
Hexaphenylcyclodisilatetrazine can also be obtained by using the dilithium derivative of azobenzene[490]:

$$(C_6H_5)_2SiCl_2 + C_6H_5NLiNLiC_6H_5 \rightarrow [(C_6H_5)_2SiNC_6H_5NC_6H_5]_2 + 4\,LiCl\ .$$

The chemical properties of the cyclic disilatetrazines depend on the degree of substitution at the nitrogen atoms. Tetraphenylcyclodisilatetrazine $[(C_6H_5)_2SiNHNH]_2$ is very sensitive to hydrolysis, hexaphenylcyclodisilatetrazine $[(C_6H_5)_2SiNC_6H_5NH]_2$ is not hydrolysed by water or dilute acids, and octaphenylcyclodisilatetrazine $[(C_6H_5)_2SiNC_6H_5NC_6H_5]_2$ is completely stable in air and in the presence of water.

4. CYCLOSILTHIANES

A number of inorganic and organic derivatives of the four-, six-, and eight-membered rings containing 2, 3, and 4 SiS units respectively have been described:



(XV) (XVI) (XVII)

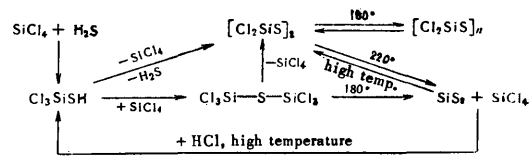
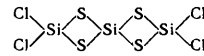


Fig. 3.

In the known inorganic compounds the silthiane rings are substituted by halogen atoms. The first representative of this type of compound, silicon thiochloride Cl_2SiS, was obtained, together with Cl_3SiSH, from silicon tetrachloride and hydrogen sulphide[494,495]. In the presence of pyridine, silicon tetrachloride reacts with hydrogen sulphide to form the cyclic dimer $[Cl_2SiS]_2$.[496] In the gaseous state $SiCl_4$ reacts with hydrogen sulphide only above 500° (optimum temperature 650°) to give Cl_3SiSH, $Cl_3SiSSiCl_3$, and $[Cl_2SiS]_4$ (XVII) (R = Cl).[497] The complex nature of this reaction was elucidated by studying it at 700°–1000°; it was shown[498] that the reaction products depend on the temperature (Fig. 3).

The compound $Si_3S_4Cl_4$ has also been isolated, and has been given structure (XVIII):



(XVIII)

On heating at 180° the crystalline dimer $[Cl_2SiS]_2$ is converted into a liquid polymer of molecular weight near that of the tetramer $[Cl_2SiS]_4$, but the tetramer could not be isolated in the pure state. Its Raman spectrum has confirmed the cyclic structure of the dimer $[Cl_2SiS]_2$, with a planar Si_2S_2 ring[499].

Organocyclosilthianes were first described in 1952.[500] The passage of hydrogen sulphide through a solution of $(C_2H_5)_2SiCl_2$ in petroleum ether in the presence of pyridine gives the cyclic dimer $[(C_2H_5)_2SiS]_2$ (XV) (R = C_2H_5). This reaction,

$$R_2SiCl_2 + H_2S + 2\,C_5H_5N \rightarrow 1/n\,[R_2SiS]_n + 2\,C_5H_5N\cdot HCl,$$

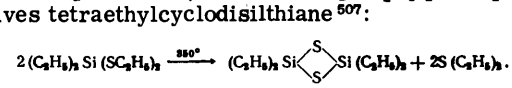
has since been used to prepare cyclosilthianes substituted by methyl[501-503], ethyl[500,504], n-propyl[501,504], and phenyl[505] groups.

This thiohydrolysis of dimethylchlorosilane at normal temperatures produces the cyclic trimer $[(CH_3)_2SiS]_3$,[502,503] which on heating in a stream of hydrogen sulphide[503] undergoes an interesting change in the silthiane ring, with formation of the dimer $[(CH_3)_2SiS]_2$. The conversion of the trimer to the dimer on heating has also been observed with the ethyl- and propyl-derivatives; the reverse change of dimer to trimer is also possible[504].

Tetraethyldisilthiane[501] and tetramethyldisilthiane[506] have also been obtained from the dialkyldiiodosilane and silver sulphide:

$$2\,R_2SiI_2 + 2\,Ag_2S \rightarrow [R_2SiS]_2 + 4\,AgI.$$

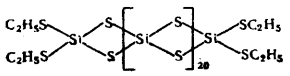
Cyclosilthianes can be obtained by the thermal decomposition of mercaptosilanes; thus heating $(C_2H_5)_2Si(SC_2H_5)_2$ at 350° gives tetraethylcyclodisilthiane[507]:



and heating tetra-(ethylmercapto)silane yields another substituted cyclodisilthiane[507]:

$$2\,Si(SC_2H_5)_4 \rightarrow (C_2H_5S)_3Si\langle S\rangle Si(SC_2H_5)_3 + 2\,S(C_2H_5)_2,$$

as well as a product of composition $Si_{22}S_{42}(SC_2H_5)_4$:



which is an intermediate in the production of silicon sulphide $[SiS_2]_x$ by the decomposition of mercaptosilanes.

Organocyclosilthianes are colourless liquid or crystalline substances, which in the presence of water (or even atmospheric moisture) are readily hydrolysed to the corresponding organosilanols or organosiloxanes and hydrogen sulphide.

Various physical methods have been used to investigate the structure of the organocyclosilthianes. The dipole moments of the methyl compounds have been determined[228] as $\mu = 0.0$ D for $[(CH_3)_2SiS]_2$ and $\mu = 1.03$ D for $[(CH_3)_2SiS]_3$; consequently the four-membered Si_2S_2 ring is planar and the six-membered Si_3S_3 ring is non-planar. Electron diffraction has confirmed the cyclic structure of the dimer and trimer, and has given the following interatomic distances and bond angles: Si–S 2.18 ± 0.03 Å (dimer) and 2.15 ± ± 0.03 Å (trimer), ∠ SSiS 105° (dimer) and 115° (trimer), and ∠ SiSSi 75° (dimer) and 110° (trimer)†.

The infrared spectra of the methylcyclosilthiane dimer and trimer[502] and the Raman spectrum of the dimer[499] $[(CH_3)_2SiS]_2$ have also confirmed their cyclic structure. The "boat" conformation has been suggested for the six-membered Si_3S_3 ring[502].

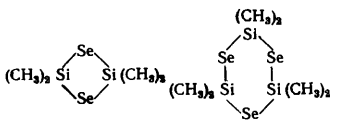
The possible utility of organosilthianes is limited, because of their low resistance to hydrolysis. However, the patent literature indicates the possibility of using them as additives for organosiloxane and hydrocarbon oils and as insecticides and fungicides[505].

5. CYCLOSILSELENANES

Only methyl derivatives of ring compounds containing silicon and selenium have been obtained[509], by the reaction of dimethyldichlorosilane with sodium selenide:

$$(CH_3)_2SiCl_2 + Na_2Se \rightarrow 1/n\,[(CH_3)_2SiSe]_n + 2\,NaCl.$$

Two products were isolated, the dimer and trimer:



The dimer is a crystalline solid, and the trimer is a liquid of unpleasant smell. Both have low stability to hydrolysis.

† These data are contained in a paper by M. Yokoi, T. Nomura, and K. Yamasaki, J. Amer. Chem. Soc., 77, 4484 (1955) (Ed. of Translation).

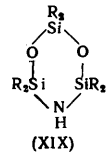
III. MIXED CYCLIC SILICON COMPOUNDS

The structure and properties of organocyclosiloxanes show them to be prototypes of inorganic silicon rings, partial replacement of silicon and oxygen atoms in these rings by other elements producing rings containing aluminium, boron, phosphorus, titanium, nitrogen, or other elements, in addition to silicon. Thus oxygen may be partially replaced by nitrogen or sulphur to obtain cyclosilazoxanes or cyclosilthioxanes respectively, and silicon may be partially replaced by boron, aluminium, phosphorus, arsenic, antimony, or titanium to form the corresponding organocyclo("elemento")siloxanes. These mixed heterocycles are transitional between organocyclosiloxanes and other inorganic rings.

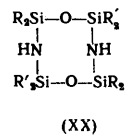
Organocyclosilazoxanes were obtained by the low-temperature ammonolysis of $\alpha\omega$-dichlorosiloxanes[75,122,510]:

$$Cl[R_2SiO]_{n-1}SiR_2Cl + 3\,NH_3 \rightarrow \left[\begin{array}{c}-R_2SiO-_{n-1}SiR_2-\\ \diagdown\!\!\diagup\ NH\ \diagdown\!\!\diagup\end{array}\right] + 2\,NH_4Cl.$$

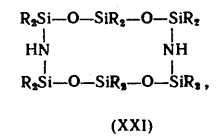
The reaction had previously been described in a patent[511], but the pure cyclic compounds had not been isolated. The organocyclosilazoxanes



(XIX)



(XX)



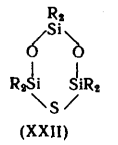
(XXI)

where R = CH_3 and R′ = C_2H_5 or CH_3, have been described[75,510]. These compounds are colourless, except for octamethylcyclotetrasiladiazadioxane; this forms prismatic or acicular crystals melting at 40°. They are all readily soluble in the usual organic solvents.

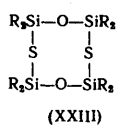
Organocyclosilthioxanes were obtained by the thiohydrolysis of $\alpha\omega$-dichlorosiloxanes in the presence of pyridine[512]:

$$Cl[R_2SiO]_{n-1}SiR_2Cl + H_2S \xrightarrow{C_5H_5N} \left[\begin{array}{c}-[R_2SiO]_{n-1}SiR_2-\\ \diagdown\!\!\diagup\ S\ \diagdown\!\!\diagup\end{array}\right] + 2\,C_5H_5N\cdot HCl.$$

The compounds



(XXII)

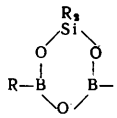


(XXIII)

where R = CH_3, have been prepared. Hexamethylcyclotrisilthiadioxane is a transparent colourless liquid boiling at 172.5°; octamethylcyclotetrasildithiadioxane is a crystalline solid melting at 38°–42°. Both dissolve well in various organic solvents.

Cyclodiborasiltrioxanes of structure (XXIV) have been prepared by heating 2–3 moles of an aryl or cycloalkyl boric acid with a diarylsilanediol in the presence of an acid catalyst[513]. It is interesting that, if the reactants are taken in proportions to give Si : B = 1 : 1, no

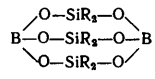
rings containing these elements in this proportion are obtained, but only the cyclodiborasiltrioxane, part of the diarylsilanediol remaining unreacted.



(XXIV)

The organocycloborasiloxanes produced are said to be of use as additives to polymers to render them incombustible and neutron-absorbing, and as scintillators, active components of fungicidal, bactericidal, and insecticidal compositions, heat-exchange media, lubricant additives, etc.[513]; these claims are probably exaggerated.

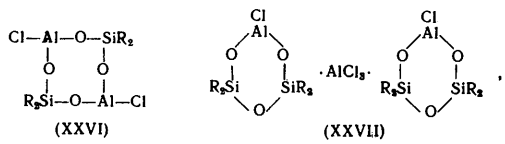
There is a report[198] of the preparation[514] of the bicyclic borasiloxane (XXV)



(XXV)

but the method of preparation and properties were not described.

Cycloaluminosiloxanes. The first reports on the preparation of cycloaluminosiloxanes appeared in the patent literature[264], where it was stated that the reaction of aluminium trichloride with organocyclotetrasiloxanes produces cyclic aluminosiloxanes of structure (XXVI):



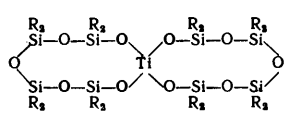
(XXVI) (XXVII)

where R = CH_3 or C_2H_5.

Others have said[515] that $AlCl_3$ reacts with cyclotetrasiloxanes to form the 1,3-dichloro(tetraalkyl)disiloxane and a complex compound of structure (XXVII).

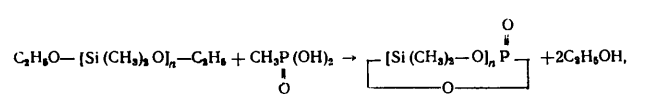
Rings made up of aluminium, silicon, and oxygen atoms, but not containing organic substituents, are found in certain natural silicates. The monocyclic anion $[AlSi_5O_{18}]^{13-}$, obtained by replacing one silicon atom in the ring of $[Si_6O_{18}]^{12-}$ by aluminium, has been found in cordierite α-$Mg_2Al_3[AlSi_5O_{18}]$[516] and indialite γ-$Mg_2Al_3[AlSi_5O_{18}]$.[517]

Cyclotitanosiloxanes. Although several titanosiloxane compounds have been described, there has been only one report[518] of the preparation of an organocyclotitanosiloxane: tetrabutoxytitanium reacts with diphenylsilanediol to give the compound of structure (XXVIII):

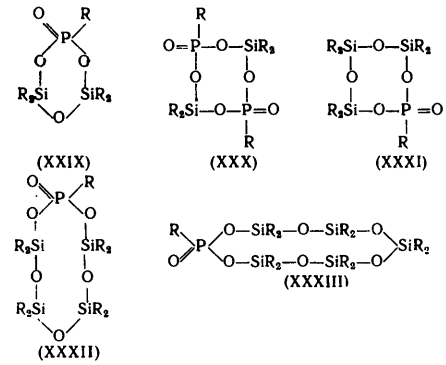


(XXVIII)

The reaction between $\alpha\omega$-diethoxydimethylsiloxanes and methylphosphonic acid has given a number of cyclophosphorosiloxanes[519]:



where $n = 1-5$. The following types of compounds in this new class of inorganic rings with organic substituents have been isolated[519]:



(XXIX) (XXX) (XXXI)

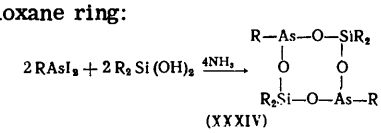
(XXXII) (XXXIII)

These compounds are very readily hydrolysed by water to form methylphosphonic acid and polydimethylsiloxanes.

Unlike dimethylcyclosiloxanes, dimethylcyclophosphorosiloxanes have been shown to polymerise very poorly in the presence of an acid or alkali as catalyst[520]; however, they copolymerise smoothly with octamethylcyclotetrasiloxane to give a dimethylsiloxane polymer containing phosphorus in the chain. Rubbers obtained from such polymers containing 0.02–0.03% of phosphorus in the polymer chain have a higher resistance to rupture and a larger relative elongation than dimethylsiloxane rubber.

The reaction between $\alpha\omega$-diethoxydimethylsiloxanes and methylphosphonic acid was also studied by Orlov and Voronkov[521], who obtained viscous or rubber-like polymers of high molecular weight. Different products were obtained because of the different reaction temperatures used.

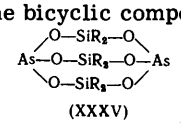
Cyclic compounds containing arsenic have been described[198,522]. Phenyldiiodoarsine and diphenylsilanediol react to produce a compound having an eight-membered arsinosiloxane ring:



(XXXIV)

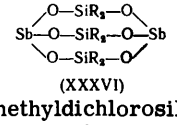
This is a crystalline product, melting at 145°.

The reaction between arsenic trichloride and diphenylsilanediol has given the bicyclic compound



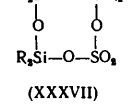
(XXXV)

The only antimony-containing compound of this type described in the literature is the product obtained from triethoxyantimony and dimethyldiacetoxysilane, which has been assigned the structure[523]



(XXXVI)

The reaction of dimethyldichlorosilane with 100% sulphuric acid yields a compound which by composition and molecular weight corresponds to the cyclic structure[524-526]



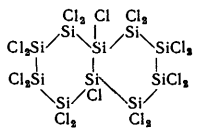
(XXXVII)

Tetramethylcyclodisulphatodisiloxane is a crystalline substance melting at 103°–120°. Above 150° it decomposes to polydimethylsiloxane and SO_3. Compounds of this class are very sensitive to hydrolysis; water destroys the cyclic structure, giving sulphuric acid and polysiloxanes.

IV. POLYCYCLIC SILICON COMPOUNDS

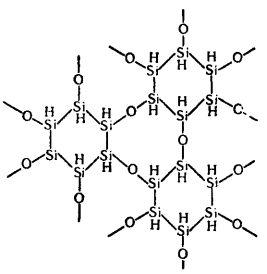
Polycyclic silicon compounds can also be divided into homocyclic and heterocyclic compounds[2–5].

Homopolycyclic compounds contain rings made up of silicon atoms only; few such compounds are known at present. An example is persilicochlorodecalin $Si_{10}Cl_{18}$, obtained by heating $Si_{10}Cl_{20}H_2$:[527]



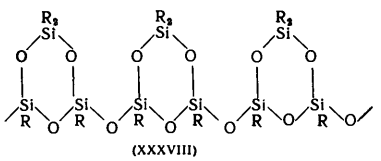
Substances of formulae $[SiCl]_x$ and $[SiH]_x$ are known, which are polycyclic compounds of high molecular weight containing condensed six-membered rings.

Many more heteropolycyclic compounds, containing rings made up of silicon atoms alternating with atoms of other elements, such as oxygen, nitrogen, and sulphur, are known, as well as polycyclic structures containing both homocyclic and heterocyclic rings, *e.g.* the siloxene $[Si_6O_3H_6]_n$ and its derivatives[528–535], which are made up of six-membered Si_6H_6 rings joined by oxygen bridges:



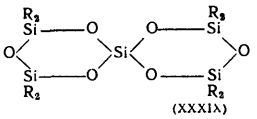
The known polycyclic silicon structures can be classified thus[3–5]:

(a) linear or cyclic chain polycyclic compounds:

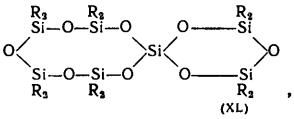


(XXXVIII)

(b) spirane compounds, in which the rings have one common atom:



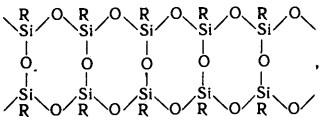
(XXXIX)



(XL)

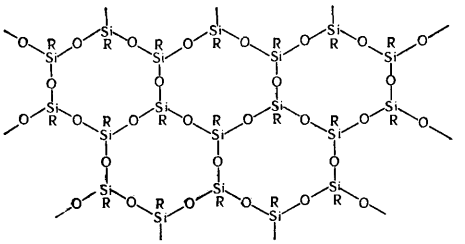
(c) condensed polycyclic compounds, in which the rings have two or more common atoms.

The rings may condense in a single direction, producing ribbon (cyclolinear) polycyclic polymers:



(XLI)

or in two directions (in a plane), producing reticular structures:



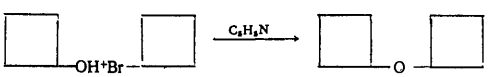
(XLII)

or in three dimensions, producing complex cross-linked three-dimensional structures.

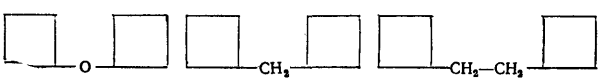
All these types of polycyclic compounds are found in natural silicates[26] and in the synthetic organic siloxane derivatives. We have not the space to discuss the polycyclic silicates here.

Polycyclic compounds of low and high molecular weight are known; most of the former are based on a silicon–oxygen skeleton. Polycyclosiloxanes give all the above types of polycyclic structure.

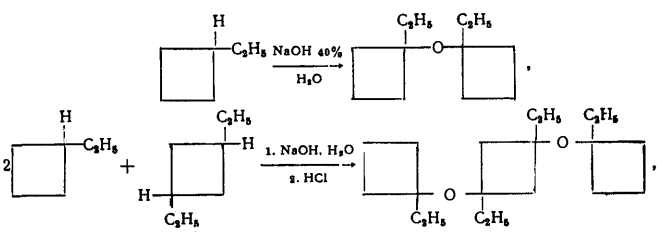
Compounds in which the rings are joined by bridges are obtained by condensation[536]:



where □ = $(CH_3)_7Si_4O_4$, or by the action of high-energy particles (irradiation) on octamethylcyclotetrasiloxane, which gives products in which the rings are joined by oxygen, methylene, or ethylene bridges:



Polycyclosiloxanes have been obtained by alkaline hydrolysis of hydrocyclosiloxanes and condensation of the resulting hydroxycyclosiloxanes[537]:

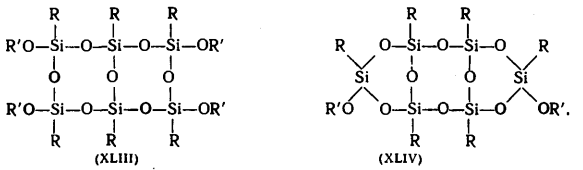


where □ is the methyl-substituted Si_4O_4 ring.

The simultaneous hydrolysis of $(CH_3)_2SiCl_2$ with RCH_3SiCl_2 (where R = CH_2CH_2CN)[427] yields monocyclic products and also a polycyclic compound which analysis and infrared spectroscopy indicated to be tricyclic.

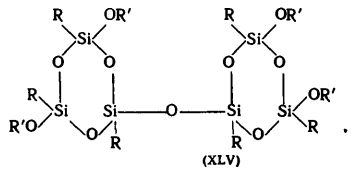
Spirocyclosiloxanes (XXXIX) and (XL) have been obtained in the thermal decomposition of the product of simultaneous hydrolysis of dimethyldichlorosilane with silicon tetrachloride [538,539]. The structure of octamethylspirocyclopentasiloxane has been confirmed by X-ray diffraction [540,541], which gave Si–O = 1.64 ± 0.03 Å.

Hydrolysis of methyl- and ethyl-triethoxysilane [542,543] has yielded compounds corresponding to (XLIII) and (XLIV). The bridged structure (XLV) is also possible:



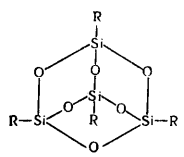
(XLIII)

(XLIV)



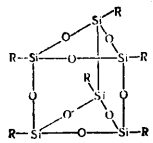
(XLV)

The hydrolysis of trisubstituted derivatives produces various types of polycyclic organosiloxanes. Compounds with the hexamethylenetetramine type of structure have been described — (XLVI) (R = iso-C_3H_7, t-C_4H_9) [544,545]:

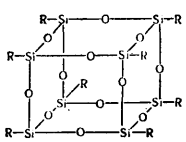


(XLVI)

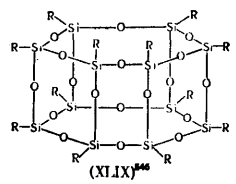
The interesting three-dimensional polycyclic compounds (XLVII), (XLVIII), and (XLIX) were obtained by the thermal degradation of the hydrolysis products of $RSiX_3$: [542–548]



(XLVII) [542,546]



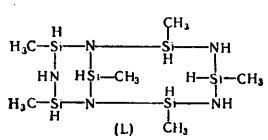
(XLVIII) [542,543,546–548]



(XLIX) [546]

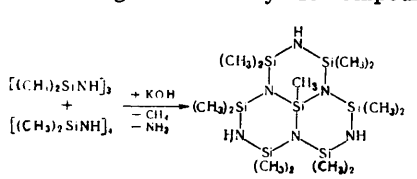
Polycyclic compounds containing Si–N and Si–S bonds have also been described.

Ammonolysis of CH_3SiHCl_2 has produced compound (L): [462]

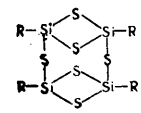


(L)

Catalytic rearrangement of a mixture of hexamethylcyclotrisilazane and octamethylcyclotetrasilazane in the presence of KOH has given the tricyclic compound [549]



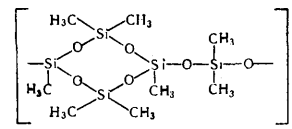
The reaction of alkyltrichlorosilanes with hydrogen sulphide produces the polycyclic compounds (LI): [550,551]



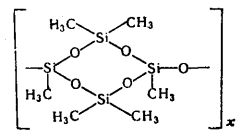
(LI)

Cyclolinear macromolecular compounds (XXXVIII) are obtained by simultaneous hydrolysis of organotrichlorosilanes and a diorganodichlorosilane [552–555], by oxidation of the ethyl groups in $[(C_6H_5)(C_2H_5)SiO]_3$, or by splitting-off of phenyl groups from the same compound by the action of sulphuric acid [374–377].

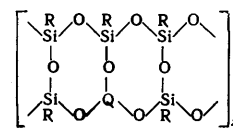
Simultaneous hydrolysis of hexamethyl-1,5-dichlorocyclotetrasiloxane and dimethyldichlorosilane [556] produces polymers of the following structure:



Simple hydrolysis of hexamethyl-1,5-dichlorocyclotetrasiloxane gives the linear polymer

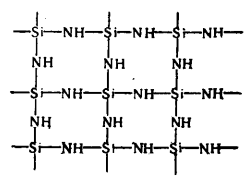


Cyclolinear condensed polysiloxanes of structure (XLI) are obtained by hydrolysis of organotrichlorosilanes $RSiCl_3$ (where R = H, alkyl, or aryl). The inorganic prototypes of this class are known [557], as well as organic derivatives. The phenyl-substituted polysiloxanes $[C_6H_5SiO_{1.5}]_x$ are said to have a stereoregular structure [558,559] (*cis*-syndiotactic). The polyorganosiloxanes obtained by simultaneous hydrolysis of organotrichlorosilanes with aluminium, titanium, or tin halides have the same polycyclic structure [1,2,560]:



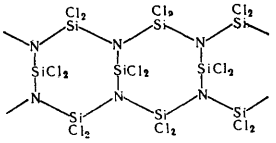
where Q = Al, Ti, or Sn. Thermogravimetric data show that these polymers are highly thermostable.

Polycyclosilazanes are produced by ammonolysis of the silicon polychlorides $HSiCl_3$ or $SiCl_4$; the latter gives "silicodiimide" $[Si(NH_2]_x$, which has the polycyclic structure (LII) [561–563], and it can be assumed that trichlorosilanes also yield a polycyclic product.



(LII)

The reaction between silicon tetrachloride and nitrogen under the action of an electric discharge produces monocyclic and linear products, and also complex polycyclic polymers[454,455]:



The inorganic cyclic silicon compounds and their organic derivatives form a large group of substances, which fall into various classes of inorganic and organic–inorganic compounds. The inorganic rings which form the basis of their molecules impart to them a range of specific properties which are greatly different from those of cyclic organic compounds. The high reactivity towards nucleophilic and electrophilic reagents shown by inorganic rings containing silicon is a characteristic of all inorganic cyclic compounds known at present; this is not shown by organic carbocyclic compounds, and opens up great possibilities in respect of their use in the preparation of organic–inorganic and inorganic compounds, particularly polymers, by various methods.

Inorganic cyclic compounds containing silicon are of special significance for the production of polymers whose main chains are composed of inorganic atoms. Furthermore, the study of the structure, properties, and reactivity of inorganic cyclic silicon compounds and their organic derivatives may help in solving many theoretical problems in organic–inorganic and inorganic chemistry.

Not all the preparative methods possible in this interesting branch of chemistry have yet been applied; very little has been done, but there are great prospects for the future. These compounds lie on the boundary between organic and inorganic chemistry, and further studies may exert a fruitful influence on the development of this little-studied branch of chemistry.

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PERCHLORIC ACID

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1. INTRODUCTION

Perchloric acid $HClO_4$ differs substantially from other inorganic oxyacids in many respects, for example the volatility of anhydrous perchloric acid, its instability on storage, especially above room temperature, the difference in properties between the anhydrous acid and its hydrates.

Anhydrous perchloric acid contains more than 63% of available oxygen, *i.e.* oxygen which can be used in the oxidation of various reductants or liberated as gas.

This determines the value of perchloric acid as an oxidant, its oxidising properties being maintained on slight dilution of the acid with water. A diminution in the concentration of perchloric acid affects its redox potential far more rapidly than in the case of nitric acid.

Perchloric acid finds varied application both in industry and in the laboratory, for example in the electrolytic polishing of metals, as catalyst for hydrolysis or esterification and various rearrangements in organic compounds. It is used also, instead of or in addition to nitric and sulphuric acids, in wet combustion in quantitative organic analysis, to break down complicated minerals and ores in their quantitative analysis, etc.

Although perchloric acid has been known for more than 150 years, it has not yet been adequately investigated.

2. BRIEF HISTORICAL OUTLINE

Perchloric acid was discovered by Stadion in 1816.[1,2] On treating the product obtained by the cautious fusion of potassium chlorate with sulphuric acid, he found that the residue left after removal of excess of the acid, contained, in addition to potassium sulphate, the potassium salt of a new, hitherto unknown acid. Analysis of this salt showed its oxygen content to be 45.92%, its composition corresponding to the formula $KClO_4$.

Stadion found that this salt can be obtained also by the anodic oxidation of potassium chlorate, for which purpose he used a battery of twenty voltaic cells. On heating the new salt with three parts by weight of sulphuric acid containing 30% of water, he obtained in the distillate a fraction consisting of an aqueous solution of a new acid, which he termed "oxychloric" acid; later the name "perchloric acid" was applied to it. Stadion showed that it can be obtained also by the electrochemical oxidation in aqueous solution of chlorine dioxide, which he had discovered.

The preparation of perchloric acid by Stadion's method is seen to be based on the reactions

$$4KClO_3 = 3KClO_4 + KCl;$$

$$KClO_4 + H_2SO_4 + aq. = KHSO_4 + HClO_{4aq}.$$

Sérullas reported[3] that attempts to obtain perchloric acid by Stadion's method invariably terminated in explosions, which he attributed to the explosive decomposition, under the experimental conditions, of chloric acid formed from potassium chlorate by the action of sulphuric acid. Sérullas probably had not noticed that Stadion had treated the chlorate after fusion, *i.e.* actually the perchlorate obtained from the chlorate, with sulphuric acid. This suggestion is supported by the fact that, in another paper[4] and also in a German translation thereof[5], Sérullas reported his discovery of the conversion of chlorate into perchlorate on careful fusion.

Hence Sérullas assumed that in Stadion's method the perchloric acid is formed, not from the perchlorate by the action of sulphuric acid, but from chloric acid. It may be supposed that it was precisely this erroneous interpretation of Stadion's process that led Sérullas to develop a new method for obtaining perchloric acid. The method is based on the gradual decomposition of chloric acid when its solutions are concentrated by evaporation under any conditions. Decomposition of chloric acid occurs when its concentration reaches a critical value, above which the acid cannot exist. The process is completed by distilling off the water present in the system and then distilling over the perchloric acid in the form of an azeotrope.

Sérullas was also able to obtain a "solid perchloric acid"[6]. This was done on distilling a mixture of the constant-boiling perchloric acid (azeotrope) and sulphuric acid in the proportions 1 : 4–5 by volume. A mixture of the solid and liquid forms of perchloric acid passed into the distillate. Sérullas was unable to isolate the pure solid acid from this mixture, and hence did not establish its composition.

To Sérullas belongs the honour of introducing the use of perchloric acid for the quantitative determination of potassium in the presence of other cations[7]. This analytical method is based on the extremely low solubility of $KClO_4$ in alcohol.

The following rather clumsy procedure was suggested by Henry[8] for the preparation of perchloric and chloric acids. A solution of $ZnSiF_6$ is first obtained by the interaction of ZnO and H_2SiF_6, and this is then heated with $KClO_4$ or $KClO_3$ respectively to give $Zn(ClO_4)_2$ or $Zn(ClO_3)_2$ in solution, which with aqueous $Ba(OH)_2$ gives a solution of $Ba(ClO_4)_2$ or $Ba(ClO_3)_2$. Finally, the action of an equivalent amount of dilute sulphuric acid on these solutions yields aqueous perchloric or chloric acid.

Nativelle published[9] a more convenient recipe for obtaining perchloric acid by Stadion's method. Kolbe[10] reported the preparation of perchloric acid by the electrochemical oxidation of hydrochloric acid, and this possibility was confirmed a little later by Riche[11]. Subsequently, especially during recent years, this method of obtaining perchloric acid has formed the subject of many patents issued in various countries. At the present time it is used to produce perchloric acid industrially.

After Stadion and Sérullas the most important results were obtained by Roscoe[12–14], who found that perchloric acid obtained by the evaporation of dilute aqueous solutions until dense white fumes appeared had a constant boiling point of 203° and remained unchanged in composition on being distilled. He proved that the solid perchloric acid discovered by Sérullas was a monohydrate of the acid $HClO_4.H_2O$.

To Roscoe is due also to the credit of discovering anhydrous perchloric acid, which he obtained by distilling a mixture of the constant boiling perchloric acid and 96.5% sulphuric acid in the proportions 1 : 4 by volume. According to him, a mobile yellowish liquid begins to pass into the receiver at 110°, but on continued distillation the temperature gradually rises to 200°, and a thick oily liquid begins to enter the receiver, this giving a white crystalline mass on contact with the more volatile portion of the distillate.

It was established that the readily volatile mobile liquid was anhydrous perchloric acid; while the involatile oily

liquid was a constant-boiling acid of composition approximating to a dihydrate of the acid $HClO_4.2H_2O$. The anhydrous acid and the dihydrate react to give the monohydrate, a crystalline solid.

Hence formation of the monohydrate takes place according to the equation

$$HClO_4 + HClO_4 \cdot 2H_2O = 2HClO_4 \cdot H_2O \ .$$

Roscoe found that the reverse reaction takes place above 110°: *i.e.* the anhydrous acid and the dihydrate are formed from the monohydrate. He regarded this latter method of obtaining anhydrous perchloric acid as the better, since the monohydrate, being completely stable on storage, makes it possible to obtain the unstable anhydrous acid at any time.

The oxidation of ammonium perchlorate with a mixture of nitric and hydrochloric acids, reported by Schloesing[15], must also be mentioned. He suggested using the free perchloric acid obtained from the NH_4ClO_4, without isolating it from the solution, for the quantitative determination of potassium by Sérullas' method[7]. Later this reaction was employed by Willard[16] to obtain the azeotrope of perchloric acid from ammonium perchlorate.

Kreider[17] suggested obtaining the azeotrope by the double decomposition of sodium perchlorate and fuming hydrochloric acid:

$$NaClO_4 + HCl \rightleftarrows HClO_4 + NaCl.$$

The equilibrium is shifted to the right owing to the limited solubility of NaCl in this system. After removal of the bulk of the NaCl, the perchloric acid is obtained from the reaction as an aqueous solution, and freed from salts and water by distillation.

Vorländer and Schilling[18] found that, when a mixture of $KClO_4$ and 96–97% H_2SO_4 is heated in a vacuum, anhydrous perchloric acid at once distils over, not its hydrates as found by Roscoe and his predecessors, who had carried out the distillation of perchloric acid under atmospheric pressure. Michael and Conn[19] also suggested the use of a vacuum in the distillation.

Smith[20] suggested the use of oleum to remove water from the azeotrope and thus obtain the anhydrous acid. This resulted in a mixture of the latter with sulphuric acid, from which the perchloric acid was isolated by distilling it off in a vacuum. Zinov'ev[21] proposed to carry out this unsafe operation in a continuous-flow apparatus consisting essentially of a slightly inclined externally heated tube. The mixture to be separated is fed into one end of the tube, and from the other end the spent sulphuric acid flows out into a receiver, while the perchloric acid vapour escapes through an outlet in the middle of the tube into another, well cooled receiver. The perchloric acid distils off in a vacuum.

The distillation process is completely safe, since only a small quantity of the mixture undergoing separation is present in the hot zone of the apparatus, and also because it remains hot for only a few seconds, considerably less than the induction period for decomposition of the acid.

The anhydride of perchloric acid was first obtained by Michael and Conn[22].

3. FORMS OF PERCHLORIC ACID

Perchloric acid is the only oxyacid of chlorine which can exist in the anhydrous state, although it is unstable in this form. Even at room temperature, only a few hours after being prepared, it begins to decompose, at a rate which increases with time. Being extremely hygroscopic, perchloric acid vigorously adds on water to form several hydrates. The monohydrate $HClO_4.H_2O$ was discovered by Sérullas[6], but its composition was established by Roscoe[12], who obtained data indicating the existence of a dihydrate $HClO_4.2H_2O$ as well. The chief properties of the dihydrate were studied by van Wijk[23,24], who also discovered and characterised the higher hydrates of perchloric acid.

Fig. 1 shows the melting-point diagram constructed by van Wijk, and Fig. 2 the part corresponding to high water contents. The maxima in Fig. 1, corresponding to 50.0 and 33.3 mole% $HClO_4$, show the existence in the $HClO_4$–H_2O system of a monohydrate and a dihydrate of perchloric acid, which are only slightly dissociated at their melting points (50° and -17.8° respectively, according to van Wijk).

At the higher water contents the diagram is very complicated (Fig. 2).

Steady crystallisation of the dihydrate (33.3 mole % $HClO_4$) at -17.8° is observed also with rather more dilute perchloric acid, but at an $HClO_4$ content of ~29 mole% the character of the crystallisation depends on the degree and conditions of cooling of the acid. This is evident simply from the fact that the lower part of the right-hand curve representing crystallisation of the dihydrate (Fig. 2) contains three eutectic points, two of which lie in the metastable region.

The hydrate $HClO_4 \cdot 2.5H_2O$ melts at -29.8°, which is very close to the eutectic point of this hydrate with the dihydrate. The temperature at which a eutectic mixture of the two hydrates solidifies is almost the same (-29.8°). The hydrate $HClO_4.3H_2O$ can exist in two forms, the β form being metastable throughout its range of existence, and the α form being stable only over a very narrow range of compositions, 23.7–25.0 mole % $HClO_4$. Over the rest of the range the α form is metastable.

The α-$HClO_4.3H_2O$ is formed from the β form on cooling. The melting point of the α form of the trihydrate is -37°, and its eutectic with the dihydrate crystallises at -39.4°.

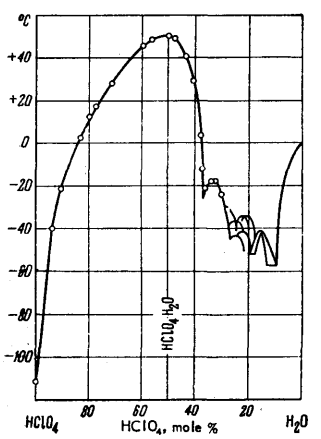


Fig. 1. Melting-point diagram for the perchloric acid–water system over the concentration range 0–100% $HClO_4$.[24]

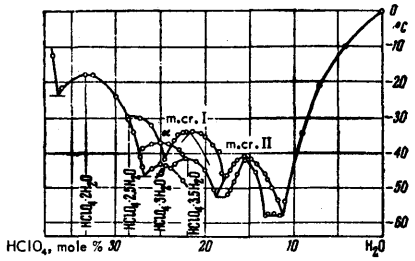


Fig. 2. Melting-point diagram of the perchloric acid–water system over the concentration range 0–36 mole % $HClO_4$.[24]

To the left of its maximum the curve for β-$HClO_4.3H_2O$ joins the dihydrate curve at the eutectic point having a crystallisation temperature of -46.5°, which is the final temperature of crystallisation of perchloric acid containing rather less than 29 mole% $HClO_4$. To the right of the extreme point of stable existence of the α form of the trihydrate its liquidus curve enters the region of mixed crystals I, in relation to which α-$HClO_4.3H_2O$ is metastable.

The hydrate $HClO_4.3.5H_2O$ crystallises poorly, only after prolonged cooling, and always from the vitreous state. For this reason, van Wijk did not analyse this hydrate. For the same reason its melting point was not determined exactly (about -41°).

The liquidus curve of $HClO_4.3.5H_2O$ covers the range of compositions from 23.8 to 18.8 mole% $HClO_4$, where it intersects the liquidus of the mixed crystals II at -52.5°. The hydrate $HClO_4.3.5H_2O$ forms a eutectic with β-$HClO_4.3H_2O$ crystallising at -44.3°. This and also the fact that the hydrate $HClO_4.3.5H_2O$ remains in a metastable state below the curve for the mixed crystals I throughout its range of existence do not inspire complete confidence in the existence of the hydrate $HClO_4.3.5H_2O$, as van Wijk himself pointed out[24].

Van Wijk was unable to separate the mixed crystals I from the liquid phase, and so he was unable to analyse them. The liquidus of this phase extends from 24.6 to 17.7 mole% $HClO_4$, so that on the left-hand side this curve approaches from below the liquidus curve of the hydrate α-$HClO_4.3H_2O$.

The mixed crystals II were also investigated very tentatively. Their liquidus extends from 17.7 to 11.6 mole% $HClO_4$. Kurnakov[25] noted the existence of berthollide phases in these mixed crystals.

When an acid containing less than 11.3 mole% $HClO_4$ is cooled, crystals of ice separate. The crystallisation curve for water intersects that for the mixed crystals II at -58.0°.

Thus according to van Wijk the hydrates of perchloric acid are characterised by the following melting points:

$HClO_4.H_2O$	50° (according to Smith[26] 49.905°)
$HClO_4.2H_2O$	−17.8°
$HClO_4.2.5H_2O$	−29.8°
$HClO_4.3H_2O$:	
α form	−37°
β form	−43.2°
$HClO_4.3.5H_2O$.	−41.4°

4. PROPERTIES OF PERCHLORIC ACID HYDRATES

According to Berthelot[27], the heat of solution of anhydrous perchloric acid is $L_{600}^{13°} = 20.3$ kcal mole^{-1}. This value is inexact, since Berthelot did not work with the completely anhydrous acid. Krivtsov *et al.*[28] determined the heats of solution of perchloric acid over the concentration range 21–100 mole% $HClO_4$. They give a table and a graph showing the dependence of the heat of solution on the initial acid concentration (Fig. 3).

The heats of solution $L_{800}^{25°}$ of the anhydrous acid, the monohydrate, and the dihydrate are[28] 21.15 ± 0.04, 7.81 ± ± 0.04, and 5.43 ± 0.04 kcal mole^{-1} respectively. Therefore the enthalpy of hydration of anhydrous perchloric acid to the monohydrate is $\Delta H_{25} = -13.34 \pm 0.07$ kcal mole^{-1}, and that to the dihydrate is -15.72 ± 0.07 kcal mole^{-1}.

The heat of fusion of the monohydrate of perchloric acid is[28] 2.48 ± 0.08 kcal mole^{-1}.

The density and the viscosity of perchloric acid up to 70% concentration have been studied by many investigators, beginning with Roscoe[12] and van Wijk[24], and including Reyher[29], van Emster[30], Brickwedde[31], Clark and Putmann[32], Garret and Woodruff[33], Simon and Weist[34], Simon and Richter[35], and also Smith and Goehler[26].

The density has been determined over the whole range of concentrations only by van Wijk[24] (at 20° and 50°) and by Zinov'ev and Babaeva[36] (at 20°, 55°, and 75°, Fig. 4).

As can be seen from Fig. 4, the density of perchloric acid increases on hydration, reaching a maximum with the monohydrate. Since this occurs in the liquid state, the high density of the monohydrate must be assumed to depend on peculiarities of its molecular structure. It must be noted in this connection that the volume of water in the monohydrate of perchloric acid, found as the difference in molar volume between the monohydrate and the anhydrous acid, is only ~7.5 compared with 12–15 cm^3 mole^{-1} in the hydrates of other acids and various salts.

It must be borne in mind that no free water is present in concentrated perchloric acid. If the acid concentration exceeds 84.8%, the whole of the water is present as the

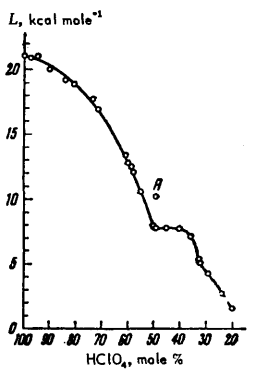


Fig. 3. Heat of solution in the perchloric acid–water system[28].

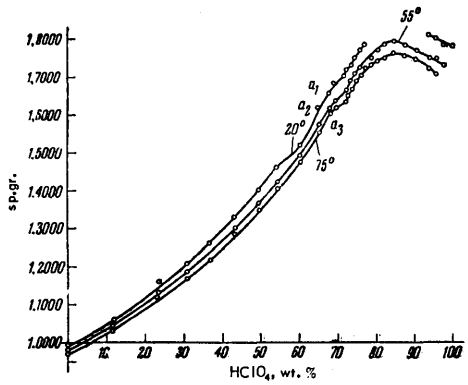


Fig. 4. Density isotherms (at 20°, 55°, and 75°) for the perchloric acid–water system [36].

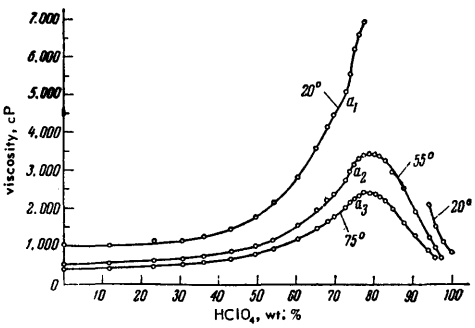


Fig. 5. Viscosity isotherms (at 20°, 55°, and 75°) for the perchloric acid–water system [36].

monohydrate, and such a specimen consists of the anhydrous acid and the monohydrate. When concentrated perchloric acid is strongly cooled, the monohydrate which it contains separates as a solid phase.

The viscosity of perchloric acid has been determined over the whole concentration range only by van Wijk [24], Simon and Weist [34], and Zinov'ev and Babaeva [36]. The graphs (Fig. 5) show that maximum viscosity occurs below the concentration than corresponding to the monohydrate. At 50° maximum viscosity occurs [35] with the 80% acid, at 55° with the 79% acid [36], and at 75° with 78% of perchloric acid [36]. The shift in maximum viscosity can be explained by an increasing degree of disproportionation of the monohydrate with rise in temperature:

$$2HClO_4 \cdot H_2O \rightleftarrows HClO_4 + HClO_4 \cdot 2H_2O.$$

5. MOLECULAR STRUCTURE OF PERCHLORIC ACID HYDRATES

The very considerable difference in properties between anhydrous perchloric acid and its monohydrate has led to a detailed study of their molecular structure.

Volmer [37] found that the X-ray diffraction pattern of crystals of the monohydrate was identical with that of ammonium perchlorate NH_4ClO_4. This led to the conclusion that the monohydrate, like the perchlorate, has an ionic structure, *i.e.* that it is oxonium perchlorate H_3OClO_4. Crystals of oxonium perchlorate have an orthorhombic structure with lattice constants a = 9.065, b = 5.569, and c = 7.339 Å.

Fonteyne [38], Simon [39], Redlich *et al.* [40], Simon and Weist [34], Millen and Vaal [41], and Mullhaupt and Hornig [42] investigated the Raman spectra of perchloric acid and found all the principal frequencies both of the perchlorate ion and of the pseudo-acid form of perchloric acid.

Richards and Smith [43] and at the same time, but independently, a Japanese group [44–46] employed proton magnetic resonance to study the structure of the monohydrate of perchloric acid. Lee and Carpenter [47] used an X-ray method for the same purpose, and Bethell and Sheppard [48] applied infrared spectroscopy.

The spectra of solutions containing less than 77% $HClO_4$ contain [34] lines at 460, 625, 928, and 1120 cm^{-1}. These frequencies coincide with the same lines in the Raman spectra of solutions of the salts. Hence the above frequencies are due to the perchlorate ion ClO_4^-, and at concentrations below 77% $HClO_4$ perchloric acid is entirely in the aci-form $H[ClO_4]$.

When the acid concentration is raised above 85% (the monohydrate contains 84.8% of $HClO_4$), new lines appear in the spectrum, their intensity increasing with increase in the acid concentration. At the same time the ClO_4^- lines become less intense. Above a concentration of 99% the latter lines disappear, and only those of the pseudo-acid form of perchloric acid remain: 284, 424, 577, 740, 1001, and 1210 cm^{-1}, and also a line at 3300 cm^{-1}.

These results obtained by Simon and Weist were confirmed by later work. Thus Millen and Vaal [41] published a table of frequencies due to ClO_4^-, H_3OClO_4, and anhydrous $HClO_4$. The spectra were determined at -185°. The frequencies which they found differed little from those obtained earlier [34].

Mullhaupt and Hornig [42] obtained data showing that the spectrum of perchloric acid monohydrate contains two bands, one at 1500–1690 cm^{-1} and the other at 2400–3600 cm^{-1}. These bands were assigned to the oxonium ion (H_3O^+).

Taylor and Vidale [49] published more exact data, assigning to the oxonium ion the frequencies 1175 ± 2, 1577 ± 5, 3100 ± 50, and 3285 ± 10 cm^{-1} at 20°. Among those assigned by Simon and Weist [34] to the anhydrous acid was also 3300 cm^{-1}, as mentioned above. It follows from Taylor and Vidale's work that this frequency is due to the oxonium ion, which must therefore be present in anhydrous perchloric acid. This was established too by Richards and Smith [43], and also by the group of Japanese workers [44–46]. The oxonium ion was found to have a pyramidal structure, in which the O–H distances were 1.02 Å and the H–H distances 1.72 Å. Below -123° the oxonium ion is fixed in the lattice, but above this temperature it acquires an additional degree of freedom.

Lee and Carpenter [47] confirmed that the ClO_4^- ion present in oxonium perchlorate is almost exactly tetrahedral, with a mean Cl–O distance of 1.42 Å. Each oxonium ion in the crystal lattice is surrounded by twelve oxygen atoms.

Rosolovskii and Zinov'ev [50] reported the occurrence of polymorphism in oxonium perchlorate. They established that the enantiotropic transition temperature is -24.9°. The high-temperature modification can exist in a supercooled

condition for a long time. The densities of the high-temperature and low-temperature modifications are $d_4^{25^\circ}$ = = 2.095 and 2.040 respectively. Zinov'ev and Babaeva reported[51] that the H_3OClO_4–CH_3COOH system contains the compound $H_3OClO_4.2CH_3COOH$. Hence perchloric acid monohydrate (oxonium perchlorate) does not lose water of hydration in anhydrous acetic acid, and behaves as a chemical individual.

The molecular structure of perchloric acid hydrates containing two and more molecules of water has been studied by Michelsen[52]. The length of the Cl–O bond in the ClO_4^- ion in the higher hydrates was determined from the X-ray distribution curve. Its mean value was found to be 1.49 Å, whence it follows that the distance between the oxygen atoms is 2.43 Å. Hydrogen bond formation was found to occur between molecules in melts of the hydrates.

Smith and Goehler[53] put forward the view that the dihydrate of perchloric acid is a monohydrate of oxonium perchlorate:

$$HClO_4 \cdot 2H_2O \longrightarrow H_3OClO_4 \cdot H_2O.$$

They extended this view to the other, higher hydrates. Hence

$$HClO_4 \cdot 2{,}5H_2O \longrightarrow H_3OClO_4 \cdot 1{,}5H_2O,$$
$$HClO_4 \cdot 3H_2O \longrightarrow H_3OClO_4 \cdot 2H_2O,$$
$$HClO_4 \cdot 3{,}5H_2O \longrightarrow H_3OClO_4 \cdot 2{,}5H_2O.$$

In their opinion, the difference between the α and β forms of perchloric acid trihydrate is that one represents an ordinary trihydrate $HClO_4.3H_2O$, while the other form is the dihydrate of oxonium perchlorate $H_3OClO_4.2H_2O$. However, these workers gave no adequate grounds in support of this view.

6. VOLATILITY OF PERCHLORIC ACID

Anhydrous perchloric acid is very volatile, but it is impossible to distil it at atmospheric pressure owing to decomposition.

The distillation of both anhydrous perchloric acid and its hydrates was described in detail by van Wijk[24]. He found that on prolonged distillation the boiling point of the acid passes through a maximum, regardless of the initial concentration. If acid containing less than 72.4% $HClO_4$ is distilled, the distillate consists initially of water until the concentration of the liquid undergoing distillation reaches 72.4%. The vapour then has the same composition: *i.e.* ultimately an azeotrope of perchloric acid and water is obtained. The same occurs, *i.e.* an azeotrope is formed, when highly concentrated perchloric acid, for example the 100% acid, is distilled. In this case the vapour is a mixture of $HClO_4 + Cl_2O_7$, the boiling point of the acid gradually rising, while its concentration gradually falls, tending to the composition of the azeotrope.

Discussing his results on the distillation of perchloric acid, van Wijk concluded: "Concentrated perchloric acid must be regarded as a mixture of the anhydride of perchloric acid and water".

Since water which appears in the presence of 100% perchloric acid will pass into the monohydrate, the above conclusion of van Wijk must be restated: "Concentrated perchloric acid is a mixture containing the anhydride and the monohydrate of perchloric acid". In other words, concentrated perchloric acid is an equilibrium system:

$$3HClO_4 \rightleftarrows Cl_2O_7 + H_3OClO_4. \quad (1)$$

TABLE. Published data on the boiling point of perchloric acid.

Pressure, mm Hg	B.p., °C	References
11	19	19
15—20	14—17.3	30
18	16	24
56	39	18

No systematic investigation has yet been made of the variation of the vapour pressure of perchloric acid with temperature. Isolated data available in the literature are given in the Table.

Application of the Clausius–Clapeyron equation to these data enables an equation to be derived, relating the logarithm of the vapour pressure to the reciprocal of the absolute temperature:

$$\log P\,(\text{mm}) = -\frac{1923}{T} + 7.91. \quad (2)$$

Calculation based on this equation gives the boiling point of perchloric acid under atmospheric pressure as 109°, not 130°, as was found by Hantzsch[54], also by extrapolation. The value obtained for the heat of vaporisation is 8.80 kcal mole^{-1}, and for the Trouton constant 23.0.

It must be emphasised that the data in the Table give only a very rough characterisation of perchloric acid.

7. PERCHLORIC ACID AS AN ELECTROLYTE

Perchloric acid acts solely as a monobasic acid both in the anhydrous state and in the form of its hydrates, thus differing substantially from, for example, iodic acid, whose hydrates are polybasic acids.

On the basis of conductivity measurements on aqueous solutions of perchloric acid, Ostwald[55] included it among the strongest electrolytes. This has been confirmed many times by other workers. However, it cannot be regarded as sufficient to assess the strength of an acid from the electrical conductivity of its aqueous solutions. Many attempts have therefore been made to employ solvents other than water and also other methods to assess strong acids as electrolytes. One of these methods is based on the measurement of special functions giving an estimate of acidic properties, for example the Hammett function H_0 [56] or the similar function J_0 (otherwise symbolised as C_0 and H_R).

Lemaire and Lucas[57], Smith *et al.*[58], and Ludwig and Adams[59] have given values of the Hammett function for solutions of perchloric acid in acetic acid (anhydrous and containing up to 5% of water). It has been shown that in acetic acid perchloric acid behaves as a very strong electrolyte. The same conclusion was reached by Dahn *et al.*[60], who determined the function J_0 for solutions of perchloric acid in a mixed solvent (dioxane–water).

Deno *et al.*[61] determined the functions H_0 and H_R for aqueous solutions of perchloric and nitric acids over the concentration range 0–60%. Perchloric acid was found to be a stronger electrolyte than nitric acid. A similar result was obtained by Bonner and Lockhart[62].

A common feature of all the measurements of H_0, J_0, etc. has been the not very high concentration of the samples of perchloric acid examined. Thus Hammett and Deyrup[56] confined their investigations to acid containing 64% $HClO_4$. Bonner and Lockhart[62] examined a higher concentration, 71.3%.

A comparative appraisal of perchloric and nitric acids as electrolytes was given by Redlich[63] on the basis of the Raman spectra and nuclear magnetic resonance. It was established that dissociation in the highly concentrated acid was due to the presence of water, according to the equation

$$H_2O+HClO_4 = H_3O^+ + ClO_4^- .$$

Hood *et al.*[64] showed that three species exist throughout the concentration range, including 100% perchloric acid, these being the pseudo-acid form $[O_3ClOH]$ and the ions H_3O^+ and ClO_4^-. This is the reason why perchloric acid conducts electricity at all concentrations.

Redlich points out[63] that nitric acid behaves differently: the acid having the composition $HNO_3.H_2O$ undergoes very little dissociation, and the more concentrated acid is practically undissociated. He explains such behaviour by not only the anhydrous acid but even the monohydrate being in the pseudo-acid form $[HNO_3.H_2O]$.

According to Simon and Weist's results[34], 100% nitric acid exists in the pseudo-acid form $[O_2NOH]$ only in the liquid state. Simon and Weist found that the Raman spectrum of the anhydrous acid in the solid state contains practically no NO_2 lines, but does contain a strong NO_3 line (at ~1050 cm^{-1}), and also a characteristic NO_3 line at 1400 cm^{-1}.

From nuclear magnetic resonance measurements, Redlich[63] obtained the following dissociation constants: $HClO_4$ 38, HNO_3 22, and CF_3COOH 1.8. According to old data, the dissociation constant of nitric acid is 21. It is evident from these results that perchloric acid is a stronger electrolyte than nitric acid.

8. PERCHLORIC ACID IN THE FORMATION OF ACIDIUM SALTS

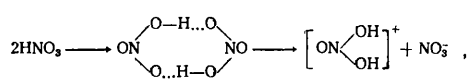
A study of the optical properties of acids made by Schäfer[65] showed that anhydrous nitric acid is similar to its esters but substantially different from its alkali-metal salts in optical properties, and that on dilution with water, nitric acid and its salts become identical in this respect.

This discovery was developed by Hantzsch and his co-workers[66–70], who showed that this property is not specific to nitric acid, but that similar relations are observed with other acids, except those which cannot be studied optically.

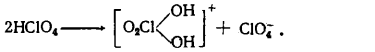
The results led Hantzsch to put forward a theory which postulates that acids exist in two forms, the so-called pseudo-acid form and the true or aci-form.

Measurements showed that nitric, sulphuric, and perchloric acids are able to conduct electricity even in the anhydrous state, *i.e.* in the pseudo-acid form. This indicates the presence of ions, and hence of salts, in anhydrous acids.

Hantzsch explained salt formation in terms of some of the molecules of the anhydrous acid reacting as proton-acceptors, obtaining their protons from the remaining molecules of the same acid, which act as proton-donors. According to this view, these acids undergo self-protonation, for example in the case of nitric acid



and in the case of perchloric acid



Hantzsch wrote the equation for perchloric acid by analogy, since this acid gives no absorption spectra in the ultraviolet, but does possess electrical conductivity.

He suggested[66] the following equations for a mixture of nitric and perchloric acids:

$$HNO_3 + HClO_4 = H_2NO_3^+ + ClO_4^-,$$
$$HNO_3 + 2HClO_4 = H_3NO_3^{2+} + 2ClO_4^- .$$

In support of these equations Hantzsch and Berger[68] reported that the conductance of the substance obtained in the first equation corresponds to a binary electrolyte, while the substance obtained in the second equation has a conductance corresponding to a ternary electrolyte. Furthermore, they found that, on electrolysis of these acidium salts, the nitric acid migrates to the cathode.

A paper by Hughes *et al.*[71] on the kinetics and mechanism of the nitration of aromatic compounds gives data indicating that the nitrating mixture contains high concentrations of NO_2^+. However, these workers postulate the existence also of the ion $H_2NO_3^+$ (mentioned by Hantzsch, but only as an intermediate stage), as follows from their equations

$$HNO_3 + H_2SO_4 \rightleftarrows H_2NO_3^+ + HSO_4^-,$$
$$H_2NO_3^+ \rightleftarrows NO_2^+ + H_2O .$$

Thus Hughes *et al.*[71] consider that the ion $H_2NO_3^+$ is unstable, and in H_2SO_4 medium readily passes into NO_2^+ by splitting off water. The same paper notes the possibility of the formation of $H_2NO_3^+$ even in the absence of sulphuric acid:

$$HNO_3 + HNO_3 \rightleftarrows H_2NO_3^+ + NO_3^-,$$
$$H_2NO_3^+ \rightleftarrows NO_2^+ + H_2O,$$
$$H_2O + HNO_3 = HNO_3 \cdot H_2O,$$

i.e. the self-protonation of nitric acid, as indicated by Hantzsch, is admitted.

In revising the results obtained by Hantzsch on acidium salts, Goddard *et al.*[72] prepared various acidium salts containing the NO_2^+ cation: $(NO_2^+)(ClO_4^-)$, $(NO_2^+)(HS_2O_7^-)$, $(NO_2^+)_2.(S_2O_7^{2-})$, etc.

The existence of the NO_2^+ cation in these salts was proved by numerous spectroscopic investigations by Goddard *et al.*[73], Ingold *et al.*[74,75], and Millen[76–78].

Gillespie made a series of investigations involving cryoscopic measurements on systems in concentrated sulphuric acid. In one of six papers on this topic[79] he gave results for solutions of ammonium perchlorate (NH_4ClO_4) and nitryl perchlorate (NO_2ClO_4) in sulphuric acid.

In contrast to the results discussed above and to be discussed below, Gillespie found that sulphuric acid is considerably stronger than perchloric acid, which is stronger than pyrosulphuric acid, *i.e.* that the strengths of these acids are in the order

$$H_2S_2O_7 < HClO_4 < H_2SO_4.$$

These views of Ingold, Goddard, and the other English workers differ from those of Hantzsch in assuming the existence, not of hydrated ions $H_2NO_3^+$, $H_3NO_3^{2+}$, etc., but of the ion NO_2^+ obtained from them by loss of water, in anhydrous acid systems capable of forming acidium salts. A second difference is that acidium salt formation is accompanied by the production of oxonium perchlorate, for example according to the equation

$$HNO_3 + 2HClO_4 = NO_2ClO_4 + H_3OClO_4.$$

Hantzsch's equations do not provide for the formation of oxonium perchlorate. The presence of H_3OClO_4 in the reaction mixtures was demonstrated experimentally by Ingold and others by extracting the oxonium perchlorate with nitromethane.

Simon and Weist[34], who made a thorough study of the Raman spectra of perchloric acid over the concentration range 41–100 wt.% $HClO_4$, found no frequencies which would indicate the existence of the ClO_4^- ion in the 100% acid, whose spectrum showed only lines due to the pseudo-acid form of perchloric acid. On this basis they rejected[34] both Hantzsch's and Ingold's equations. According to Simon and Weist, the conductivity of anhydrous perchloric acid depends on the possible contamination of the acid with moisture during the experiments, the amount being so minute that the monohydrate $HClO_4.H_2O$ formed cannot be detected spectroscopically, although it gives rise to conductivity. However, these workers mentioned also another possible reason for conductivity, which is that perchloric acid decomposes very readily into Cl_2O_7 and water, resulting in the formation of oxonium perchlorate, which dissociates in the acid. As a result, Simon and Weist[34] regard Hantzsch's hypothesis of the self-protonation of perchloric acid as incorrect.

Even in mixtures with various acids, perchloric acid forms acidium salts not as a proton-acceptor but solely as a proton-donor. This indicates that it is a stronger electrolyte than the other acids. A possible exception to this principle is pyrosulphuric acid, which gives the compound $(ClO_3^+)(HS_2O_7^-)$, obtained by the interaction of anhydrous perchloric acid with sulphur trioxide[80]. However, this single indication of the possibility of perchloric acid acting as a proton-acceptor has not yet been confirmed by anyone. Furthermore, it contradicts Gillespie's sequence[79]

$$H_2S_2O_7 < HClO_4 < H_2SO_4.$$

In the HNO_3–H_2SO_4 system Usanovich[81] demonstrated the existence of the compounds $HNO_3.H_2SO_4$ and $HNO_3.2H_2SO_4$. According to Ref. 72, these compounds readily rearrange into acidium salts of pyrosulphuric acid, $[NO_2^+][HS_2O_7^-]$ and $(NO_2^+)_2[S_2O_7^{2-}]$.

Usanovich *et al.*[82] were unable, from a study of the conductivity of mixtures of $HClO_4 + H_2SO_4$ in different proportions, to establish the existence of a compound. Perchloric and sulphuric acids are obviously unable to form acidium salts. Nevertheless, the self-protonation of sulphuric acid, for example according to the equation

$$4H_2SO_4 = H_3SO_4^+ + HS_2O_7^- + H_2SO_4 \cdot H_2O$$

has been proved.

In spite of Gillespie's sequence[79], however, it may be supposed that the strengths of sulphuric and perchloric acids are of the same order of magnitude, while that of pyrosulphuric acid is probably somewhat higher.

It is of interest to examine how perchloric acid behaves towards considerably weaker acids.

Hantzsch and Langbein[69] reported that they had obtained the compound $CH_3COOH.HClO_4$, and Usanovich and Sumarokova[83] also found the compound $2CH_3COOH.HClO_4$ to be formed in this system.

In the H_3PO_4–$HClO_4$ system Simon and Weist[34] detected the existence at room temperature of a 1 : 1 crystalline compound melting at 41°. The Raman spectrum of the molten compound at 50° contains lines due to anhydrous phosphoric and perchloric acids and also to the perchlorate ion. These workers concluded from an analysis of the spectra that, of the two possible mechanisms for the process

$$H_3PO_4 + HClO_4 = P(OH)_4ClO_4 \qquad \text{(according to Hantzsch)}$$

and

$$H_3PO_4 + 2HClO_4 = PO(OH)_2^+ + H_3O^+ + 2ClO_4^- \qquad \text{(according to Ingold)},$$

Hantzsch's scheme is the more probable.

Usanovich and his collaborators investigated the systems $HClO_4$–$CH_2ClCOOH$,[84] $HClO_4$–$CHCl_2COOH$,[85] and $HClO_4$–CCl_3COOH.[86] They showed that $CH_2ClCOOH$ and $CHCl_2COOH$ form equimolecular compounds with perchloric acid, and also compounds in which the molar ratio of perchloric acid to substituted acetic acid is 1 : 2. But CCl_3COOH and H_2SO_4 form no compounds with perchloric acid.

These facts show that the electrical conductivity of anhydrous perchloric acid depends, not on its self-protonation, but on the presence of ClO_4^- ions formed spontaneously in the anhydrous acid and present as an integral part thereof. This is readily explained on the assumption that the composition of perchloric acid is represented by the equilibrium

$$3HClO_4 \rightleftarrows Cl_2O_7 + H_3OClO_4. \qquad (1)$$

As mentioned above, the behaviour of the acid on distillation leads to the same conclusion.

The presence of Cl_2O_7 in perchloric acid was proved by Missan and Sukhotin[87] from the polarisation curves. They found that the Cl_2O_7 content in the acid increases as the concentration of the latter approaches 100%.

9. CHLORINE HEPTOXIDE

Preparation and Properties

Chlorine heptoxide was first obtained by Michael and Conn[22], who added perchloric acid slowly to phosphorus pentoxide cooled to -10°. After 24 h the resulting anhydride was distilled off under atmospheric pressure, and again distilled at 82°.

Meyer and Kesler[88] obtained chlorine heptoxide by the interaction of 3 parts of potassium perchlorate and 5 parts of chlorosulphonic acid at 75°. After purification by repeated vacuum distillation, a slightly coloured chlorine heptoxide of 98–99% purity was obtained in ~50% yield.

Goodeve and Powney[89] gradually added phosphorus pentoxide to perchloric acid which had been cooled to -78°. The mixture was allowed to reach room temperature, after which it was heated to 40°, and the resulting anhydride was distilled off under a vacuum, its vapour being led through phosphorus pentoxide and over active copper.

Zinov'ev and Rosolovskii[90] added anhydrous perchloric acid, allowing it to run in a thin film over the walls of the reaction vessel, on to phosphorus pentoxide dispersed on glass wool and cooled to -78°. The temperature of the reaction mixture was then raised to -38°, subsequently rising to -34°. The process was carried out at a pressure of 1–2 mm Hg, and the resulting chlorine heptoxide was distilled into a receiver cooled to -78°. The product obtained in this way was quite colourless, *i.e.* free from lower oxides of chlorine, and it contained also no perchloric acid, oxygen, or other contaminant. Later these workers[91] developed a method in which, instead of liquid perchloric acid, the vapour, formed from the liquid in a vacuum at room temperature, was fed to the phosphorus pentoxide.

Rosolovskii *et al.*[92] have also worked out an original method for obtaining chlorine heptoxide based on the reaction of oleum (for example 60%) with 70–75% perchloric acid. If the proportions of the reactants are chosen correctly, the oleum not only combines with the water of hydration but also removes the constitutional water from the perchloric acid. The resulting anhydride, being practically insoluble in sulphuric acid, separates as an upper layer on standing. It can be decanted from the sulphuric acid, and distilled.

These workers remark that all experiments with chlorine heptoxide require special care owing to its tendency to explode with great violence, the reason being unknown. In particular, the use of separating funnels with ground taps is excluded.

Chlorine heptoxide is a very mobile, heavy, colourless liquid which is immiscible with water. Therefore its interaction with water is slow. In spite of this, chlorine heptoxide fumes in air as a result of its reaction with moisture present in the latter, the monohydrate of perchloric acid being formed.

According to Goodeve and Marsh[93], the heat of solution of chlorine heptoxide in water is 50.0 ± 0.5 kcal mole^{-1} (sufficient water to produce a 0.01 *N* $HClO_4$ solution). According to Rosolovskii *et al.*[94] the value at a final dilution of 1 mole of Cl_2O_7 in 1758 moles of H_2O is 50.4 ± 0.3 kcal × × mole^{-1}. According to the same data, the heat of the reaction $Cl_2O_7 + H_2O = 2HClO_4$ is 8.1 kcal mole^{-1}.

Goodeve and Powney[89] reported the melting point and the boiling point of chlorine heptoxide as -91.5° and 80° respectively. They measured the vapour pressure at temperatures between -2.9° and 30.0°. From the results the following equation was deduced:

$$\log P(\text{mm}) = -\frac{1818}{T} + 8.03.$$

The heat of vaporisation of the anhydride calculated from Goodeve and Powney's data is 8.29 kcal mole^{-1} and the Trouton constant 23.4. According to Michael and Conn, the boiling point of the anhydride is 82°. The vapour pressure at 0° calculated from the above equation is 23.7 mm Hg, which considerably exceeds the vapour pressure of perchloric acid at 0° (7.4 mm Hg, calculated from the equation given earlier for the acid:

$$\log P(\text{mm}) = -\frac{1923}{T} + 7.91).$$

The enthalpy of formation of chlorine heptoxide is, according to Goodeve and Marsh[93], $\Delta H_{17°} = -63.4 \pm 3$ kcal × × mole^{-1}, while that of perchloric acid is $\Delta H = 8.62$ kcal × × mole^{-1} from the data of Vorob'ev *et al.*[95]

According to Zinov'ev and Rosolovskii[90], the melting point of chlorine heptoxide is -90 ± 2°, and the compound exists in two polymorphic modifications of enantiotropic type with a transition point at -100 ± 2°. They established[90] that above -23° chlorine heptoxide and carbon tetrachloride are miscible in all proportions.

The literature† contains only one mention of the density of chlorine heptoxide, a paper by Goodeve and Richardson[96] quoting the value $d_4^0 = 1.86$ found by Marsh.

The density of chlorine heptoxide according to Rosolovskii *et al.*[97] is shown in the following table:

Temperature, °C	20	10	0	−10	−20	−30	−40	−50
d_4^t	1.811	1.834	1.855	1.878	1.900	1.922	1.945	1.967

From these data the following equation was derived for the variation of density with temperature expressed in °K:

$$d_4^T = 2.4632 - 0.0022243\,T.$$

The viscosity of chlorine heptoxide was first determined by Zinov'ev and Rosolovskii[98], who obtained the following data:

Temperature, °C	20	10	0	−10	−20	−30
Viscosity, cP	0.698	0.776	0.867	0.975	1.087	1.200

These data show that the viscosity of chlorine heptoxide is rather lower than that of anhydrous perchloric acid. Actually, the values at 20° are 0.698 and 0.859 cP[36] respectively.

10. MOLECULAR STRUCTURE OF PERCHLORIC ACID AND OF CHLORINE HEPTOXIDE

Simon[39] concluded from a study of the Raman spectrum that 100% perchloric acid in the liquid state contains only monomeric molecules, which are in the pseudo-acid form $[O_3ClOH]$. According to him, the ClO_3 group forms a trigonal pyramid, and the hydroxy-group is located on the extension of its height. This model belongs to the symmetry group C_{3v}.

Akishin *et al.*[99] used diffraction of fast electrons to study the molecular structure of the acid. They found that perchloric acid vapour consists of monomeric molecules, having the structure of a trigonal pyramid with the chlorine atom at its apex and the oxygen atoms at the corners of the triangular base. The OH group lies on the continuation of the height of the pyramid.

† Presumably "literature prior to 1960" is intended. (Ed. of Translation).

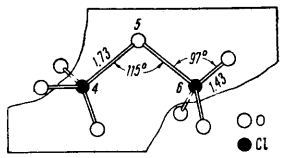


Fig. 6. Model of chlorine heptoxide molecule[99].

The chief parameters of the molecule are:

$$\begin{aligned} Cl=O &\quad 1.42 \pm 0.01\ Å \\ Cl-O &\quad 1.64 \pm 0.02\ Å \\ O-Cl-O &\quad 100° \pm 2° \end{aligned}$$

The position of the hydrogen was not determined.

From a study of the Raman spectrum of a solution of chlorine heptoxide in carbon tetrachloride, Fonteyne concluded that the structure of the anhydride consists of two trigonal pyramids (ClO_3 atomic groupings) linked by an oxygen atom. The ClO_3 groups have symmetry C_v.

Akishin *et al.*[99] used diffraction of fast electrons to study the structure of chlorine heptoxide, and suggested the model illustrated in Fig. 6. In such a structure any oxygen atom of one ClO_3 group is situated between two oxygen atoms of another ClO_3 group, giving a minimum repulsion potential between unlinked oxygen atoms. The chief geometrical parameters of the molecule are as follows.

Distances: (Cl=O) 1.42±0.01 Å, (Cl—O′) 1.725±0.03 Å, ∠ClO′Cl = =115°±5°, ∠OClO′=97°±3°,

where O′ represents the oxygen atom linking the two trigonal pyramids. The length of the Cl_2O_7 molecular dipole is 0.15 Å, while the dipole moment is $\mu = 0.72 \pm 0.02\ D$.

The principal parameters of the $HClO_4$ and Cl_2O_7 molecules, namely the Cl=O distance and the OClO′ angle, are identical. However, the difference between the Cl—O distances in perchloric acid (1.64 Å) and in the anhydride (1.73 Å) considerably exceeds the experimental error in their determination.

Unlinked oxygen atoms in the Cl_2O_7 molecules are ~2.50 Å apart, which is less than the sum of the intermolecular radii (~2.80 Å), and this prevents free rotation of the ClO_3 group.

11. MELTING-POINT DIAGRAM OF THE Cl_2O_7–H_2O SYSTEM

The complete melting-point diagram of perchloric acid over the concentration range 0–100% $HClO_4$ given by van Wijk[24] shows no line for the crystallisation of perchloric acid (Fig. 1). Consequently he observed neither a maximum which would correspond to $HClO_4$ nor a eutectic of the latter with the monohydrate $HClO_4.H_2O$, although he assumed that they did exist, but that the curve representing the crystallisation of perchloric acid was so short that the analytical methods available could not provide data from which it could be plotted. This point was checked experimentally by Zinov'ev and Rosolovskii[91], who studied fusibility in the Cl_2O_7–H_2O system both thermographically and by visual observations over a range of temperatures (the visual polythermal method), their results being given in the form of a table and a diagram (Fig. 7). The points represented by circles were plotted from these results[91], while the triangles represent van Wijk's data[24]. The essential difference between the two set of results is that the lower portion of the crystallisation curve for the monohydrate, drawn by van Wijk on the basis of only two points, terminates in the point corresponding to -112° and precisely 100% $HClO_4$, *i.e.* 50 mole % Cl_2O_7. The lower portion of the curve representing crystallistion of the monohydrate of perchloric acid, plotted from seven experimental points[91], intersects the eutectic line at -100 ± 2° and 53 mole% Cl_2O_7 (*i.e.* a mixture of $HClO_4$ + Cl_2O_7).

But the diagram plotted from the later work[91] also shows no line for the crystallisation of anhydrous perchloric acid. One component of the eutectic (point *A* on Fig. 7) is the monohydrate of perchloric acid, while the nature of the other component was not entirely clear, since, when the content of the anhydride was increased from 53 to about 72 mole%, a drop in temperature resulted not in the separation of crystals but a breakdown in the homogeneity of the solutions, shown visually by the appearance of turbidity. This is entirely to be expected, since the monohydrate of the acid is an ionic substance, while the anhydride is a substance of low polarity (length of dipole ~0.15 Å); since homogeneity broke down above the melting point of the anhydride: the latter separates from the system as a liquid.

When the anhydride content of the mixture was increased, turbidity was found to appear at higher temperatures. This indicates a progressive diminution in the stability of the system with increase in concentration. But mixtures containing more than 72 mole% Cl_2O_7 deposited crystals on being cooled. Since the anhydride melts at -90°, the horizontal line on Fig. 7 at -90° ± 2° was regarded as corresponding to the crystallisation of chlorine heptoxide. Therefore, since separation into layers first occurs, and is followed by crystallisation of the anhydride, it was concluded that it is the anhydride which is the second component of the eutectic. Since, nevertheless, no points

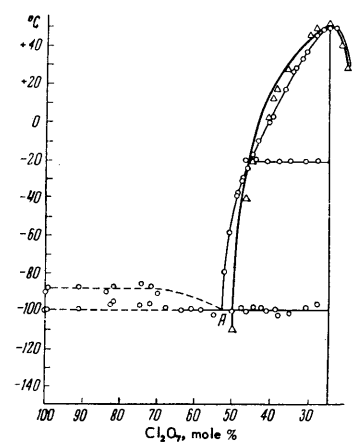


Fig. 7. Melting-point diagram for the chlorine heptoxide–water system[91]. Δ — van Wijk's data.

were obtained representing crystallisation over the range 53–72 mole%, this part of the diagram (Fig. 7) was shown as a broken line.

The horizontal straight line at -100 ± 2°, to the right and to the left of the point corresponding to 53 mole% Cl_2O_7, is a eutectic line. It was found that the polymorphic transition of chlorine heptoxide fortuitously also takes place at -100 ± 2°, [90] and the eutectic line and the polymorphic transition line have coalesced into one in Fig. 7.

Therefore the melting-point diagram constructed from the data in Ref. 91 also did not reveal the existence of $HClO_4$ in the Cl_2O_7–H_2O system. The branch representing crystallisation of the monohydrate intersected the ordinate corresponding to 100% perchloric acid, and entered the region of compositions in which the anhydride content is 53 mole%. When acids containing somewhat less than 50 mole% Cl_2O_7 are cooled, it is not the anhydrous perchloric acid but its monohydrate which crystallises.

These peculiarities of perchloric acid were explained [91] by assuming that the very concentrated acid is not a chemical individual but represents a mixture characterised by the equilibrium $3HClO_4 \rightleftharpoons Cl_2O_7 + H_3OClO_4$ [Eqn. (1)], which is shifted far to the right, *i.e.* towards oxonium perchlorate at very low temperatures.

12. DENSITY OF Cl_2O_7–$HClO_4$ SYSTEMS

In order to check the soundness of equilibrium (1), Rosolovskii *et al.* [97] studied the dependence of several physical properties on composition, in particular the densities of Cl_2O_7 + $HClO_4$ mixtures, at various temperatures. The density was determined for mixtures over the composition range 100–43 mole% Cl_2O_7 at temperatures between 20° and -50°. These were the first data on the density of such mixtures. As mentioned above, there had been only one previous indication of the density of pure chlorine heptoxide (Marsh, private communication [95]): $d_4^{20} = 1.86$.

The densities of Cl_2O_7 + $HClO_4$ mixtures are presented in the paper [97] as a table and a series of isotherms (Fig. 8). The isotherms show that the density of the mixtures increases almost linearly from $HClO_4$ to Cl_2O_7. There are no singular points on the density isotherms between 50 mole% and 100% Cl_2O_7. There are practically no deviations from additivity. This all points to the absence of interaction between the components. As the concentration decreases from $HClO_4$, *i.e.* towards oxonium perchlorate, the density increases rapidly. The maximum density in the Cl_2O_7–H_2O system occurs at $HClO_4.H_2O$. The composition $HClO_4$ corresponds to a sharp minimum on the 20° and 10° isotherms. As the temperature falls, the character of the minimum changes, and the singularity, which is clearly marked at higher temperatures, disappears.

It was concluded that these facts also support equilibrium (1), which as the temperature falls is displaced to the right, *i.e.* in the direction of the anhydride and the monohydrate of perchloric acid. Since both these compounds are denser than anhydrous perchloric acid, an increase in the content of Cl_2O_7 and $HClO_4.H_2O$ should be accompanied by an increase in density, which is actually the case.

The shift in equilibrium and consequent change in composition with decrease in temperature also explains the diminished sharpness of the minima on the density isotherms in Fig. 8.

13. VISCOSITY OF Cl_2O_7–$HClO_4$ SYSTEMS

No information was available in the literature on the viscosity of chlorine heptoxide or of anhydrous perchloric acid below 0° before the work of Zinov'ev and Rosolovskii [98]. Viscosity measurements have been made [98] on Cl_2O_7 + $HClO_4$ mixtures covering the range 100–42.8 mole% Cl_2O_7 at temperatures between 20° and -30°. Results are presented as a table and the six isotherms reproduced in Fig. 9. Each isotherm consists of two parts. With diminishing Cl_2O_7 content the left-hand portions of the isotherms rise slightly to ~54–52 mole% Cl_2O_7, after which the isotherms (the right-hand portions) begin to rise very steeply, breaking off at the boundary with the heterogeneous region (solid monohydrate of perchloric acid).

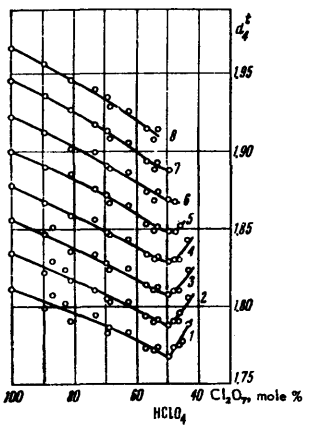


Fig. 8. Density in the chlorine heptoxide–anhydrous perchloric acid system [97]. Isotherms at:
1) 20°; 2) 10°; 3) 0°; 4) -10°; 5) -20°; 6) -30°; 7) -40°; 8) -50°.

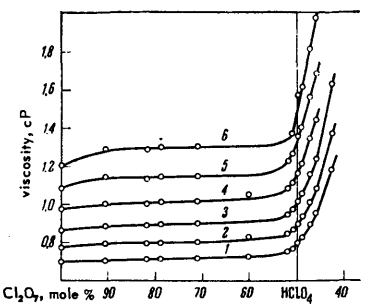


Fig. 9. Viscosity in the chlorine heptoxide–anhydrous perchloric acid system [98]. Isotherms at:
1) 20°; 2) 10°; 3) 0°; 4) -10°; 5) -20°; 6) -30°.

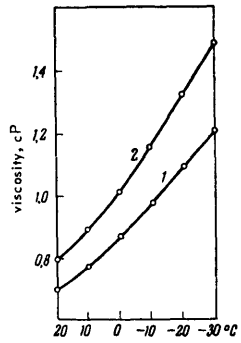


Fig. 10. Temperature variation of viscosity[98]: 1) chlorine heptoxide; 2) perchloric acid.

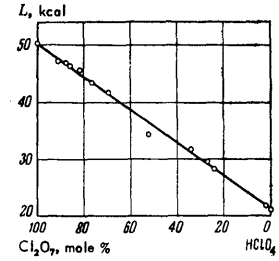


Fig. 11. Heats of solution in the chlorine heptoxide–anhydrous perchloric acid system[94].

The maximum viscosity, like the maximum density, occurs at a composition close to the monohydrate. As the temperature falls, the shape of the isotherm changes slightly, and over the range 55–100 mole% Cl_2O_7 the shape of the isotherms indicates the absence of interaction between Cl_2O_7 and $HClO_4$.

The inflection in the viscosity isotherms (Fig. 9) corresponding to formation of the compound $HClO_4$ is displaced somewhat towards the anhydride, especially at low temperatures. This shape of the isotherm supports equilibrium (1). Actually, since the viscosity of the monohydrate of perchloric acid is substantially grater than the viscosity of either the anhydrous acid or its anhydride, an increasing content of the monohydrate should result in an increase in viscosity. This is actually the case. The rise begins sooner in the viscosity isotherms (Fig. 9) the lower the temperature. This in turn indicates a shift in equilibrium (1) towards the monohydrate as the temperature is lowered.

Fig. 10 shows viscosity polytherms[98] for chlorine heptoxide and perchloric acid. They indicate that the increase in viscosity with fall in temperature is considerably greater with the acid than with the anhydride. This also points to a shift in equilibrium (1), with fall in temperature, towards oxonium perchlorate, increase in the concentration of which entails an increase in viscosity.

14. INTEGRAL HEATS OF SOLUTION IN THE Cl_2O_7–$HClO_4$ SYSTEM

Integral heats of solution in the $HClO_4$–H_2O system have been indicated above[27,28]. Apart from this work, a paper published by Goodeve and Marsh[93] on the determination of the heat of solution of chlorine heptoxide gave a value of 50.0 ± 0.5 kcal mole^{-1}.

Rosolovskii *et al.*[94] have made a systematic investigation of the heats of solution of mixtures of perchloric acid and its anhydride. It was found that the acid passes into solution very rapidly (within 1–2 min), while the remaining anhydride dissolves with characteristic slowness, at a rate determined by the volume of the drops of anhydride, *i.e.* by the intensity of stirring. The results are tabulated in the paper[94] and are shown graphically in Fig. 11.

The additivity of the heats of solution suggests that Cl_2O_7 and $HClO_4$ do not interact, but give what may be regarded as true solutions. Absence of interaction is indicated also by the independent dissolution of the components of mixtures and the density and melting-point results for the Cl_2O_7–$HClO_4$ system. The heat of reaction was found to be

$$Cl_2O_7 + H_2O = 2HClO_4 + 8.1 \text{ kcal.}$$

The thermochemical data were also used to find the heat of the reaction

$$3HClO_4 = Cl_2O_7 + HClO_4 \cdot H_2O + 2.8 \text{ kcal.}$$

The positive heat of reaction in this case confirms the assumption that lowering the temperature shifts the equilibrium towards chlorine heptoxide and the monohydrate of perchloric acid. The content of $HClO_4$ in this mixture at about -100° is obviously so low that $HClO_4$ does not crystallise. For this reason the melting-point diagram does not contain a line representing crystallisation of the acid, as was stated above.

15. THERMAL STABILITY OF PERCHLORIC ACID

Anhydrous perchloric acid is unstable. A few hours after its preparation it already shows clear signs of decomposition, first becoming yellowish (owing to the lower oxides of chlorine which are formed), the colour then deepening, becoming darker, and finally almost black, and the acid becomes opaque. In this condition perchloric acid may explode.

At slightly elevated temperatures (not above 100°) perchloric acid passes through these stages considerably more rapidly, in periods measured in minutes, and at about 100° even in seconds. At all temperatures (up to 95°–99°), however, there is an interval during which decomposition of the perchloric acid has not yet occurred: *i.e.* the decomposition is preceded by an induction period. The kinetic curves for the decomposition are S-shaped, the isotherms for the rate of decomposition passing through a maximum. This and also the possibility of delaying the decomposition for some time by means of inhibitors give grounds for supposing that the thermal decomposition of perchloric acid takes place by a chain mechanism. If

decomposition occurs at a temperature not exceeding 100°, the residue contains the monohydrate, present in the theoretical quantity based on Eqn. (1).

Zinov'ev and Babaeva [101] cite data showing that the decomposition of perchloric acid begins with the formation and subsequent decomposition of chlorine heptoxide. The following stages in the decomposition may be noted.

1. Vigorous evolution of a small amount of oxygen (10–15 $cm^3 g^{-1}$ of acid) within a short period of time (1–2 min). The yield of oxygen varies from one specimen to another. It is obviously oxygen dissolved in the acid which is being evolved.

2. A second stage during which only slight changes are taking place in the acid, the initially colourless acid becoming coloured, accompanied by slight oxygen evolution (at a constant rate, since the isotherm is linear). The volume of oxygen evolved during this stage does not exceed 10–12% of the total quantity of oxygen obtained from a given weight of the acid.

3. The following stage of decomposition is characterised by the high rate and considerable complexity of the reactions which develop. The rate of decomposition of the acid at this stage increases rapidly with time, tending to a maximum.

4. The stage of decomposition after the maximum rate has been passed, tending to die away.

In the presence of inhibitors the duration of the second stage increases several hundred times, and the portions of the isotherms corresponding to this stage become more distinct and completely linear. This implies that the reaction is of zero order during this stage, while the activation energy is ~33 kcal $mole^{-1}$, [101] which coincides with the activation energy found by Figini *et al.* [102] ($E = 32 \pm 1.5$ kcal × × $mole^{-1}$) for the decomposition of chlorine heptoxide. Since this agreement is hardly fortuitous, and also as uncombined Cl_2O_7 is always present in perchloric acid, Zinov'ev and Babaeva concluded that the decomposition of perchloric acid begins with that of Cl_2O_7 formed from the acid.

The decomposition of chlorine heptoxide is assumed [102] to involve the intermediate formation of free radicals: $Cl_2O_7 = ClO_3 + ClO_4$, followed by very complicated and not yet elucidated reactions in which they take part. The following end-products of the decomposition of perchloric acid can be regarded as firmly established provided that the temperature does not exceed 100°: perchloric acid monohydrate $HClO_4.H_2O$, chlorine dioxide ClO_2, and elemental chlorine Cl_2. A probable decomposition product is Cl_2O_6.

The water formed in the reaction combines completely with still undecomposed perchloric acid, which is the reason for the formation of the monohydrate.

Above 110°, according to Roscoe [12], the monohydrate begins to decompose too. This has been confirmed by Zinov'ev and Tsentsiper [103].

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The above account of perchloric acid indicates that it differs substantially from other inorganic acids. The most remarkable fact is that perchloric acid is not chemically unique, but exists under all conditions as a component of a mixture of $HClO_4 + Cl_2O_7 + H_3OClO_4$. The composition of this mixture varies considerably with change in conditions, especially temperature, and at very low temperatures, in particular, Cl_2O_7 and H_3OClO_4 predominate to a very great extent over $HClO_4$.

Another peculiarity of perchloric acid is that, of all the forms in which it exists, only the monohydrate, better described as oxonium perchlorate H_3OClO_4, satisfies the requirements of an individual chemical species. In the Cl_2O_7–H_2O system such requirements are met also by chlorine heptoxide.

The very different volatility of the various forms of perchloric acid is of considerable interest. Anhydrous perchloric acid is extremely volatile, but at atmospheric pressure it cannot be distilled without decomposition. Its distillation is readily achieved only at reduced pressure. The monohydrate of perchloric acid does not distil without decomposition either at atmospheric pressure or in a vacuum, but an azeotrope, whose composition is close to a dihydrate of the acid, can be distilled almost without decomposition even at atmospheric pressure (evaporation of the azeotrope from a dish takes place without any signs of decomposition, while distillation from a flask fitted with a condenser is accompanied by slight decomposition).

A substantial increase in density must be noted on passing from the anhydrous acid to its monohydrate, and the viscosity of the latter is several times greater than that of the anhydrous acid.

It is remarkable that the viscosity of the anhydrous acid is less than that of water under the same conditions.

Perchloric acid is among those acids which contain so-called available oxygen. It has a higher content of the latter (63.7%) than have other acids (nitric, chloric, etc.), but its oxidising power is very greatly dependent on its water content. Thus the ClO_4^- ion exhibits no oxidising properties in aqueous solution. Above 100°, however, free perchloric acid, in the form of the azeotrope, readily oxidises many metals, ores, and especially organic compounds. On passing from the dihydrate to the monohydrate, the oxidising activity of the perchloric acid increases considerably, the monohydrate readily oxidising various reducing agents even below 100°.

The oxidising activity of perchloric acid increases very sharply when its composition approaches 100% $HClO_4$. Such an acid instantly sets fire to all oxidisable organic compounds, and oxidises almost all metals in the most vigorous fashion (with the exception of noble metals and those which can be passivated by oxidation), the heats of reaction usually being sufficient for the instantaneous decomposition of the acid, accompanied by a powerful explosion.

Colourless perchloric acid, *i.e.* an acid containing no lower oxides of chlorine, does not explode out of contact with reductants, and is therefore safe when handled carefully.

In spite of the great amount of work done on perchloric acid, its properties have not yet been adequately determined. This applies primarily to the dependence of vapour pressure on temperature, and then to the way in which the stability of the acid varies with temperature and other conditions. In this connection the problem of the stabilisation of perchloric acid still remains unsolved, its instability being a serious obstacle not only to its wide industrial use but also to its employment in laboratory experiments.

In spite of the work of many investigators, the nature of perchloric acid requires further study. In particular, it must be made clear why perchloric acid behaves as a mixture and how the properties of this mixture vary with the external conditions, especially with temperature.

Much work has been done on perchloric acid salts (perchlorates), but the diverse properties of these salts and mixtures thereof have been altogether insufficiently studied; it is even true that not all possible perchlorates have been prepared, which applies especially to those of the rare metals.

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THE NATURAL PIGMENTS

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1. INTRODUCTION

The natural pigments are complex organic compounds produced by living organisms and by colouring various animal and plant cells and tissues they determine the entire diversity of colour of animate nature.

Even from most ancient times, in the early stages of civilisation, man began to use the natural pigments for the satisfaction of his aesthetic needs. In the second half of the XIXth century many natural dyestuffs were used for colouring textiles, hides, paper, perfumes, food products, etc. With the development of the organic chemical industry, and especially of the aniline dyestuffs industry, the natural pigments were unable to compete with the synthetic dyes and in the great majority of cases lost their former practical value. However, the value of the natural pigments is not exhausted by their practical use for the purpose of dyeing. Most of them play an essential role in the life of those organisms by which they are produced. Many natural pigments exhibit marked physiological and antibiotic activity and are often used as medicines.

The pigments are extremely widely distributed in nature and are extremely diverse chemically[1]. Their classification is possible according to various features, for example, by their origin and occurrence in nature (animal dyestuffs, plant pigments, butterfly wing pigments, flower and fruit pigments, and so forth). However, in many cases the same pigment (or pigments of similar structure) is encountered in different natural sources, and therefore the most desirable classification, used in this paper, is the usual classification of organic compounds by their functional features[2].

2. PIGMENTS OF THE ALIPHATIC AND ALICYCLIC SERIES

This class consists mainly of the so-called polyene pigments or carotenoids[3-5]. These are compounds containing long chains of carbon atoms with a system of conjugated double bonds which is responsible for their colour. The colour deepens as the length of the conjugated system is increased. The pigments of this group include hydrocarbons (some with alicyclic rings at the end of the carbon chain), alcohols (sometimes encountered in the form of esters), ketones, keto-alcohols, aldehydes, acids, esters, epoxides, and compounds with a furan ring[6] (Table 1).

The carotenoids are encountered in both the plant and the animal kingdoms. Many of them (such as carotene) exhibit a high physiological activity (provitamin A). The polyenes of unestablished structure include several antibiotics (capacidin, pentamycin, filipin, mediocydin, trichomycin, etc.) produced by various species of *Streptomyces*[7].

Most of the carotenoids have a completely *trans* configuration, but partly isomerised *trans–cis*-isomers[8] are encountered (most frequently isomerised at the central double bond).

TABLE 1. The carotenoids:

R–C(CH_3)=CHCH=CHC(CH_3)=CHCH=CHCH=C(CH_3)CH=CHCH=C(CH_3)–R′*.

R	R′	Name	Colour	M.p., °C	Occurrence in nature
Hydrocarbons					
1	1	neurosporene	orange-yellow	124	in the fungus *Neurospora crassa*; in mutants of the red yeast *Rhodotorula rubra*
2	2	lycopene	red	173	in fruits of *Solanum lycopersicum* and many others
3	3	β-carotene	violet	181—184	widely distributed in the vegetable kingdom, microorganisms, fungi, algae, egg-yolk, milk, etc.
3	4	α-carotene	violet	187—188	accompanies β-carotene
2	3	γ-carotene	violet	176.5—178	accompanies β-carotene
Alcohols					
2	5	lycoxanthin	violet-red	168	in fruits of *Solanum dulcamara*, etc.
2	6	rubixanthin	red	160	in fruits of *Rosa rubiginosa*, etc.
2	22	celaxanthin	dark red	204—210	in berries of *Celastrus scandens L.*
3	6	cryptoxanthin	red	169	widely distributed in the plant world (berries, fruit, flowers, lichens, fungi, microorganisms)
6	6	zeaxanthin	yellow-red	204—206	ditto
					in feathers of birds *Chrysoena victor, Rupicola peruviana*
6	7	xanthophyll	red	192—193	as for zeaxanthin; in feathers of birds *Emberiza citrinella, E. icterica, Oriolus oriolus*
5	5	lycophyll	violet-red	179	in fruits of *Solanum dulcamara*
7	7	eschscholtzxanthin	violet	185—190	in petals of *Eschscholtzia californica*
Ketones and keto-alcohols					
3	8	myxoxanthin	violet	168—169	in the algae *Rivularia nitida*, etc.
9	9	rhodoxanthin	blue-black	219	in leaves of *Cryptomeria japonica, Cupressus naitnocki*, etc. in feathers of birds *Phoenicircus nigricollis, Megalopreria magnifica*
10	10	xanthoxanthin		213	in the fungus *Cantharellus cinnabarinus*; in the orange mutants of *Corynebacterium michiganense*
11	11	astacene	violet	240—243	in the shell of the lobster *Astacus gamarus L.*; in feathers of birds *Laniarius atrococineus, L. barbarus, L. erythrogaster*, etc.
12	12	astaxanthin	red	215—216	in lower plants and feathers of birds *Laniarius atrococcineus, L. erythrogaster*, etc.
6	8	capsanthin	red	175—176	in fruit of *Capsicum annum L.*; in flowers of *Tecoma radicans*, etc.
14	14	capsorubin	violet-red	201	in the skin of fruits of *Capsicum annum L.*
15	15	fucoxanthin	brownish red	166—168	in various algae
Aldehydes, acids, esters					
6	21	β-citraurin		147	in the rind of oranges
16	17	bixin	violet-red	198	in the skin of seeds of *Bixa orellana L.*
3	18	torularhodin	red	201—203	in the yeast *Torula rubra*
19	19	crocetin	red	275—276	in fruits of *Gardenia grandiflora*, etc.
20	20	crocin	brownish red	186 (decompn.)	in *Crocus sativus L.*
Epoxides					
3	23	β-carotene epoxide	orange	≈160	in the rind of oranges
4	23	α-carotene epoxide	orange	175	in flowers of *Tragopogon pratensis* and *Raminculus acer*
4	24	trollixanthin		155—156	in flowers of *Trollius europaeus*
24	6	antheraxanthin		205—207	in fruit and flowers of *Capsicum annuum*, etc.
24	24	violaxanthin	brownish yellow	200	in flowers of *Viola tricolor*
Furanoxides					
3	26	citroxanthin	yellow-orange	163—164	in the rind of oranges
4	26	flavochrome	yellow	176—178	in flowers of *Ranunculus acer*
2	26	rubichrome	reddish violet	154	in flowers of *Tagetes patula*
7	26	flavoxanthin	yellow		in flowers of *Ranunculus acer, Ulex europaeus*, etc.
27	27	auroxanthin	yellow	203	in flowers of *Viola tricolor*

* For the significance of R and R′ see Appendix 1 on p. 289.

3. PIGMENTS OF THE AROMATIC SERIES

These pigments are based on hydroxy- and alkoxy--substituted unsaturated ketones, derivatives of a diaroylmethane: 4,4′-dihydroxydicinnamoylmethane, yellow, m.p. 224°; 4-hydroxycinnamoylferuloylmethane, orange, m.p. 168°; and diferuloylmethane (curcumin), red, m.p. 181°–183°, encountered in the roots of *Curcuma longa, C. tinctoria*, etc.; chalcones[9] (I) (Table 2), quinones[10,11], benzoquinones (II) (Table 3), naphthaquinones[12] (III) (Table 4), anthraquinones[13,14] (IV) (Table 5), and anthrones: chrysarobin (1,8-dihydroxy-3-methylanthran-9-one), m.p. 203.5°–204°, the yellow dye of *Andira araroba* wood and emodinanthrone (1,6,8-trihydroxy-3-methylanthran-9-one), m.p. 250°–258°, the yellow dye of *Rhamnus dahurica* wood. Many of these dyestuffs are encountered in nature as glycosides (only the aglycone is shown in all the tables). The structurally similar anthraquinones hypericin (V) (R = CH_3) and pseudohypericin (V) (R = CHOH.CH_3), the dark violet and dark red pigments of *Hypericum perforatum* flowers, exhibit photodynamic properties[15], as do other bianthraquinones[16].

The natural pigments of the aromatic series also include compounds displaying physiological and antibiotic acitivity (for example, vitamin K, curcumin, many quinones, etc.). The partly hydrogenated aromatic natural pigments include the antibiotics of the tetracycline group, which are yellow.

The yellow pigment aristolochine† (8-methoxy-3,4--methylene-10-nitro-dihydroxyphenanthrene-1-carboxylic acid), m.p. 281°–286°, isolated from *Aristolochia clematitis* roots is somewhat different from the compounds considered above.

TABLE 2. Chalcones (I)*.

Substituents**	Name	Colour	M.p., °C	Occurrence in nature
$R_1' = R_3' = R_3 = OH$	isoquiritigenin	yellow	200–204	in roots of *Glycyrrhiza glabra*
$R_1' = R_3 = OH$; $R_3' = OCH_3$	2,4′-dihydroxy-4-methoxychalcone	yellow	172–176	in resin from *Xanthorroea australis*
$R_1' = R_3' = R_2 = R_3 = OH$	butein	yellow	214–215	in flowers of *Butea frondosa*, etc.
$R_1' = R_2' = OH$; $R_3' = R_4' = R_5' = OCH_3$	pedicin	orange-red	143–145	in leaves of *Didymocarpus pedicellata*
$R_1' = R_2' = R_3' = R_2 = R_3 = OH$	okanin	orange	235–240	in heartwood of *Cyclicodiscus gabunensis* Harms.; in flowers of *Coreopsis maritima, C. gigantea*
$R_1' = R_3' = R_4' = R_2 = R_3 = OH$	neoplathymenin	orange	232	in heartwood of *Plathymenia reticulata* Benth.
$R_2' + R_3' = OCH_2O$; $R_1 = R_3 = R_5 = OH$	gissopin	orange	265–270	in the fungus *Capsella bursa-pastoris*
$R_1' = R_2' = R_3' = R_5' = R_3 = OH$	carthamin	yellow	–	in pollen from flowers of *Carthamus tinctorius*

* For the formulae of the compounds in all tables and text see Appendix 2, p. 289.

** In all tables unspecified R = H.

† Or aristolochic acid (Ed. of Translation).

TABLE 3. Benzoquinones (II).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_1 = R_4 = OCH_3$	2,6-dimethoxybenzoquinone	yellow	250–251	in stalks of *Adonis vernalis L.*
$R_1 = R_3 = OH$; $R_4 = n\text{-}C_{11}H_{23}$	embelin	orange-yellow	142–144	in the berries of *Embelia ribes* Burm., etc.
$R_1 = R_3 = OH$; $R_4 = n\text{-}C_{13}H_{27}$	rapanone	orange	141–142	in the root and wood of *Rapanea maximowiszii* Koidz.
$R_1 = R_3 = OH$; $R_2 = CH_3$; $R_4 = C_{10}H_{37}$	maesaquinone	orange-red	122	in fruits of *Maesa japonica* Moritz
$R_1 = R_3 = OH$; $R_2 = R_4 = C_6H_5$	polyporic acid	brown-violet	305	in the fungi *Polyporus rutilans*, etc.
$R_1 = R_3 = OH$; $R_2 = R_4 = p\text{-}C_6H_4OH$	atromentin	brown		in the fungi *Agaricus atrotomentosus*, etc.
$R_1 = OH$; $R_2 = R_4 = o\text{-}C_6H_4COOH$; $R_3 = CH = CHCH = CHCOOH$	muscarufin	orange-red	275.5	in the fungus *Amanita muscaria L.*

TABLE 4. Naphthoquinones (III).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_1 = OH$	lawsone	light yellow	192–195	in leaves of *Lawsonia inermis L.*
$R_3 = OH$	juglone	brown-red	153–154	in the shells of the Grecian walnut *Juglans regia*
$R_1 = OCH_3$	2-methoxy-naphthoquin-1,4-one	yellow	183.5	in leaves of *Impatiens balsamina L.*
$R_1 = CH_3$; $R_2 = OH$	phthiocol	yellow	173–175	pigment of tuberculosis bacterium
$R_1 = CH_3$; $R_3 = OH$	plumbagin	golden yellow	76–78	in roots of *Plumbago europaea L.*, etc.
$R_1 = CH_3$; $R_2 = R_3 = OH$	droserone	yellow	178–181	in roots of *Drosera peltata*
$R_1 = CH_3$; $R_2 = R_3 = R_4 = OH$	hydroxydroserone	red	192–193	in the tubers of *Drosera whittakerii*
$R_1 = OH$; $R_2 = CH_2CH = C(CH_3)_2$	lapachol	yellow	139–142	in the heartwood of *Avicennia tomentosa*
$R_1 = CH(OH)CH_2CH = C(CH_3)_2$; $R_3 = R_4 = OH$	alkannin	brownish red	147–149	in roots of *Anchusa tinctoria*, etc.
$R_1 = OH$; $R_2 = CH_2CH = C(CH_3)CH_2OH$	lomatiol	yellow	127–128	in seeds of *Lomatia ilicifolia*, etc.
$R_1 = CH_3$; R_2 = phytyl	vitamin K	yellow	oil	in *Alfalfa* and other green plants

TABLE 5. Anthraquinones (IV).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_2 = OH$	2-hydroxyanthraquinone	yellow	302–306	in roots of *Oldenlandia umbellata L.*
$R_1 = R_2 = OH$	alizarin	orange-red	289–290	in roots of *Rubia tinctorum*
$R_1 = OCH_3$; $R_2 = OH$	α-methyl ester of alizarin	orange	178–179	in roots of *Oldenlandia umbellata L.*
$R_2 = OCH_3$; $R_3 = OH$	monomethyl ether of hystazarin	yellow-orange	232–235	ditto
$R_1 = R_3 = OH$	purpuroxanthin (xanthopurpurin)	yellow	268–270	in roots of *Rubia tinctorum, R. sikkimensis*
$R_1 = R_2 = R_3 = OH$	anthragallol	orange	310–314	in bark of *Coprosma lucida*
$R_1 = R_3 = OH$; $R_2 = OCH_3$	2-methyl ether of anthragallol	yellow	218–220	in bark of *Coprosma lucida*
$R_1 = R_2 = OCH_3$; $R_3 = OH$	1,2-dimethyl ether of anthragallol	yellow	230–232	in bark of *Coprosma lucida, Oldenlandia umbellata L.*
$R_1 = R_3 = OCH_3$; $R_2 = OH$	1,3-dimethyl ether of anthragallol	yellow	209	in bark of *Oldenlandia umbellata L.*
$R_1 = R_2 = R_4 = OH$	purpurin	orange-yellow	253–259	in bark of *Rubia tinctorum*
$R_2 = CH_3$	tectoquinone	light yellow	175–177	in wood of *Tectona grandis*
$R_2 = CH_3$; $R_3 = OH$	3-hydroxy-2-methyl-anthraquinone	yellow	302	in bark of *Coprosma lucida*

TABLE 5 (contd.)

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_1 = R_3 = OH$; $R_2 = CH_3$	rubiadin	yellow	297	in roots of *Rubia tinctorum*, in bark of *Coprosma lucida*
$R_1 = OCH_3$; $R_2 = CH_3$; $R_3 = OH$	1-methyl ether of rubiadin	golden yellow	290–291	in roots of *Morinda longiflora*
$R_1 = OCH_3$; $R_2 = OH$; $R_3 = CH_3$	digitolutein	yellow	222	in leaves of *Digitalis lutea, D. purpurea*
$R_1 = R_3 = OH$; $R_2 = CH_3$	chrysophanic acid	golden yellow	193–196	in roots of *Rumex patientia, R. obtusifolius*
$R_1 = R_6 = OH$; $R_2 = CH_3$	soranjidiol	orange-yellow	287–289	in bark of rhizomes of *Morinda umbellata, M. citrifolia*
$R_1 = R_4 = R_5 = OH$; $R_2 = CH_3$	1,4,5-trihydroxy-2-methyl-anthraquinone	dark red	218	in mycelia of *Penicillium islandicum* Sopp.
$R_1 = R_5 = R_6 = OH$; $R_2 = CH_3$	morindone	orange-red	281–284	in bark of rhizomes of *Morinda umbellata*
$R_1 = R_5 = R_6 = OH$; $R_2 = CH_3$	chrysarone	golden yellow	165–166	in roots of *Rheum rhaponticum L.*
$R_2 = R_5 = R_6 = OH$; $R_3 = CH_3$	rhabarberone	orange-yellow	212	in roots of *Rheum palmatum, R. officinale*
$R_4 = R_5 = R_7 = OH$; $R_2 = CH_3$	emodin	orange-red	254–256	in bark of *Rhamnus purshiana*; in roots of *Rheum palmatum*
$R_4 = R_5 = OH$; $R_7 = OCH_3$; $R_2 = CH_3$	physcion	orange-yellow	203–207	in lichens *Parmelia parietina*
$R_4 = R_5 = R_8 = OH$; $R_2 = CH_3$	helminthosporin	reddish brown	226–227	in mycelia of *Helminthosporium graminneum* Rabenhorst
$R_1 = R_4 = R_5 = OH$; $R_2 = CH_3$	islandicin	red	218	in mycelia of various moulds of *Penicillium islandicum* Sopp.
$R_1 = R_4 = R_5 = R_7 = OH$; $R_2 = CH_3$	catenarin	red	246	in mycelia of *Helminthosporium graminneum* Rabenhorst
$R_1 = R_4 = R_5 = OH$; $R_7 = OCH_3$; $R_2 = CH_3$	erythroglaucin	red	205–206	in mycelia of *Penicillium glaucum*
$R_1 = R_4 = R_5 = R_8 = OH$; $R_2 = CH_3$	cynodontin	reddish brown	260	in mycelia of *Helminthosporium cynodontis* Marignoni
$R_1 = R_3 = R_6 = R_7 = OH$; $R_2 = CH_3$	copareolatin	dark red	298	in bark of *Coprosma areolata*
$R_1 = R_5 = OH$; $R_3 = CH_2OH$	aloe-emodin (rottlerin)	orange-yellow	223–225	in bark of *Rhamnus purshiana*
$R_1 = R_3 = OH$; $R_2 = CH_2OH$	lucidin	yellow	> 330	in bark of *Coprosma lucida, C. acerosa*
$R_4 = R_5 = R_7 = OH$; $R_2 = CH_2OH$	citreorosein	dark orange	288	in mycelia of *Penicillium cyclopium*
$R_5 = R_7 = OH$; $R_4 = OCH_3$; $R_1 = CH_2OH$	carviolin	yellow	280 (decompn.)	in mycelia of *Penicillium carminoviolaceum*
$R_4 = R_5 = OH$; $R_7 = OCH_3$; $R_2 = CH_2OH$	fallacin	yellow-brown	245–248	in lichens *Xanthoria fallax* Arc.
$R_3 = R_4 = R_5 = R_6 = R_7 = OH$; $R_2 = CH_2OH$	asperthecin	orange-red	–	in mycelia of *Aspergillus quadrillineatus*
$R_4 = R_5 = OH$; $R_7 = OCH_3$; $R_2 = C_5H_9OH$	nalgiovensin	orange	199–200	in mycelia of *Penicillium nalgiovensis* Laxa
$R_1 = Cl$; $R_4 = R_5 = OH$; $R_7 = OCH_3$; $R_2 = C_5H_9OH$	nalgiolaxin	yellow	248–248.5	ditto
$R_1 = OCH_3$; $R_2 = CHO$; $R_3 = OH$	damnacanthal	orange-yellow	208	in roots of *Damnacanthus major, D. indicum*
$R_4 = R_5 = OH$; $R_2 = COOH$	rhein	orange	321	in roots of *Rheum palmatum*
$R_1 = R_3 = OH$; $R_2 = COOH$	munjistin	orange-yellow	231	in roots of *Ribia munjista*
$R_1 = R_2 = R_4 = OH$; $R_3 = COOH$	pseudopurpurin	red	220–224 (decompn.)	in roots of *Rubra cordifolia*
$R_4 = R_5 = R_7 = OH$; $R_2 = COOH$	emodic acid	orange-yellow	363–365 (decompn.)	in mycelia of *Penicillium cyclopium* Westling
$R_1 = R_6 = R_8 = OH$; $R_2 = COOH$; $R_3 = CH_3$	endocrocin	orange	318 (decompn.)	in the lichen *Nephromopsis endocrocea* Asachina
$R_1 = R_3 = R_6 = OH$; $R_2 = COOCH_3$; $R_7 = CH_2OH$	rhodocladonic acid	ruby red		in fruits of the *Cladonia* series
$R_1 = R_3 = R_4 = R_6 = OH$; $R_5 = CH_3$; $R_8 = COOH$; $R_2 = CO(CHOH)_4CH_2$	carminic acid	red		colouring substance of cochineal
$R_1 = R_3 = R_4 = R_6 = OH$; $R_5 = CH_3$; $R_8 = COOH$; $R_2 = COCH_3$	kermesic acid	red		ditto

Many natural pigments of the aromatic series were earlier widely used for dyeing silk; for example, alizarin (the principal dyestuff of madder, which also contains purpurin, xanthopurpurin, munjistin, and rubiadin), carthamin, curcumin (also used today as an indicator in acidometry), cochineal, etc.

4. PIGMENTS OF THE HETEROCYCLIC SERIES

a. Oxygen-Containing Heterocyclics

In this class are the yellow pigment pongamol (4-methoxy--5-acetylbenzoylbenzofuran), m.p. 128°–129°, isolated from *Tephrosia lanceolata* roots and usnic acid (3,8-diacetyl-7,8--dihydroxy-2-keto-4a,6-dimethyl-2,4a-dihydrobenzofuran), m.p. 203°, a yellow pigment encountered in many lichens, for example, in *Usnea barbata*. The dihydrofuran derivatives include the lactone of pulvinic acid (VI, R = H), m.p. 221°–222°, the pale yellow colouring matter of the lichen *Sticta coronata* and others, salicin (VI, R = OH), m.p. 244°–245°, the orange-red pigment of the lichen *Calycium chrysocephalum* and others, dihydrofuranones (VII) (Table 6), and also the coumaranones[9], five-membered cyclic isomers of chalcones and flavones (VIII) (Table 7).

TABLE 6. Dihydro-α-furanones (VII).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
R_1 = OH	pulvinic acid	yellow	215–217	in the lichens *Sticta coronata*
R_1 = NHCH($COOCH_3$).CH_3 – $CH(CH_3)_2$	epanorin	yellow	135–136	in the lichens *Lecanora epanora* Acl
R_1 = NHCH($COOCH_3$).CH_2 – C_6H_5	rhizocarpic acid	lemon yellow	177–179	in the lichens *Rhizocarpon geographicum*
R_1 = OCH_3	vulpinic acid	yellow	146–148	in the lichens *Cetraria vulpina*
R_1 = OC_2H_5	callopisminic acid	lemon yellow	127–128	in the lichens *Callopisma vitellinum* Ehrchardt
R_1 = R_3 = OCH_3	pinastric acid	golden yellow	203–205	in the lichens *Cetraria pinastri*
R_1 = R_2 = OCH_3	lepraric acid	golden yellow	159–160	in the lichens *Lepraria citrina*

TABLE 7. Coumaranones (VIII).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
R_2 = R_1' = R_2' = OH	sulphurein	yellow	280–285	in flowers of *Cosmos sulphureus*
R_2 = R_3 = R_1' = R_2' = OH	aureusidin	yellow	270–275	aglucone of the pigment of flowers of *Oxalis cernua*, etc.
R_1 = R_2 = R_1' = R_2' = OH	maritimein	yellow	–	in flowers of *Coreopsis maritima*
R_2 = R_1' = R_2' = OH R_1 = OCH_3	leptosin	orange-yellow	252–254	in the petals of *Coreopsis grandiflora*

The pigments which are most widely represented in nature are chroman derivatives[17], for example, flavonoids[18–25], flavones[26] (IX, X = H) (Table 8), flavonols (IX, X = OH, OCH_3, OSO_3K) (Table 9), flavanones (X, X = H) (Table 10), and flavananols (X, X = OH) (Table 10), anthocyanins[27–29] (XI) (Table 11), and isoflavones[30,31] (XII) (Table 12). The group of isoflavones also includes the yellow pigments: osajin (XIII, R = H), m.p. 189°, and pomiferin (XIII, R = OH), m.p. 200.5°, contained in the fruit of *Maclura pomifera* Raf. Other compounds which contain chroman rings are the dark red pigments dracorhodin (XIV, R = CH_3, R′ = H), m.p. 168°–169° (with decomposition), present in the resin of *Deamonorops draco*, and carajurin (XIV, R = OH, R′ = OCH_3), m.p. 205°–207°, found in the leaves of *Bignonia chika*; the red dye dracorubin (XV), m.p. 315°, also present in the resin of *Deamonorops draco*, and the other biflavanoid pigments[32,33]; the yellow pigment rottlerin (XVI), m.p. 200°–207°, and isorottlerin (XVII), m.p. 182°, present in the fruits of *Rottlera tinctoria* Roxb[34], dehydrodeguelin (XVIII, R = H), m.p. 232°–233°, present in the seeds of *Tephrosia vogelii* and dehydrotoxicarol (XVIII, R = CH_3), m.p. 234°, found in the roots of plants of the Derris family.

The coumarin derivatives include the yellow pigments: daphnetin (7,8-dihydroxycumarin), m.p. 255°–256°, aglucone of the glucoside daphnin, present in the bark of *Daphne alpina*; ellagic acid (XIX, R = OH), widely distributed in the wood of many species, for example, in *Quebracho colorado*, its dimethyl ether (XIX, R = OCH_3), m.p. 337°–338°, encountered in the roots of *Euphorbia formosana* Hay; luteic acid (XX), m.p. 338°–342° (with decomposition), the red dye of the fruits of *Terminalia chebula*, etc. Xanthones (XXI) also belong to this group (XXI) (Table 13). The oxygen--containing heterocyclic compounds also include thelephoric

TABLE 8. Flavones (IX, X = H).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
R_2 = R_4 = OH	primetin	yellow	230–231	in leaves of *Primula modesta*
R_1 = R_3 = OH	chrysin	yellow	275	in heartwood of *Pinus strobus*, etc.
R_1 = OH; R_3 = OCH_3	tectochrysin	yellow	163	in heartwood of *Pinus strobus*, etc.
R_1 = R_2 = R_3 = OH	baicalein	yellowish brown	264–265	in roots of *Oroxylum indicum* Vent.
R_1 = R_3 = OH; R_2 = OCH_3	oroxylin-A	yellow	231–232	ditto
R_1 = R_3 = OH; R_4 = OCH_3	wogonin	yellow	199–201	in roots of *Scutellaria baicalensis*
R_1 = R_3 = OH; R_2 = R_3' = OCH_3	pectolinarigenin	yellow	215–219	aglycone of flower pigment of *Linaria vulgaris L.*
R_1 = R_3 = R_2' = R_3' = OH	luteolin	yellow	328–330	in flowers of *Reseda luteola L.*, etc.
R_1 = R_3 = R_3' = OH; R_2' = OCH_3	chrysoeriol	yellow	330–331	in haulm of *Eriodictyon glutinosum* Benth.
R_1 = R_3 = R_2' = R_3' = OH; R_2 = *n*-HOC_6H_4CH–$CHCO$ (O)	fukugetin	yellow	288–290	in bark of *Garcinia spicata*
R_1 = R_2 = R_3 = R_4 = R_2' = = R_3' = OCH_3	nobiletin	yellow	134–137	in rind of *Citrus nobilis* Lour.
R_1 = R_3 = R_1' = R_3' = OH	lotoflavin	yellow	–	aglycone of pigment from *Lotus arabicus L.*
R_1 = R_3 = R_2' = R_3' = R_4' = = OH; R_4 = OCH_3	acrammerin	brown	335–340	in pods of *Gleditschia triacanthos*
R_1 = R_3 = R_3' = OH; R_2' = R_4' = OCH_3	tricin	yellow	191–192	in leaves of *Triticum dicoccum*

TABLE 9. Flavonols (IX).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
X = OH				
$R_1 = R_3 = OH$	galangin	yellow	216–221	in roots of *Alpinia officinarum* Hance
$R_1 = OH$; $R_3 = OCH_3$	izalpinin	yellow	195	in seeds of *Alpinia chinensis* Rosc.
$R_1 = R_3 = R_1' = OH$	datiscetin	yellow	268–273	aglycone of dye from wood of *Datisca cannabina L.*
$R_1 = R_3 = R_3' = OH$	kaempferol	yellow	275–277	in leaves of *Delphinium consolida*, etc.
$R_1 = R_3' = OH$; $R_3 = OCH_3$	rhamnocitrin	yellow	221–222	in berries of *Rhamnus cathartica*
$R_1 = R_3 = OH$; $R_3' = OCH_3$	kaempferide	yellow	225–229	in roots of *Alpinia officinarum* Hance
$R_1 = R_4 = R_3' = OH$	pratoletin	yellow	285	in flowers of *Trifolium pratense*
$R_1 = R_3 = R_4 = R_3' = OH$	herbacetin	yellow	280–283	in flowers of *Gossypium indicum*
$R_1 = R_3 = R_3' = OH$; $R_4 = OCH_3$	tambuletin	yellow	269–271	in seeds of *Xanthoxylum acanthopodium*
$R_1 = OH$; $R_3 = R_4 = R_3' = OCH_3$	tambulin	yellow	205	in fruit of *Xanthoxylum acanthopodium*
$R_3 = R_2' = R_3' = OH$	fisetin	yellow	330 (decompn.)	in wood of *Rhus cotinus L.*, etc.
$R_1 = R_3 = R_2' = R_3' = OH$	quercetin	yellow	312–316 (decompn.)	in stems of *Erica vulgaris* and many others
$R_2 = R_3 = R_3' = OH$; $R_1 = OCH_3$	azaleatin	yellow	~ 320	in flowers of *Rhododendron mucronatum*
$R_1 = R_2 = R_3' = OH$; $R_3 = OCH_3$	rhamnetin	yellow	220–295	in berries of *Rhamnus tinctoria*, etc.
$R_1 = R_3 = R_3' = OH$; $R_2' = OCH_3$	isorhamnetin	yellow	~ 305 (decompn.)	in petals of *Cheiranthus cheiri*, etc.
$R_1 = R_1' = OH$; $R_3 = R_2' = OCH_3$	rhamnazin	yellow	214–218	aglycone of dye from *Rhamnus* berries
$R_1 = R_2' = OH$; $R_3 = R_3' = OCH_3$	ombuin	yellowish brown	229–230	aglycone of pigment from leaves of *Phytolacca dioica L.*
$R_1 = R_2 = R_3 = R_2' = R_3' = OH$	quercetagenin	yellow	316–320	in flowers of *Tagetes patula*, etc.
$R_1 = R_3 = R_2' = R_3' = OH$; $R_1' = OCH_3$	patuletin	yellow	262–264	in flowers of *Tagetes patula*
$R_1 = R_3' = OH$; $R_2 = R_3 = OCH_3$	chrysosplenetin	yellow	158–159	aglycone of pigment from stems of *Chrysosplenium japonicum*
$R_1 = R_3 = R_4 = R_2' = R_3' = OH$	gossypetin	yellow	311–313	in flowers of *Hibiscus sabdariffa*, etc.; aglycone of flower pigment of *Gossypium* family
$R_1 = R_3 = R_1' = R_3' = OH$	morin	light yellow	286–290	in wood of *Morus tinctoria L.*
$R_3 = R_2' = R_3' = R_4' = OH$	robinetin	yellow	324–334	in wood of *Robinia pseudacacia*
$R_1 = R_3 = R_2' = R_3' = R_4' = OH$	myricetin	yellow	350–357	in bark of *Myrica nagi*, etc.
$R_1 = R_3 = R_4 = R_2' = R_3' = R_4' = OH$	hibiscetin	yellow	340–350	in flowers of *Hibiscus sabdariffa*
X = OCH_3				
$R_2 = R_3' = OH$; $R_1 = R_2 = R_4 = OCH_3$	calycopterin	yellow	224	in leaves of *Digitalis thapsi*
$R_1 = R_2' = OH$; $R_3 = R_3' = OCH_3$	ayanin	orange-yellow	172–173	in heartwood of *Distemonanthus benthamianus*
$R_1 = R_2 = R_2' = OH$; $R_3 = R_3' = OCH_3$	hydroxyayanin-B	yellow	208–209	ditto
$R_1 = OH$; $R_3 = R_2 = R_2' = R_3' = OCH_3$	artemisetin	yellow	261–264	in *Artemisia absinthium*
$R_1 = R_3' = OH$; $R_3 = R_4 = R_2' = OCH_3$	ternatin	yellow	210–210.5	in bark of *Melicope ternata, M. simplex*
$R_1 = R_3 = OH$; $R_2 = R_4 = R_2' = R_3' = OCH_3$	eriantin	yellow	161	in *Blumea eriantha*
$R_1 = R_2' = R_3' = OH$; $R_3 + R_4 = OCH_2O$	wharangin	yellow	277–278	in bark of *Melicope ternata*
$R_1 = OH$; $R_2 = R_3 = OCH_3$; $R_2' + R_3' = OCH_2O$	melisimplin	yellow	234–236	in bark of *Melicope simplex*
$R_1 = R_2' = R_3' = OH$; $R_3 = R_3' = OCH_3$	hydroxyayanin-A	yellow	229–230	in heartwood of *Distemonanthus benthamianus*
$R_1 = OH$; $R_2 = R_4 = R_2' = R_3' = R_4' = OCH_3$	gardenin	yellow	163–164	in resinous exudation from *Gardenia lucida* Roxb.

TABLE 9 (contd.)

Substituent	Name	Colour	M.p., °C	Occurrence in nature
X = OSO_2K				
$R_1 = R_3 = R_3' = OH$; $R_2' = OCH_3$	persicarin	yellow	280 (decompn.)	in leaves of *Polygonum hydropiper L.*
$R_1 = R_3' = OH$; $R_3 = R_2' = OCH_3$	7-methyl ether of persicarin	yellow	212–213	in leaves of *Polygonum hydropiper L.*

TABLE 10. Flavanols (X, X = H).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_1 = R_2 = R_3 = R_2' = OH$	carthamidin	yellow	218	aglycone of flower pigment of *Carthamus tinctorius*
$R_1 = R_2 = R_1' = R_2' = OH$	homoeriodictyol	yellow	223–225	in stems of *Eriodictyon glutinosum* Benth.
$R_2 = R_1' = R_2' = OH$; $R_3 = OCH_3$	methoxybutin	yellow	195–197	in petals of *Coreopsis grandiflora* Nutt.
$R_1 = R_3 = R_1' = OH$; $R_2' = OCH_3$	hesperetin	yellow	224–225	aglycone of citrus pigment
Flavanonol, (X, X = OH)				
$R_1 = R_2 = OH$	pinobanksin	yellow	177–178	in heartwood of *Pinus strobus*, etc.

TABLE 11. Anthocyanins (XI).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_2 = R_3 = R_2' = OH$	apigenidin chloride	red	> 300	aglycone of petal pigment of *Gesneria fulgens*
$R_1 = R_2 = R_3 = R_2' = OH$	pelargonidin chloride	reddish brown	> 300	aglycone of petal pigment of *Pelargonium zonale*, etc.
$R_1 = R_2 = R_3 = R_4 = R_2' = OH$	cyanidin chloride	reddish brown	> 300	aglycone of flower pigment of *Chrisanthemum indicum L., Aster chinensis L., Centaurea cyanus L.*, etc.
$R_1 = R_2 = R_3 = R_2' = OH$; $R_1' = OCH_3$	peonidin chloride	brown	> 300	aglycone of flower pigment of *Viola tricolor*; berries of *Oxycocos macrocaprus* Pers., etc.
$R_1 = R_2 = R_3 = R_1' = R_2' = R_3' = OH$	delphinidin chloride	dark violet	> 300	aglycone of flower pigment of *Viola tricolor, Salvia patens*; berries of *Empetrium nigrum*, etc.
$R_1 = R_2 = R_3 = R_1' = R_2' = OH$; $R_3' = OCH_3$	petunidin chloride	sulphur brown	> 300	aglycone of flower pigment of *Petunia hybrida*, etc.
$R_1 = R_2 = R_3 = R_2' = OH$; $R_1' = R_3' = OCH_3$	malvidin chloride	dark brown	> 300	aglycone of flower pigment of *Cyclamen persicum* Mill., *Primula polyantha, Iris ensata*, etc.
$R_1 = R_2 = R_2' = OH$; $R_1' = R_3' = OCH_3$	hirsutidin chloride	violet	> 300	aglycone of flower pigment of *Primula hirsuta*.

TABLE 12. Isoflavones (XII).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_3 = R_2' = OH$	daidzein	light yellow	315–323 (decompn)	aglucone of pigment from *Soja hispida*
$R_1 = R_3 = OH$; $R_2' = OCH_3$	biochanin-A	light yellow	212–216	in *Cicer arietinum*
$R_1 = R_3 = R_2' = OH$; $R_2 = OCH_3$	tectorigenin	light yellow	227–230	aglucone of pigment from *Iris tectorum*
$R_1 = R_3 = R_1' = R_2' = OH$	orobol (santol)	light yellow	270.5	aglucone of pigment from *Orobus tuberosus L.*
$R_1 = R_1' = R_2' = OH$; $R_2' = OCH_3$	santal	yellow	223	in wood of *Pterocarpus santalinus L.*
$R_1 = R_3 = R_1' = OH$; $R_2 = R_2' = R_3' = OCH_3$	irigenin	yellow	185	aglycone of pigment from *Iris florentina*

TABLE 13. Xanthones (XXI).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_1 = R_7 = OH$	euxanthone	yellow	236–240	in heartwood of *Platonia insignis* Mart.
$R_1 = R_7 = OH$; $R_3 = OCH_3$	gentisin	yellow	267–274	in root of *Gentiana lutea*
$R_1 = R_3 = OH$; $R_7 = OCH_3$	isogentisin	yellow	241	ditto
$R_1 = R_3 = R_8 = OH$; $R_6 = OCH_3$	swertianol	yellow	263–267	in *Swertia japonica*
$R_1 = R_8 = OH$; $R_3 = R_6 = OCH_3$	swertirin	yellow	185–186	in stalks of *Swertia chirata*
$R_1 = R_3 = OH$; $R_6 = R_8 = OCH_3$	swertinin	yellow	217	in stalks of *Swertia decussata*
$R_1 = OH$; $R_2 = R_6 = R_8 = OCH_3$	decussatin	yellow	149–150	in flowers and roots of *Swertia decussata*
$R_1 = R_4 = R_8 = OH$; $R_3 = CH_3$	ravenelin	yellow	267–268	in mycelia of *Helminthosporium ravenelli* Curtus
$R_3 = R_8 = OH$; $R_1 = OCH_3$; $R_7 = CH_3$ or $R_2 = R_3 = OH$; $R_8 = OCH_3$; $R_7 = CH_3$	rubrofusarin	orange-red	210–211	in mycelia of *Fusarium culmorum* Saco
$R_1 = OH$; $R_2 = R_8 = OCH_3$; $R_7 = CH_3$ or $R_3 = OH$; $R_1 = R_8 = OCH_3$; $R_7 = CH_3$ or $R_8 = OH$; $R_1 = R_2 = OCH_3$; $R_7 = CH_3$	asperxanthone	yellowish red	203	in mycelia of various moulds *Aspergillus niger*

acid (XXII), the black-violet dye of many types of Thelephora, to which the structure of a phenanthrene derivative was earlier ascribed. Brasilein (XXIII, R = H) and haematoxilin (XXIII, R = OH), isolated from the wood of the mahogany (Leguminosae family) and the logwood (*Haematoxylon campechianum*) stand somewhat apart. This last substance, although itself colourless, was widely used for mordant dyeing cotton (bluish red and violet).

Many dyes of the groups considered above are encountered as glycosides (there are some exceptions)[31,35]. The most frequent carbohydrate is glucose, but rhamnose, galactose, arabinose, and others are also found.

b. Nitrogen-Containing Heterocyclics

Indole derivatives. Among the oldest natural dyestuffs used by man in dyeing are indigo[36] and purple of the ancients (antique purple). Indigo was extracted from the leaves of the tropical plant *Indigofera tinctoria*, and also *Isatis tinctoria* and *Polygonum tinctorium*, growing in Western Europe and in the south of the USSR. The plants contain not indigo itself, but the glucoside of indoxyl, indican, which is decomposed on hydrolysis into glucose and indoxyl, and is oxidised by atmospheric oxygen into indigo. Indican is accompanied by an isomer, indirubin (also formed from indoxyl), and other dyestuffs (including kaempferol). The purple of the ancients, present in the molluscs *Murex bandaris*, is 6,6'-dibromoindigo. The indole derivatives also include the high-molecular-weight pigments, the melamines[37].

Pyrrole derivatives. Three important groups of natural pigments belong to this class; the blood pigments, chlorophyll, and the bile pigments. They all contain a skeleton consisting of four pyrrole nuclei linked by methine bridges, only in the first two is the system closed to give the so-called porphyrin ring and in the last the ring is not closed. Haemoglobin of the blood is an iron-containing complex of protoporphyrin IX and a protein, globin[38]. The prosthetic group of haemoglobin — haem — which contains iron(II), is readily oxidised to haematin, which with acids gives salts, such as haemin. Porphyrins (XXIV) which are encountered in nature[39] are shown in Table 14. Chlorocruoroporphyrin is near in structure to protoporphyrin (a formyl group replaces one vinyl group) and is the prosthetic group of the pigment chlorocruorin from Spirographis.

As well as carotene and xanthophyll, the chloroplasts of the green parts of plants contain two pigments in 3 : 1 ratio, close in structure to the blood pigments, the blue-green chlorophyll-a (XXV, R = CH_3) and the yellow-green chlorophyll-b (XXV, R = CHO), which play an important role in plant photosynthesis. In addition, plants contain protochlorophyll-a (XXV, R = C_2H_5) in which ring A is dehydrogenated[40].

Vitamin B_{12}, which is widely distributed in nature and contains coordinated cobalt, belongs to this group of natural pigments.

TABLE 14. Porphyrins (XXIV).

Substituent	Name	Occurrence in nature
$R_1 = R_5 = CH_3$; $R_2 = CH = CH_2$; $R_3 = R_4 = CH_2CH_2COOH$	protoporphyrin IX	prosthetic group of haemoglobin and cytochrome (another protein), in faeces, in yeasts, in lettuce, spinach, potatoes, etc., in bird feathers. In the form of the Mg complex in mutants of *Chlorella vulgaris*
$R_1 = R_5 = CH_3$; $R_2 = C_2H_5$; $R_3 = R_4 = CH_2CH_2COOH$	mesoporphyrin IX	in faeces, in amber
$R_1 = R_5 = CH_3$; $R_2 = H$; $R_3 = R_4 = CH_2CH_2COOH$	deuteroporphyrin IX	in faeces
$R_1 = R_5 = CH_3$; $R_2 = CH(OH)CH_3$; $R_3 = R_4 = CH_2CH_2COOH$	haematoporphyrin IX	in mutants of *Chlorella vulgaris*
$R_1 = R_4 = CH_3$; $R_2 = R_3 = R_5 = CH_2CH_2COOH$	coproporphyrin I	in faeces, urine, yeasts, bird feathers
$R_1 = R_5 = CH_3$; $R_2 = R_3 = R_4 = CH_2CH_2COOH$	coproporphyrin III	ditto
$R_1 = R_4 = CH_2COOH$; $R_2 = R_3 = R_5 = CH_2CH_2COOH$	uroporphyrin I	»
$R_1 = R_5 = CH_2COOH$; $R_2 = R_3 = R_4 = CH_2CH_2COOH$	uroporphyrin III	»

TABLE 15. Pterins (XXVIII).

Substituent	Name	Colour	Occurrence in nature
$R_2 = OH$	xanthopterin	yellow	in wings of the lemon butterfly *Gonopteryx rhamni*; in the shell of the crab *Cancer pagurus*; in the astsidiae *Microcosmus polymorphus*
$R_1 = R_2 = OH$	leucopterin	white	in wings of the cabbage butterfly *Pieris brassica*
$R_1 = CH_3$; $R_2 = OH$	chrysopterin	yellow	in wings of the butterfly *Gonopteryx rhamni*
$R_1 = C(OH) = C(OH)CH_2OH$; $R_2 = OH$	erytropterin	red	in wings of the butterfly *Gonopteryx rhamni*
$R_2 = CH(OH)CH(OH)CH_3$	biopterin	yellow	in beer yeasts

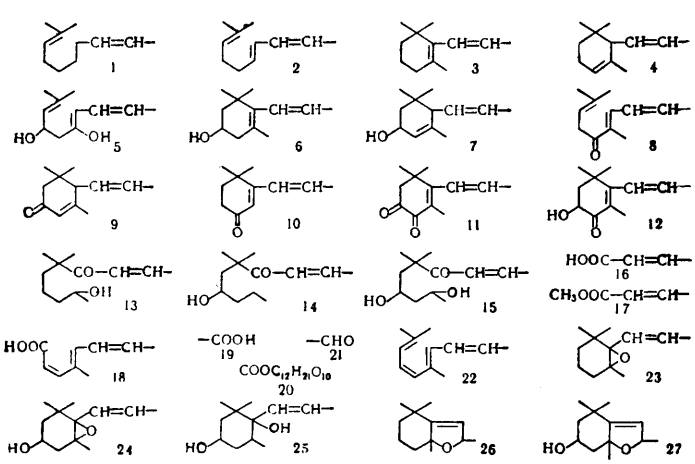
The group of bile pigments includes bilirubin (XXVI, R = $CH{=}CH_2$), mesobilirubin (XXVI, R = C_2H_5), and urobilin, distinguished from the last by the A, B, and C rings being hydrogenated[41]. Also among the pyrrole derivatives is prodigiosin, the red pigment of the bacterium *Serratia marinorubra* (XXVII), m.p. 151°–152°.

Phenazine derivatives. Hemipyocyanine, 1-hydroxyphenazine, m.p. 158°; phenazinecarbonic acid, m.p. 242°, and pyocyanine, 1-hydroxy-9-methylphenazine, m.p. 242°, which is dark blue and is found in *Pseudomonas pyocyanea* and *P. aureofaciens* all belong to this class. Vitamin B_2 (lactoflavin, riboflavin), 6,7-dimethyl-9-ribityl-isoalloxazine, which is also widely distributed in nature is similar to this group of pigments.

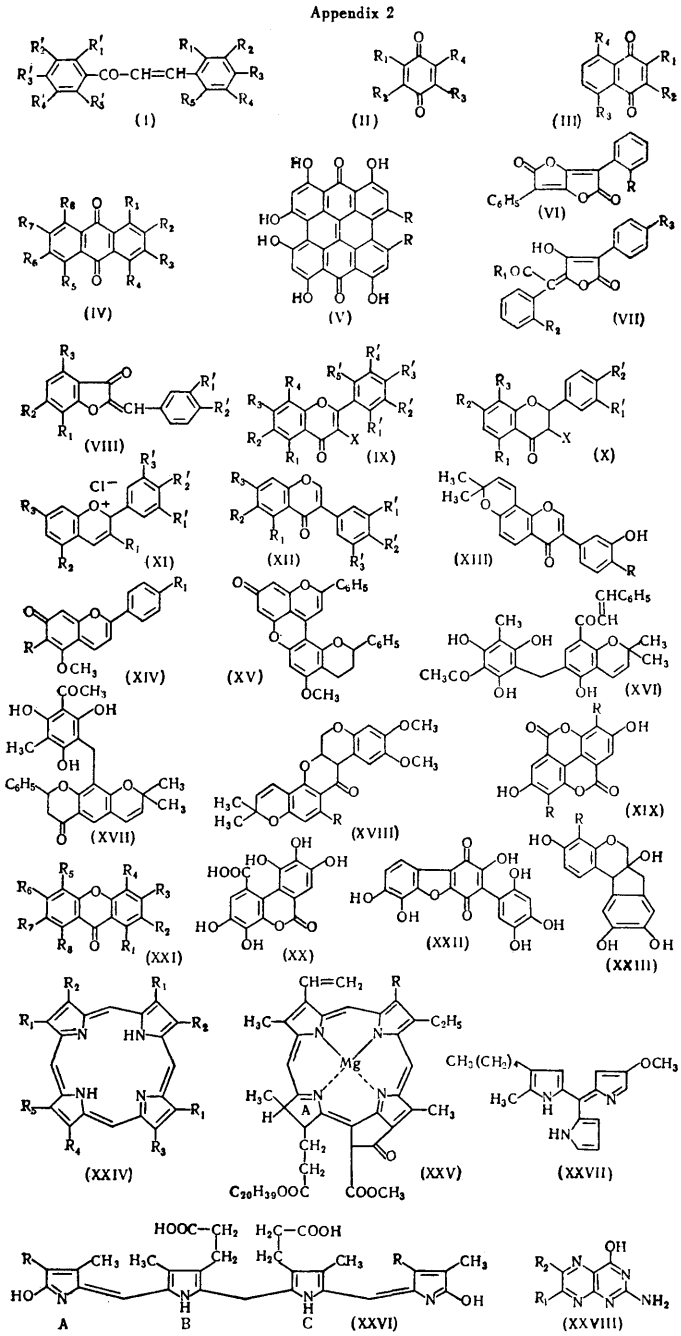
The pigments of the group of ommochromes[44] belong to the oxazine derivatives.

Another rather widely distributed group of natural pigments is the derivatives of pteridine[45–47] (XXVIII) first isolated from the dust of butterfly wings. Some of them are physiologically active and are also structurally close to folic acid.

Appendix 1 (to Table 1)



Appendix 2



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CHEMISTRY OF ALLOXAZINES AND ISOALLOXAZINES

V. M. Berezovskii and T. V. Eremenko

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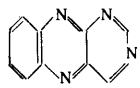
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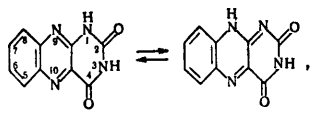
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I. INTRODUCTION

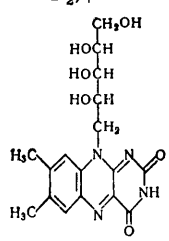
1,2,3,4-Tetrahydro-2,4-dioxo-derivatives of benzopteridine — the condensed pyrimido[4,5-*b*]quinoxaline cyclic system



are called "alloxazines". They exist in two tautomeric forms

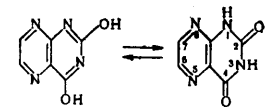


one of which, when "frozen" by substitution of the hydrogen atom at $N_{(9)}$, is the source of the isoalloxazine series. The most important naturally occurring member of this series, riboflavin (vitamin B_2)†



belongs to the yellow pigments of the "flavin" group. Riboflavin is one of the few isoalloxazines possessing biological activity; it is present in the animal organism.

Alloxazines and isoalloxazines are close in structure to the pteridines, compounds containing a condensed pyrimidopyrazine ring system. The product of condensing 2,4-dihydroxypteridine in the lactam form (called lumazine)



with benzene is alloxazine (benzolumazine).

Pteridines are widely distributed in the animal and vegetable world, as innumerable natural pterins — derivatives of 2-amino-4-hydroxypteridine such as leucopterin, xanthopterin, erythropterin, rhizopterin, folic acid (vitamin B_c).

The alloxazines were discovered in 1891 by Kühling[5], unsubstituted alloxazine being obtained for the first time by condensation of *o*-phenylenediamine hydrochloride with alloxan. In the next few years a number of compounds of this type were obtained[6,7] but then for a long time this field of chemistry failed to attract attention. The intensive examination of the alloxazine and isoalloxazine series developed only after the discovery by Osborne and Mendel[8] in 1913 that a water-soluble factor contained in milk is necessary for the growth of young rats which are on a diet of proteins and other purified components, the isolation of this factor from milk[8,9], egg yolk[10], liver[11,13], dandelions[14], malt[15], and other sources[16], and the observation (in 1932)[17-21] that 6,7,9-trimethylisoalloxazine is formed in the photolysis of the water-soluble factor (vitamin B_2) in alkaline medium. In 1935 the exact empirical formulae ($C_{17}H_{20}O_6N_4$) of a strongly fluorescing orange crystalline substance (m.p. 280°-282°), which was isolated from milk[22], was established. Simultaneously Karrer and coworkers[23,24] and Kuhn *et al.*[25] synthesised vitamin B_2 (riboflavin) and hence demonstrated its structure unequivocally.

Riboflavin is widely distributed in nature both as itself and in the form of coenzymes and flavin enzymes; it is found in almost all cells of animal and vegetable organisms and in the cells of many microorganisms. Some of them, for example *Eremothecium ashbyii*, are capable of producing riboflavin[26,27] and the coenzyme flavin-adenine dinucleotide[28,29] in quantities considerably exceeding that that required for exchange of substances in their cells.

An enzyme containing vitamin B_2, the so-called "yellow oxidising enzyme"‡, was first isolated from yeast by Warburg and Christian[17,18] in 1932, even before the structure of vitamin B_2 was established.

II. SYNTHESIS OF ALLOXAZINES FROM *o*-PHENYLENEDIAMINES AND ALLOXAN

One of the most important and most general methods for the synthesis of alloxazines is the condensation of aromatic *o*-diamines with α-dicarbonyl compounds of the pyrimidine series.

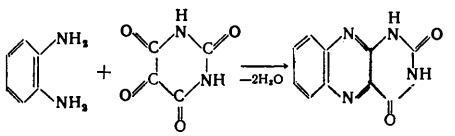
Aromatic *o*-diamines react fairly easily with aliphatic and aromatic α-dicarbonyl compounds (α-dialdehydes and

† The determination of the structure and method of synthesis of riboflavin, its physical and chemical properties, and the relation between structure and biological activity, established through the synthesis of intermediate substances and flavin coenzymes, have previously been given in review articles[1,2,3] and in "Khimiya Vitaminov" (Chemistry of the Vitamins)[4].

‡ This is normally called the "old yellow enzyme" (Ed. of Translation).

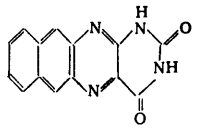
α-diketones or ketals) to form phenazines or quinoxalines. The reaction was first used by Claus[30] in 1873 to synthesise phenazine and then extended to its derivatives[31]. Quinoxaline was first obtained, by the condensation of *o*-phenylenediamine with glyoxal at 60°-70°, by Hinsberg[32] and Körner[33], and its derivatives were prepared from substituted *o*-phenylenediamines and α-dicarbonyl compounds[34,35].

This method was proposed[5] for the preparation of alloxazine from *o*-phenylenediamine hydrochloride and alloxan:



Alloxan, 5-oxobarbituric acid, is a ketone, as is confirmed by addition reactions with amines[36], substitution reactions[37], etc.; it also possesses acidic properties.

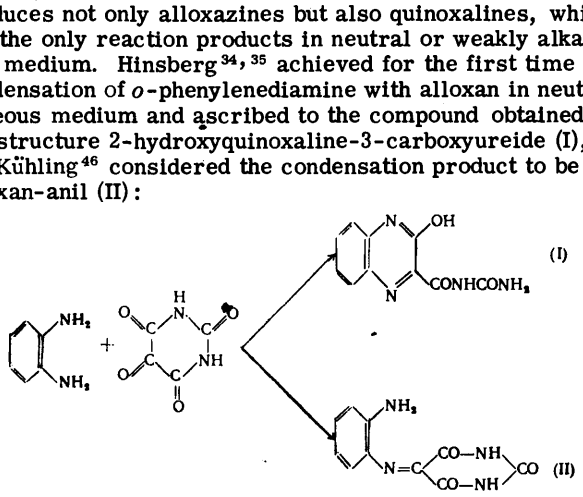
Condensation of aromatic *o*-diamines with alloxan in an acid medium has been used to obtain alloxazines with the following substituents: 6- or 7-methyl[5], 6,7-dimethyl[38,39], 6,8- or 5,7-dimethyl, 7,8- or 5,6-dimethyl[39], 5,7,8- or 5,6,8-trimethyl, 6,7,8- or 5,6,7-trimethyl, 5,6,7,8-tetramethyl[40], 6- or 7-ethyl[41], and 6- or 7-phenyl[42]. Alloxazine-6- or alloxazine-7-sulphonic acid[43], alloxazine-6- or alloxazine-7-β-acrylic acid[43], the lactone of 5(or 8)-hydroxymethylalloxazine-6(or 7)-carboxylic acid, and the lactone of 8(or 5)-amino-7(or 6)-hydroxymethylalloxazine-6(or 7)-carboxylic acid[44] have been prepared; benzoalloxazine



has been synthesised[42].

It follows from these examples that the synthesis of substituted alloxazines from alloxan and unsymmetrically substituted *o*-diamines does not always lead to a single compound. In many cases a mixture of two or more isomers of alloxazine is formed, the separation of which is very difficult.

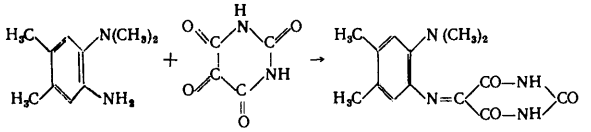
When insufficient acid is present the reaction of *o*-phenylenediamines with alloxan is not well defined and produces not only alloxazines but also quinoxalines, which are the only reaction products in neutral or weakly alkaline medium. Hinsberg[34,35] achieved for the first time the condensation of *o*-phenylenediamine with alloxan in neutral aqueous medium and ascribed to the compound obtained the structure 2-hydroxyquinoxaline-3-carboxyureide (I), but Kühling[46] considered the condensation product to be an alloxan-anil (II):



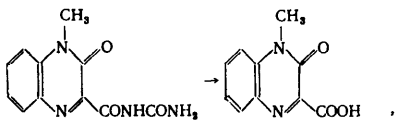
Many authors have ascribed an alloxan-anil structure to analogous substances obtained by condensation of alloxan with aromatic *o*-diamines in various solvents in the absence of mineral acids; in these syntheses the following *o*-diamines were used: *N*-methyl-*o*-phenylenediamine in methanol[36], *N* 4,5-trimethyl-*o*-phenylenediamine[47], *N*-(2-amino-4,5-dimethylphenyl)-*L*-arabitylamine in aqueous alcohol and acetic acid[48], *N*-(2-amino-4,5-dimethylphenyl)-*D*-ribitylamine in pyridine[49], etc.

However, such a structure for the condensation products is doubtful. They do not undergo cyclisation in acidic media and are easily hydrolysed by alkali to derivatives of 2-hydroxyquinoxaline-3-carboxylic acid or of the corresponding 1,2-dihydro-2-oxoquinoxaline compounds, *i.e.* the same compounds which are formed in the cleavage of alloxazines and isoalloxazines by alkali[50]. They are not cleaved by acids as is characteristic for Schiff bases and is observed, for example, with 5-(*p*-dimethylaminoanil)-alloxan.

Nevertheless, from *o*-diamines with one tertiary nitrogen atom, which excludes the possibility of condensation to quinoxalines, substances with an alloxan-anil structure are obtained[51]:



Hinsberg's quinoxaline-ureide structural formula (I) for the substances obtained from alloxan and *o*-diamines is proved, for example, by the fact that 1,2-dihydro-1-methyl-2-oxoquinoxaline-3-carboxylic acid can be obtained from its ureide:



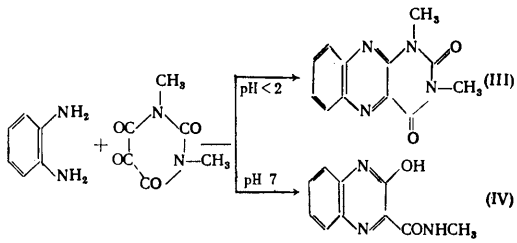
not only by alkali cleavage but by hydrolysis with 2 *N* hydrochloric acid[50], *i.e.* under conditions which would preclude cleavage of the pyrimidine ring if this were present in the molecule. Ultraviolet adsorption spectra[52] also confirm the ureide structure for the compound in question.

Alloxan is not stable towards alkaline reagents. In the presence of baryta water it is converted into alloxanic acid. According to Hinsberg[34] alloxan is converted even under milder conditions to the acyclic alloxanic acid, which then condenses with *o*-diamines to a quinoxaline derivative.

It is possible that the initial unstable product of the reaction of alloxan with aromatic *o*-diamines is the alloxan-anil which in acidic medium undergoes cyclisation without cleavage of the pyrimidine ring to give alloxazines and isoalloxazines, but under acid-free condensation conditions in the presence of free *o*-diamine cyclises to the quinoxaline-ureide.

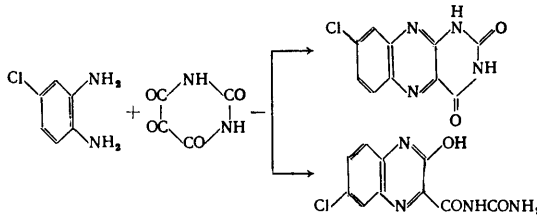
The condensation of *o*-phenylenediamine hydrochloride with dimethylalloxan produces 1,3-dimethylalloxazine (III)[5,53] while condensation in a neutral medium gives the

methylamide of 2-hydroxyquinoxaline-3-carboxylic acid (IV)[53]:



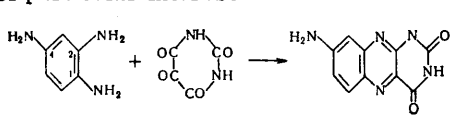
The formation of the second condensation product evidently occurs because even in a neutral medium dimethylalloxan is broken down to the monomethylamide of mesoxalic acid, which then condenses with the *o*-diamine[53]. This is proved by previously treating dimethylalloxan with an equivalent amount of alkali, the dimethylalloxan easily decomposing to methylamine, carbon dioxide, and the monomethylamide of mesoxalic acid; the last condenses with *o*-diamine to give (IV)[54].

Depending on the medium the 5-CO group of alloxan reacts preferentially with one of the amino-groups of 4-chloro-*o*-phenylenediamine with subsequent closing of the pyrazine ring. 7-Chloroalloxazine is obtained on heating in 1-5 *N* hydrochloric acid or in glacial acetic acid in the presence of 0.1 mole boric acid at 18°-20°; in 10% aqueous acetic acid or alcohol the ureide of 6-chloro-2-hydroxyquinoxaline-3-carboxylic acid is formed in 96% yield[55]:



Condensation in glacial acetic acid without boric acid produces an equal mixture of both substances[55]. In this reaction the catalytic effect of boric acid, which was established earlier in the formation of isoalloxazines[56], is shown clearly.

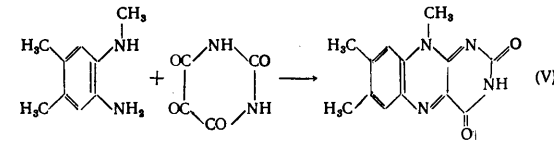
The reaction of 1,2,4-triaminobenzene with alloxan, which gives 7-aminoalloxazine in the presence of boric acid[57] is of particular interest



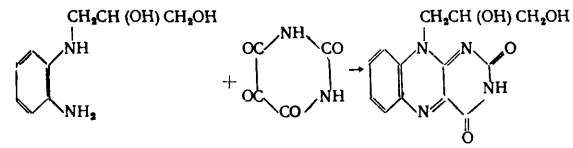
Evidently the opposed inductive effects of the amino-groups in the *para*-positions and, to some extent, in the *ortho*-positions diminish the conjugation of the *p* electrons of the nitrogen atom with the π electrons of the benzene ring to a different degree for the various amino-groups, and the amino-groups must occur in the following order as regards their nucleophilic character: 1-NH_2 > 4-NH_2 > 2-NH_2. Hence the electrophilic centre of the carbonyl group is preferentially attacked by the most nucleophilic nitrogen atom, that in position 1, which also determines the further course of the reaction with the second amino-group and the structure of the substance formed.

III. SYNTHESIS OF ISOALLOXAZINES FROM PRIMARY-SECONDARY AROMATIC *o*-DIAMINES AND ALLOXAN

Isoalloxazines were first obtained in 1934. Kuhn and his coworkers[47,58,59] prepared 9-methylisoalloxazine by the condensation of *N*-methyl-*o*-phenylenediamine hydrochloride with alloxan in water at 50°-60°, and 6,7,9-trimethylisoalloxazine (lumiflavin, 9-methylflavin§) in 75% yield by the condensation of *N* 4,5-trimethyl-*o*-phenylenediamine hydrochloride with alloxan under the same conditions



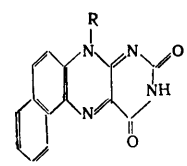
At the same time Karrer *et al.*[60] obtained 9-(2,3-dihydroxypropyl)isoalloxazine by heater *N*-(2,3-dihydroxypropyl)-*o*-phenylenediamine dihydrochloride with alloxan in alcohol



In contrast to alloxazines, isoalloxazines with a strictly definite structure are formed from primary-secondary aromatic *o*-diamines, as a consequence of the predominating reaction of the primary amino-group with the 5-oxo-group of alloxan.

Isoalloxazines have been synthesised with the following substituents in the 9-position: ethyl, benzyl[61], cyclohexyl[62], 2-hydroxyethyl[41], 2-hydroxypropyl[63], 3-hydroxypropyl[64], and carboxyethyl[65]. Derivatives which have been prepared with substituents in other positions are as follows: 9-(2-hydroxyethyl)-8-methyl[40,66], 6,8,9-trimethyl[61,62,67], 9-(1-*D*-dulcityl)-7-methyl[24,68], 7-methyl-9-(1-*D*-ribityl)[69-71], 9-(1-*D*-mannityl)-7-methyl[68], 7-ethyl-9-(1-*D*-ribityl)[72], 9-(1-*L*-arabityl)-6,7-tetramethylene[73], 9-(1-*D*-arabityl)-6,7-trimethylene[73], 5,7-and 6,8-dimethyl-9-(1-*D*-ribityl), 9-(1-*D*-arabityl)-6,8-dimethyl, 5,6-and 5,7-dimethyl-9-(1-*L*-arabityl)[74,75], 5,6,7-trimethyl-9-(1-*D*-ribityl), 9-(1-*D*-arabityl)-5,6,7-trimethyl, 5,6,7-trimethyl-9-(1-*D*-xylityl), and 9-(1-*D*-lyxityl)-5,6,7-trimethyl[76].

Other derivatives obtained are *D*- and *L*-arabo-[22,68,77], *D*- and *L*-ribo-[23-25,77,78], *D*-lyxo-[77], *D*-2′-deoxyribo-[69], and *D*-gluco-[68], flavins, 2′,3′-dihydroxypropylflavin[41,62], flavin acetic acid[62,79], and also benzoisoalloxazines such as 9-(1-*D*-ribityl)- and 9-(1-*L*-arabityl)-benzo[*h*] isoalloxazines[72]



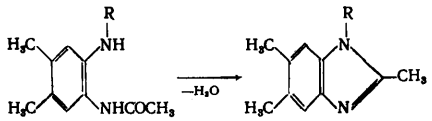
where R = *D*-ribityl or *L*-arabityl.

§ In accordance with a terminology frequently used but not very systematic, we use the term flavins for derivatives of 6,7-dimethylisoalloxazine.

In trivial names pentose and hexose substituents are designated by the name of the corresponding sugar, *e.g.* 6,7-dimethyl-9-(1-*D*-sorbityl)isoalloxazine is called *D*-glucoflavin.

Some isoalloxazines can be synthesised in good yields using hydrochloric acid as a catalyst. By this means compounds have been obtained with simple alkyl, aryl, or alkylaryl substituents in position 9, such as 9-methyl[58,80], 6,9-dimethyl (80%)[81], 9-(1-naphthyl)[42], 9-(1,3-dihydroxy--2-propyl)[82], 9-(2-phthalimidoethyl)[83], 9-methyl-6-sulphonic acid[80], and also 9-benzylbenzo[*h*]isoalloxazine[42].

Monoacyl derivatives of *o*-phenylenediamine can also be used for the condensation with alloxan in a medium of hydrochloric acid; they are deacylated as the reaction occurs but the yield of flavins is then not high because the predominant reaction is an intramolecular removal of water, the original diamine undergoing cyclisation to a substituted benzimidazole[22,68]

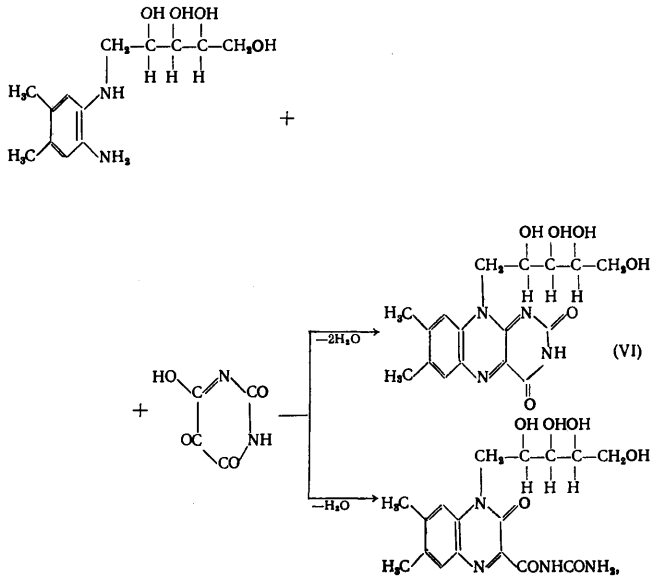


Dilute hydrochloric acid or methanol saturated with hydrogen chloride are successfully used as catalysts for synthesis of isoalloxazines, mainly when the original *o*-diamines contain aminoalkyl or alkyl derivatives of nitrogen heterocycles as *N*-substituents, the isoalloxazines formed being isolated as the hydrochlorides. The reactions are usually carried out by heating to 100° or by boiling the reaction mixture; the isoalloxazines are obtained in good yield. Under these conditions isoalloxazines with the following substituents in position 9 have been obtained: 2-aminoethyl[83], 2-diethylaminoethyl[84], 3-aminopropyl (65% yield), 4-diethylaminobutyl (33.8%), 3-diethylamino-2--hydroxypropyl (65%), 2-(2-hydroxyethylamino)ethyl (68.2%), 3-piperidinopropyl (59.5%), and 3-morpholinopropyl (70%)[85].

Isoalloxazines with substituents in other positions have also been obtained: 9-(2-diethylaminoethyl)-6-methyl (62%), 9-(3-diethylaminopropyl)-6-methyl (48.8%), 9-(2-diethylaminoethyl)-6-methoxy, 9-(3-diethylaminopropyl)-6--methoxy[84], 9-(3-diethylaminopropyl)-6,7-dimethoxy, 9--(3-diethylaminopropyl)-6,7-dimethyl[86], 6-chloro-9-(2--diethylaminoethyl), and 6-chloro-9-(3-diethylaminopropyl)[84].

However, many isoalloxazines are synthesised in the presence of hydrochloric acid in very poor yields. It was found that, if 9-alkylisoalloxazines are obtained in good yields on condensing *o*-diamine hydrochlorides with alloxan in aqueous or alcoholic medium, the condensation of many *N*-hydroxyalkyl-*o*-diamines occurs with low yields of 9-hydroxyalkylisoalloxazines, and with pentose substituents the yield of isoalloxazines falls to as low as 5-10%.[55] Increasing the acidity of the medium for the reaction in dilute hydrochloric acid, for example, in the preparation of isoalloxazines with the substituents: 9-(1-*L*-arabityl), 9-(1-*L*--arabityl)-7-methyl, 7-methyl-9-(1-*D*-xylityl), 7-methyl--9-(1-*D*-sorbityl), 6,7-dimethyl-9-(1-*L*-rhamnityl)[22,68], 6,7-dimethyl-9-(1-*L*-xylityl)[77], and 9-(2-hydroxyethyl)--6,8-dimethyl[66], only increases the yields a little and they all remain below 20%.

If acetic acid is used in place of the mineral acid, for example, in the condensation of *N*-(2-amino-3,4-dimethylphenyl)-*D*-ribitylamine with alloxan, apart from the reaction in which two molecules of water are removed to produce riboflavin (VI) in 5-10% yield, there is a second reaction in which only one molecule of water is lost[48,87] and a substance with a quinoxaline structure is formed[49,50];



the latter is 1,2-dihydro-6,7-dimethyl-2-oxo-1-(*D*-ribityl)-quinoxaline-3-carboxylic acid ureide.

It was found, in a systematic study of the effect of substituents in the aromatic ring, that in some cases addition of boric acid gives a higher yield of flavins. However the catalytic activity of boric acid does not depend on complex formation with the hydroxyl groups because its presence in the reaction medium also increases the yield of isoalloxazines which do not contain hydroxyl groups in the side chain[56]. Crystalline pyroboroacetate $[(CH_3COO)_2B]_2O$, which is obtained from acetic anhydride and boric acid, can be used as a catalyst[56].

The following substances were synthesised with high yields using a boric acid catalyst in a medium of acetic acid: *D*-, *DL*-, and *L*-araboflavins[56,88,89], *D*-riboflavin (over 70% yield); methyl-, pentyl-, and allyl-flavins[88], and 9-phenyl-[56,88], 6,9-diphenyl-[42], 6,9-dimethyl- (80% yield)[81], 9-(1-*D*-dulcityl)-6-methyl-(65%), 9-(1-*D*-dulcityl)-6--methoxy-(51%)[90], 6-methyl-9-(1-*D*-ribityl)-[91], 6-ethyl-7--methyl-9-(1-*D*-ribityl)-, and 9-(1-*L*-arabityl)-6-ethyl-7--methyl-[72] isoalloxazines were also synthesised. 5,6-Dimethyl-9-(tetraacetyl-*D*-ribit-1-yl)isoalloxazine has also been obtained[72]; this is hydrolysed by sodium methoxide to 5,6-dimethyl-9-(1-*D*-ribityl)isoalloxazine, or isoriboflavin, antivitamin B_2.[92,93] 9-Phenylbenzo[*j*]- and 9-benzylbenzo[*h*]-isoalloxazines have been prepared[42].

The increase in the yields of some isoalloxazines was nevertheless small: thus, 6-ethyl- and 6,7-diethyl-9-(1--*D*-ribityl)isoalloxazines were obtained with only 29% and 30% yields respectively[90,95].

Extensive searches were made for bacterial inhibitors and therapeutically active agents among halogen-substituted isoalloxazines. The condensation of alloxan with halogen--substituted aromatic *o*-diamines was accomplished in the presence of boric acid. The following compounds were obtained:

A. 6-Chloroisoalloxazines with the following substituents in position 9: 1-*D*-arabityl (66% yield)[90,96], 1-*L*-arabityl (67%),

1-*D*-xylityl (52%)[91], 1-*D*-dulcityl (70%), 1-*D*-mannityl (64%), 1-*D*-sorbityl[91,97], 1-*D*-ribityl[98], and 3-diethylaminopropyl[99].

B. 6,7-Dichloroisoalloxazines with the following substituents in position 9: 1-*D*-ribityl (80%)[97,99,100], 1-*D*--arabityl[90,96,97], 1-*L*-arabityl[96], 1-*D*-xylityl[90,96], 1-*D*--sorbityl[96,100], 1-*D*-dulcityl[96,97,101], 1-*D*-rhamnityl[97], 1-*D*-mannityl[90,96], 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 5-hydroxypentyl[102], diethylaminoethyl, 4-diethylamino-1-methylbutyl[98], diethylaminodecyl, diethylaminoundecyl[102].

C. Chloroisoalloxazines with substituents in various positions: 7-chloro-8-diethylaminoethyl (41%), 7-chloro-9--diethylaminopropyl (70%)[103,104], 7-chloro-9-(4-diethylamino-1-methylbutyl) (82%)[104], 6-chloro-7-methyl-9-(1-*D*--ribityl), 7-chloro-6-methyl-9-(1-*D*-ribityl) (64%)[105], and 6-methyl-7-chloro-9-(1-*D*-sorbityl) (48%)[90].

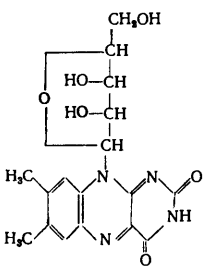
D. 6,7-Dibromoisoalloxazines with the following substituents in position 9: 1-*D*-ribityl, 1-*L*-arabityl, and 1-*D*--galactyl.[97] 6-Fluoroisoalloxazines with the following substituents in position 9: 1-*D*-ribityl, 1-*D*-arabityl, and 1-*D*-galactyl.[97]

Boric acid in an acetic acid medium catalyses the condensation of alloxan with primary-secondary aromatic *o*-diamines which contain aminoalkyl derivatives as *N*-substituents, but the isoalloxazines are not always obtained with good yields.

The yields of isoalloxazines fall as the aminoalkyl substituent in position 9 becomes more complex and as the number of substituents in the benzene ring increases: 9--(3-diethylaminopropyl) (77%), 9-(3-diethylaminopropyl)--8-methyl (62%), 9-(3-diethylaminopropyl)-6,8-dimethyl (50%), 9-(4-diethylamino-1-methylbutyl)-6,7-dimethyl (68%)[105], 9-(4-diethylamino-1-methylbutyl)-7-methoxy (40%), 9-(4-diethylamino-1-methylbutyl)-6,8-dimethyl (20%), 9-(4-diethylamino-1-methylbutyl)[106].

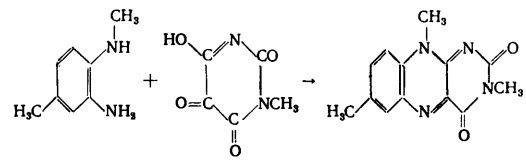
The method discussed gives good results in the condensation of initial diamines containing also negative substituents such as the nitro-group; 9-(2-hydroxyethyl)-6--nitro-[107] and -6,7,9-trimethyl-8-nitro-isoalloxazines[108] have been obtained.

Condensation of *O*-acetylated *N*-glycosyl-*o*-diamines and alloxan under mild conditions in a mixture of acetic and boric acids at 20° gave the corresponding *O*-acetylated *N*-glycosylisoalloxazines (65%) from which *D*-, *DL*-, and *L*--arabofuranosylflavins and *D*-ribofuranosylflavin were obtained by mild deacetylation in an alcoholic solution of ammonia[109]



There is no information as to which configuration (α- or β-) the substances obtained have. They are easily decomposed in cold dilute acid to form lumichrome[109].

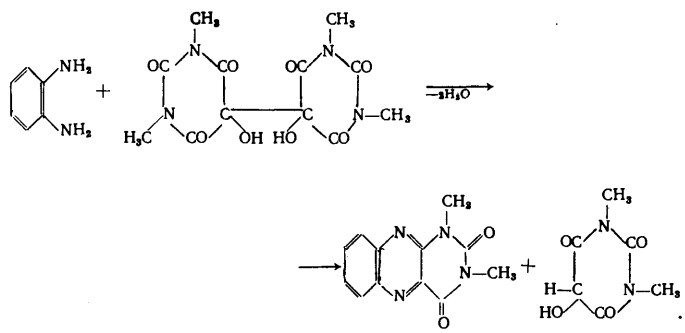
Since monomethylated alloxan is capable of lactam-lactim tautomerism only through the group with the unsubstituted hydrogen atom, -NH-CO-, the condensation of methylalloxan with *N*-phenyl(alkyl)-*o*-phenylenediamines gives, in contrast to the alloxazines, *N*-methylated isoalloxazines with unequivocal structure. 3-Methyl-9-phenyl- and 3,9-dimethyl-isoalloxazine were obtained by this means from, respectively, *N*-phenyl- and *N*-methyl-*o*--phenylenediamine in water or in acetic acid in the presence of boric acid[56,67,110,111]. 3,6,9-Trimethylisoalloxazine was obtained, in hydrochloric acid solution, from 3-amino-4-methylaminotoluene and methylalloxan[81]



The following have also been obtained from methylalloxan: 3-methylriboflavin[101] and 6,7-dichloro-9-(1-*D*--dulcityl)-3-methylisoalloxazine[101].

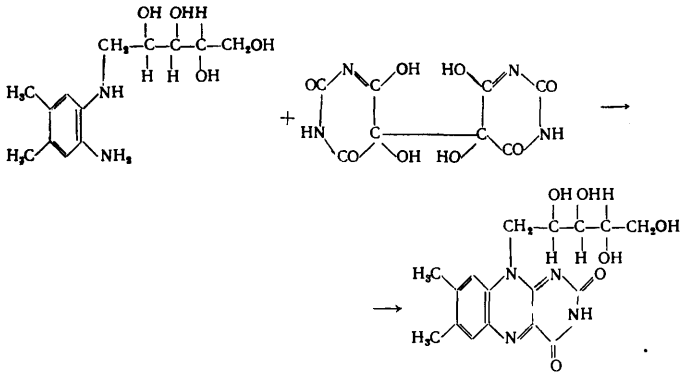
IV. SYNTHESIS OF ALLOXAZINES AND ISOALLOXAZINES FROM AROMATIC *o*-DIAMINES AND ALLOXANTIN OR DIALURIC ACID

Besides alloxan, the products of its reduction — alloxantin and its methylated derivatives — enter into the condensation reaction with *o*-phenylenediamine. However, the reaction takes place somewhat differently than with alloxan; one of the hetero-rings of alloxantin is split off in the form of dialuric acid. Thus, in the condensation of 3,4-diaminotoluene with symmetrical dimethylalloxantin 1,6-, 1,7-, 3,6-, or 3,7-dimethylalloxazine is formed[5,112] while 1-(or 3-(methylalloxazine is obtained from *o*-phenylenediamine[5,113]; condensation of 3,4-diaminotoluene with tetramethylalloxantin produces 1,3,6- or 1,3,7-trimethylalloxazine while *o*-phenylenediamine gives 1,3-dimethylalloxazine[5,112].



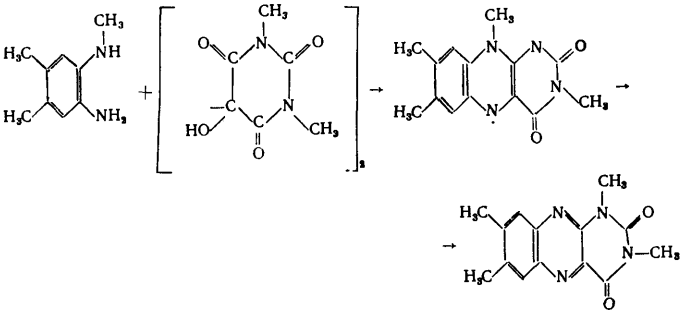
The reaction takes place in acetic acid in the presence of boric acid. The dialuric acid formed is slowly oxidised by atmospheric oxygen to alloxantin.

Unsubstituted alloxantin condenses with *N*-(2-amino-4,5-dimethylphenyl)-*L*-lyxitylamine hydrochloride on heating in alcohol to form *L*-lyxoflavin [114]:



Riboflavin is obtained from *N*-(2-amino-4,5-dimethylphenyl)-*D*-ribitylamine and a mixture of alloxantin with alloxan [115,116] or alloxantin alone, or dialuric acid in the presence of atmospheric oxygen in alcoholic hydrochloric acid [117,118].

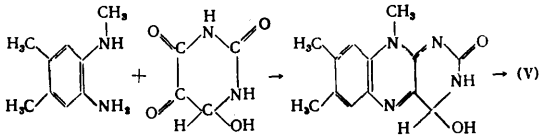
2′,3′,4′-Triacetyl-*D*-araboflavin was obtained from alloxantin and *N*-(2-nitro-4,5-dimethylphenyl)-2,3,4-triacetyl-5-trityl-*D*-arabitylamine [119]. The reaction of tetramethylalloxantin with *N*,4,5-trimethyl-*o*-phenylenediamine proceeds in the absence of air in glacial acetic acid with formation of a semiquinonoid radical of a substituted isoalloxazine, which is oxidised slowly with demethylation and formation of a colourless alloxazine — 1,3-dimethyl lumichrome [80]:



It is not clear at what intermediate stage the demethylation at position 9 takes place. The semiquinonoid intermediate separates from dilute hydrochloric acid in the form of violet rhodoflavin with the grouping:



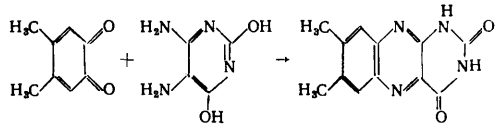
The possibility of using isodialuric acid is of interest. For example, the condensation of *N*,4,5-trimethyl-*o*-phenylenediamine with isodialuric acid in glacial acetic acid takes place with difficulty through the intermediate 4,4-dihydro isoalloxazine, which is unstable and is oxidised in an acidic medium in the presence of air to lumiflavin [120,121]:



6-Methylisodialuric acid can be used in place of isodialuric acid in the reaction with *o*-diamine; under the influence of atmospheric oxygen the C–C bond of the methyl group at position 4 in the isoalloxazine ring of the intermediate compound is broken and lumiflavin is again formed [121]. It should be noted that in alkali solutions isodialuric acid isomerises to dialuric acid.

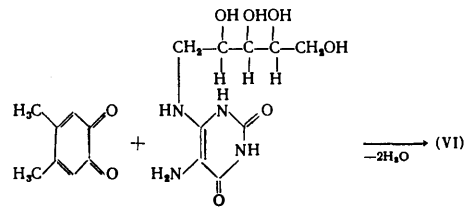
V. SYNTHESIS OF ALLOXAZINES AND ISOALLOXAZINES FROM AROMATIC *o*-QUINONES AND DIAMINODIHYDROXYPYRIMIDINES

The synthesis of an alloxazine molecule from *o*-diamines and α-dicarbonyl compounds can be achieved starting not from aromatic *o*-diamines but from *o*-diaminopyrimidines, condensing them with α-dicarbonyl aromatic compounds. Thus, lumichrome is formed (68% yield) on boiling 4,5-dimethyl-1,2-benzoquinone with 4,5-diamino-2,6-dihydroxypyrimidine in acetic acid [122]



(VII)

Isoalloxazines are obtained in a similar way. For example, riboflavin (VI) is formed (29% yield) in the reaction of 5-amino-4-(*D*-ribitylamino)uracil with 3,4-dimethyl-1,2-benzoquinone:



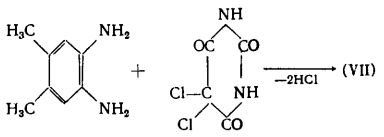
and from the corresponding diaminopyrimidines lumiflavin (40% yield) and 9-hydroxyethyl-, 9-(1-*D*-mannityl)-, and 9-(1-*D*-sorbityl)-flavins are obtained [123].

VI. SYNTHESIS OF ALLOXAZINES AND ISOALLOXAZINES FROM AROMATIC *o*-DIAMINES AND HALOGENOBARBITURIC ACIDS

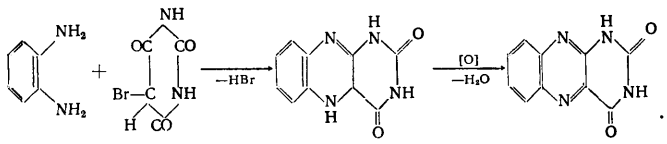
To build up the pyrazine ring in alloxazines and isoalloxazines, Matsukawa and coworkers [124,125] and Tishler and coworkers [49,126,127] proposed the condensation of α-halogenoketones of the pyrimidine series, in particular 5,5-dibromo- and 5,5-dichloro-barbituric acid, with *o*-phenylenediamines. The 4-oxo-group of the halogen-substituted barbituric acid takes part in the ring formation.

Hinsberg [35] had already observed in 1886-1887 the formation of quinoxalines in the reaction of aliphatic α-halogenoketones with aromatic *o*-diamines. It has been noted that 5,5-dibromobarbituric acid reacts easily with aliphatic amines and aniline [128]. The halogen atoms in 5,5-dibromobarbituric acid are not equivalent and they differ in their reactivity [129,130]. On the basis of spectroscopic data 5,5-dihalogenobarbituric acids have been ascribed the structure of trioxohexahyropyrimidines [131].

The condensation of 1,2-diamino-4,5-dimethylbenzene with 5,5-dichlorobarbituric acid at 100° in acetic acid produces 6,7-dimethylalloxazine in 59% yield; in pyridine the yield of lumichrome is increased to 90%:[49]



The use of 5-bromo- or 5,5-dibromo-barbituric acid in the condensation leads to lower yields[49], particularly with the monosubstituted compound. Thus, in the condensation of 5-bromobarbituric acid with *o*-phenylenediamine at 100° in pyridine, alloxazine is obtained in only 20.7% yield[49]:



However, aromatic *o*-diamines substituted in the ring with alkyl groups give better yields than *o*-phenylenediamine; the yield of lumichrome from the corresponding substituted *o*-phenylenediamine is 30%.[49]

The reaction with monohalogenobarbituric acids takes place through the formation of intermediate dihydroalloxazines which undergo dehydrogenation to alloxazines in the presence of atmospheric oxygen. However, the low yield is apparently not connected with the dehydrogenation reaction but with the difficulty of condensing amines with monohalogenated, as compared with dihalogenated, barbituric acids. The analogous dehydrogenation of dihydro- and tetrahydro-derivatives of pyrimidopyrazine ring systems (*e.g.* pterins) by atmospheric oxygen occurs very easily[4].

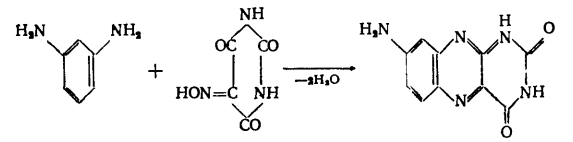
Besides acetic acid and pyridine, methanol and isopentanol are used as media for the condensation. Sodium acetate and borates can be used as catalysts but they are significantly inferior to pyridine[49].

Isoalloxazines are obtained in good yields from the condensation of 5,5-dichlorobarbituric acid with primary-secondary *o*-phenylenediamines in pyridine. Lumiflavin, benzylflavin (78% yield; 70% from 5-chlorobarbituric acid), *L*-araboflavin, and tetraacetylriboflavin have been synthesised from the corresponding starting materials[49,132]. Riboflavin was obtained in 85% yield from *N*-(2-amino-4,5-dimethylphenyl)-*D*-ribit-1-ylamine and 5,5-dichlorobarbituric acid in pyridine[49,126,127,132].

Riboflavin, *D*-araboflavin, and 9-hydroxyethyl-6-methylisoalloxazine were obtained previously from the corresponding primary-secondary *o*-phenylenediamines and 5-bromo- or 5,5-dibromo-barbituric acid in acetic acid in the presence of sodium acetate, sodium borate, or pyridine[124].

VII. SYNTHESIS OF ALLOXAZINES AND ISOALLOXAZINES FROM AROMATIC *m*-DIAMINES AND VIOLURIC ACID

In 1938 Ganapati[57] showed that *m*-phenylenediamine can be condensed with 5-isonitrosobarbituric acid (violuric acid) to obtain 7-aminoalloxazine. In this condensation the pyrazine ring in the alloxazines is obtained from the nitrogen atom of one amino-group of the *m*-phenylenediamine and the nitrogen of the isonitroso-group of violuric acid instead of from the two nitrogen atoms of *ortho*-substituted aromatic compounds:



The method has a limited value because it leads to formation only of 7-aminoalloxazines or 7-aminoisoalloxazines. An attempt to use *meta*-substituted anilines with nitro-, hydroxy-, and carboxy- or methyl groups for the condensation with violuric acid did not give positive results[133].

The condensation of *m*-phenylenediamine (or its derivatives) with violuric acid (or its *N*-substituted derivatives) is carried out in a neutral or weakly alkaline aqueous medium. 7-Methylamino- and 7-dimethylamino-alloxazine (66.5% yield)[103], 6-methyl-[133] and 1,3-dimethyl-7-aminoalloxazine[134] have been obtained. In the preparation of alloxazines, violuric acid reacts with the carbon atom in the position *para* to the most alkylated amino-group in the *m*-phenylenediamine derivatives.

In further study of the reactivity of *meta*-substituted anilines it was found that a methoxy-group provides sufficient electron density in the position *para* to itself for the condensation with violuric acid and furthermore this position is *ortho* to the amino-group. By this method, 6,7-dimethoxyalloxazine was obtained from 3,4-dimethoxyaniline[103].

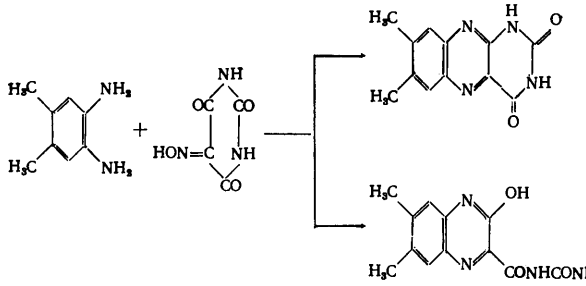
Condensation of *m*-diamines with violuric acid is also used to obtain 7-aminoisoalloxazines. 7-Amino-6,9-dimethylisoalloxazine[135,136], 7-amino-9-(1-*D*-arabityl)- or 7-amino-9-(1-*L*-arabityl)-6-methylisoalloxazine[137], 9-(2-diethylaminoethyl)-7-dimethylaminoisoalloxazine[103], 7-amino-9-methyl- and 7-dimethylamino-9-methyl-isoalloxazine (74% yield)[103] have been prepared.

The isomeric 7-amino-9-(2-diethylaminoethyl)isoalloxazine and amino-7-(2-diethylaminoethyl)alloxazine have been obtained from *N*-(2-diethylaminoethyl)-*o*-phenylenediamine and violuric acid[103].

VIII. SYNTHESIS OF ALLOXAZINES FROM AROMATIC *o*-DIAMINES AND VIOLURIC ACID

In 1962 Berezovskii and Glebova proposed a new method for synthesising compounds of the alloxazine series: the condensation of *o*-phenylenediamines with violuric acid[138]. The reaction takes place in an alcoholic solution of acetic acid in the presence of boric acid. In the absence of boric

acid or in aqueous alcohol[139] the formation of ureides of quinoxalinecarboxylic acids is observed. Thus, under the appropriate conditions either lumichrome or 2-hydroxy--6,7-dimethylquinoxaline-3-carboxyureide are obtained from 4,5-dimethyl-*o*-phenylenediamine and violuric acid:



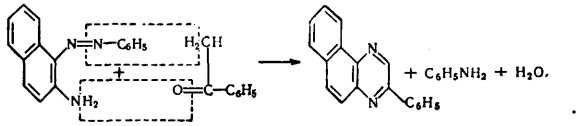
The pyrazine ring in these compounds is formed from the nitrogen atoms of the *o*-phenylenediamine; this is proved by the use of violuric acid labelled with ^{15}N in the isonitroso-group at position 5. The nitrogen atom of the isonitroso-group is split off as hydroxylamine[138]. Lumichrome is formed by reaction of 4,5-dimethyl-*o*-phenylenediamine with violuric acid and not with the product of its possible "deoximation" (alloxan); in control experiments, under the conditions of the condensation, alloxan is not detected even in the least traces[138].

In a mixture of aqueous acetic and boric acids the yield of alloxazines is raised. In dilute hydrochloric acid the yields of lumichrome and alloxazine reach 70.0% and 73.5% respectively[138].

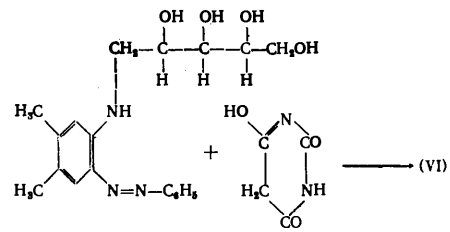
IX. SYNTHESIS OF ALLOXAZINES AND ISOALLOXAZINES FROM AROMATIC *o*-AMINOAZO-COMPOUNDS AND BARBITURIC ACID

In 1947 Tishler and coworkers obtained compounds of the isoalloxazine series by the condensation of secondary aromatic *o*-aminoazo-compounds with barbituric acid[92]. In many cases this method is simple to put into practice because barbituric acid is more readily available than alloxan or 5,5-dihalogenobarbituric acids, and secondary *o*-aminoazo-compounds more so than primary-secondary *o*-phenylenediamines.

Crippa earlier proposed the reaction of α, β-naphthylaminoazo-compounds with α-oxomethylene (or methyl) aliphatic compounds or their aromatic derivatives as a method of synthesising polycyclic quinoxaline derivatives. According to Crippa, under the influence of acid catalysts the amino-group first reacts with the carbonyl group forming an intermediate anil, after which ring formation takes place by reaction of the α-methylene (or methyl) group with the azo-group with elimination of an aromatic amine; this produces a 1,4-diazine ring[140,141,142]:



The condensation of secondary *o*-aminoazo-compounds with barbituric acid is carried out in dioxan in the presence of acetic acid. Riboflavin was obtained thus in 71% yield from *N*-(3,4-dimethyl-6-phenylazophenyl)-*D*-ribitylamine and barbituric acid[92]:

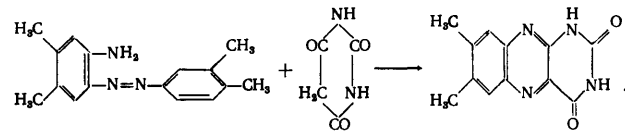


and from the corresponding *o*-aminoazo-compounds *L*-lyxoflavin (43% yield)[114,143-146], *D*-lyxoflavin[146], *D*-araboflavin, *D*-xyloflavin[147], 2′,3′,4′,5′-tetraacetylriboflavin[92], 5′-deoxyriboflavin[148], 2′-deoxyriboflavin (65.4%)[149], galactoflavin (25.6%)[150], and lumiflavin[151] were synthesised.

The substituents in the arylazo-group affect the yield of isoalloxazines in the condensation of barbituric acid with aromatic *o*-aminoazo-compounds[92].

The reaction has been shown to be catalysed by weak organic acids with dissocation constants K_a from 1.2×10^{-5} to 6.89×10^{-5}: for example, acids such as benzoic *p*-aminobenzoic, phenylacetic, nicotinic, or succinic[147]. The yield of riboflavin is raised from 21% to 62–70% when these catalysts are used.

Alloxazines have been obtained by condensation of barbituric acid with primary aromatic *o*-aminoazo-compounds[152]; for example, a naturally occurring alloxazine was synthesised from 1-amino-6-(3,4-dimethylphenylazo)--3,4-dimethylbenzene:



This reaction is catalysed by acetic and oxalic acids. 6-Methylalloxazine (88%) has been obtained by the same method[152].

The synthesis of the primary and some secondary *o*-aminoazo-compounds of the benzene series was achieved by rearrangement of triazines[149,150,153-155].

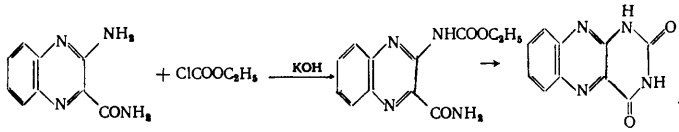
It is of interest that *o*-aminoazo-compounds of the benzene series with a methyl group in the position *ortho* to the azo-group do not condense with barbituric acid and alloxazines and isoalloxazines are not formed[152-156].

Derivatives of barbituric acid which cannot react in the α-oxomethylene form, *e.g.* 4-*O*-methylbarbituric acid and, apparently, *S*-methyl-2-thiobarbituric acid, do not condense with *o*-aminoazo-compounds and hence isoalloxazines of the corresponding types could not be obtained from these substances[121].

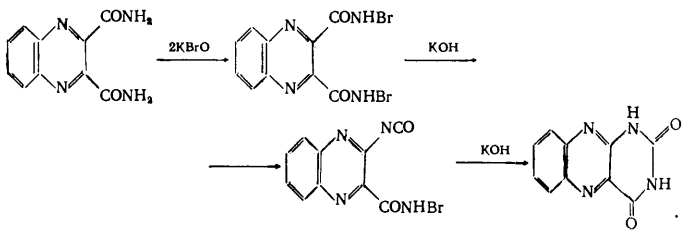
X. OTHER SYNTHESES OF ALLOXAZINES AND ISOALLOXAZINES

Quinoxalines can be converted into alloxazines by building up a pyrimidine ring on to the molecule. The action of a chloroformate ester on 2-aminoquinoxaline-3-carbonamide gives the corresponding quinoxaline urethane which

undergoes ring closure to alloxazine in good yield in the presence of sodium ethoxide[53,157]:

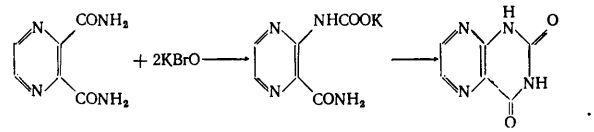


With a chloroformate ester, the methylamide of 2-methylaminoquinoxaline-3-carboxylic acid is converted into 1,3-dimethylalloxazine[53]. Alloxazine is also obtained from quinoxaline-2,3-dicarbonamide using the Hofmann reaction, by treating it with two moles of sodium hypobromite followed by alkali[158].

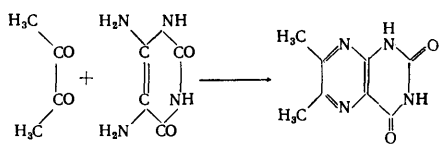


The synthesis of alloxazines and isoalloxazines from lumazines is of interest. Research was undertaken in this direction because of the suggestion that the biosynthesis of riboflavin in cells of microorganisms is achieved through lumazine derivatives[159]. The cells of *Eremothecium ashbyii* produce 6,7-dimethyl-8-ribityllumazine and a number of other substances[160]. It is curious that this compound, obtained synthetically, forms riboflavin on treatment with enzyme-containing extracts of microbic cells of *Ashbya gossypii* [161,162] but this is not the principal direction of the biochemical reaction[159].

Lumazine can be obtained by the Hofmann reaction from pyrazine-2,3-dicarbonamide and potassium hypobromite with subsequent treatment with alkali[163]:

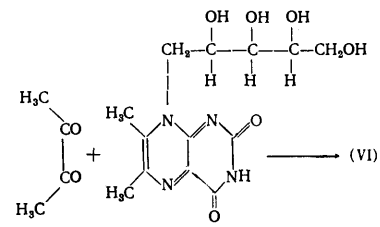


The principal method for synthesising lumazine and its derivatives, is however, the reaction of 4,5-diamino-2,6-dihydroxypyrimidines with the appropriate α-dicarbonyl compounds[164]. Thus, 6,7-dimethyllumazine was obtained from diacetyl and 4,5-diaminouracil[164]:



and 2,4-dihydroxy-6,7-dimethyl-8-*D*-ribitylpteridine (6,7-dimethyl-8-ribityllumazine) from diacetyl and 5-amino-4-*D*-ribitylaminouracil[161].

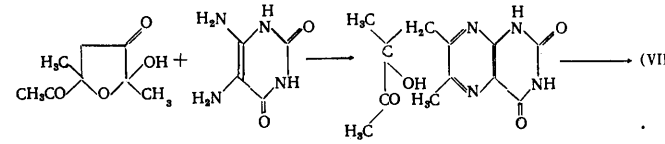
Riboflavin is obtained by the condensation of 6,7-dimethyl-8-ribityllumazine with diacetyl (130°, 6 h)[165]:



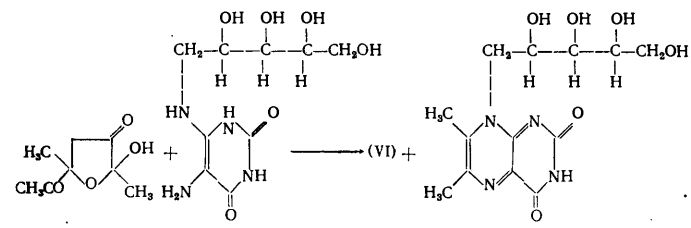
and lumiflavin from 6,7,8-trimethyllumazine by a similar condensation[165].

It has been established that in the cells of *Eremothecium ashbyii* and *Ashbya gossypii* the pyrimidine ring of riboflavin is derived from a purine precursor[166,167] and the benzene ring with *o*-dimethyl groups originates from diacetyl[167]. In connection with this, alloxazines and isoalloxazines were synthesised from 5-acetyl-2-hydroxy-2,5-dimethyl-3-oxotetrahydrofuran (a dimer of diacetyl) *via* substituted lumazines[159,167,168].

From the diacetyl dimer and 4,5-diaminouracil, 7-(2-acetyl-2-hydroxypropyl)-6-methyllumazine is obtained and under the action of 1 *N* sodium hydroxide this undergoes ring closure to lumichrome[168]:



The condensation of 5-amino-4-methylaminouracil with the same diacetyl dimer with subsequent ring closure in the presence of polyphosphoric acid gives lumiflavin[168]. A mixture of riboflavin and 6,7-dimethyl-8-ribityllumazine is obtained by the reaction of 5-amino-4-*D*-ribitylaminouracil with the diacetyl dimer followed by ring closure under the action of 0.1 *N* sodium hydroxide[159,167]:

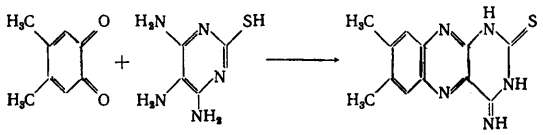


XI. SYNTHESIS OF ANALOGUES OF ALLOXAZINES AND ISOALLOXAZINES

Analogues of alloxazines and isoalloxazines are obtained by replacing the oxygen atoms of the oxo-groups in positions 2 and 4 by a sulphur atom or an imino-group. The condensation of aromatic *o*-diamines with alloxan derivatives containing sulphur or an imino-group in place of oxygen in positions 2, 4, and 6 is not used to synthesise analogues of alloxazine because the corresponding 5-oxopyrimidines are not easily available. However, it was

found possible to obtain some analogues of lumichrome by synthesising the pyrazine ring from the amino-groups of a pyrimidine compound and 4,5-dimethyl-1,2-benzoquinone.

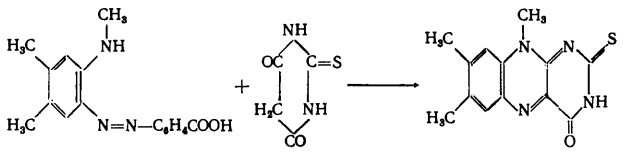
2- and 4-iminolumichrome are obtained from 2,4,5-triamino-6-hydroxy- and 4,5,6-triamino-2-hydroxy-pyrimidine, 2,4-diiminolumichrome from 2,4,5,6-tetraaminopyrimidine, and 4-imino-2-thiolumichrome from 4,5,6-triamino-2-mercaptopyrimidine [122] *e.g.* :



The reactions are carried out in boiling acetic acid; the yields are 66-90% [122].

2-Iminolumiflavin is obtained by condensation of the corresponding primary-secondary aromatic *o*-diamine with 5,5-dibromo-2-iminobarbituric acid in the presence of alkali [108].

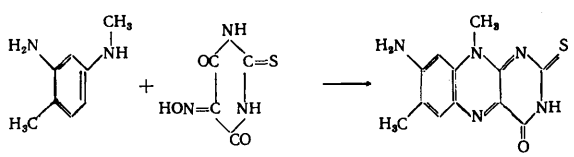
Condensation of aromatic *o*-aminoazo-compounds with barbituric acid was found suitable also for obtaining some of the simplest 2-thio- and 2-imino-analogues of isoalloxazine compounds. The condensation of 6-(*p*-carboxyphenylazo)-*N*,3,4-trimethylaniline with 2-thiobarbituric acid in the presence of acetic acid gives 2-thiolumiflavin, as reddish violet crystals, in good yield [156,169]:



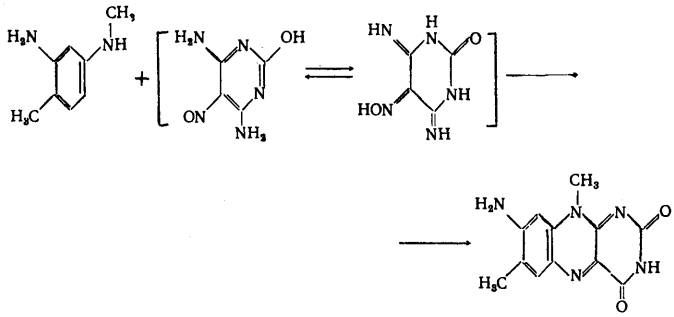
Condensation of *N*-(3,4-dimethyl-6-phenylazophenyl)-*D*-ribitylamine, 3,4-dimethyl-6-(3,4-dimethylphenylazo)-aminobenzene, 4-methyl-6-(4-tolylazo)aminobenzene, and *N*-(3,4-dimethyl-6-phenylazophenyl)-2′-deoxy-*D*-ribitylamine with 2-thiobarbituric acid gives respectively 2-thioriboflavin (60.4% yield), 2-thiolumichrome (79.7%), 6-methyl-2-thioalloxazine (73.5%) [170], and 2-thio-2′-*D*-deoxyriboflavin (69.6%) [149].

Replacement of the oxygen atom in position 2 of barbituric acid by an imino-group has a strong inhibiting effect on the condensation with *o*-aminoazo-compounds. 2-Iminobarbituric acid does not react with those compounds even when kept in pure acetic acid for 20 hours at boiling point, but if the original *o*-aminoazo-compound is converted into the hydrochloride, then 2-iminolumiflavin is formed [156].

The following have been obtained by condensation of *m*-phenylenediamines with thio- and imino-analogues of violuric acid (5-nitrosopyrimidines): from 2-thioviolurie acid, 7-amino-2-thioalloxazine [57], and also 7-amino-6,9-dimethyl-2-thioisoalloxazine [136]:



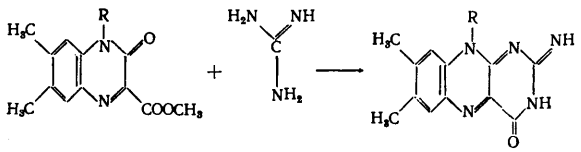
7-amino-2-imino-6,9-dimethylisoalloxazine from 2-iminoviolurie acid, 7-amino-4-imino-6,9-dimethylisoalloxazine from 4,6-diamino-2-hydroxy-5-nitrosopyrimidine, and 7-amino-2,4-diimino-6,9-dimethylisoalloxazine from 2,4,6-triamino-5-nitrosopyrimidine [136].

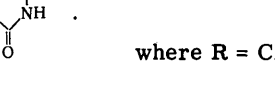


In the last two cases the pyrazine ring is closed as a result of the reaction between the secondary amino-group of the aromatic compound and the imino-group of the tautomeric form of the pyrimidine.

2-Thiolumichrome was obtained in 58% yield by the condensation of 4,5-dimethyl-*o*-phenylenediamine with 2-thioviolurie acid in an alcoholic solution of hydrogen chloride [138].

2-Iminoriboflavin and 2-iminolumiflavin were prepared by condensing esters of *N*-methyl or *N*-ribityl derivatives of 1,2-dihydro-6,7-dimethyl-2-oxoquinoxaline-3-carboxylic acid with guanidine [136,171] :

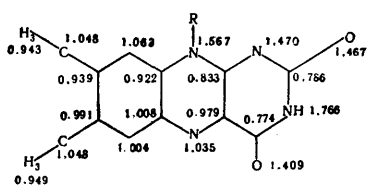


where R = CH_3 or  .

XII. PROPERTIES OF ALLOXAZINES AND ISOALLOXAZINES

All compounds of the alloxazine and isoalloxazine series are high-melting crystalline substances with melting points above 200° and often above 300°. They contain a chromophore in the forming of the azomethine grouping >C=N–, which explains their colour — yellow with shades from pale straw-yellow to bright orange; 7-amino-substituted alloxazines and isoalloxazines are red.

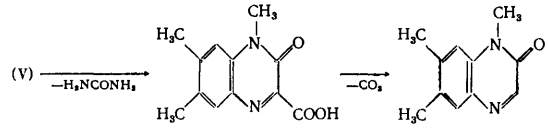
The electron density distribution in the molecule has been calculated for isoalloxazine compounds [172,173]:



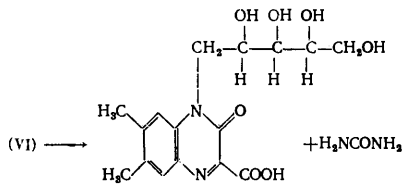
A characteristic peculiarity of compounds of the alloxazine and isoalloxazine series is the instability of the heterocyclic ring of the molecule. In alkaline solutions the

pyrimidine ring of alloxazines and isoalloxazines undergoes cleavage, particularly easily on heating, to form quinoxalines. Cleavage of alloxazine produces 2-hydroxyquinoxaline-3-carboxylic acid[45,174]. When 6,7-dimethylalloxazine is heated in sodium hydroxide solution, 2-hydroxy-6,7-dimethylquinoxaline-3-carboxylic acid is obtained[175].

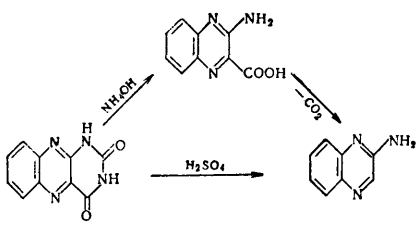
On heating with baryta water, lumiflavin gives urea[176] and 1,2-dihydro-1,6,7-trimethyl-2-oxoquinoxaline-3-carboxylic acid[21], which forms 1,2-dihydro-1,6,7-trimethyl-2-oxoquinoxaline on decarboxylation:



Riboflavin is completely decomposed by 1% sodium hydroxide in 24 h. After heating for a short time at 100° in 4% sodium hydroxide, urea and 1,2-dihydro-6,7-dimethyl-2-oxo-1-(1-*D*-ribityl)quinoxaline-3-carboxylic acid are formed[49,177]:

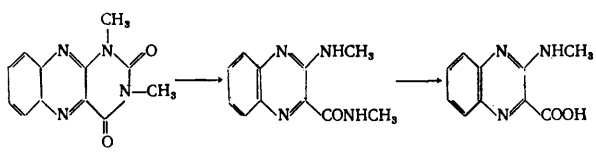


The mode of cleavage of the pyrimidine ring of alloxazine by aqueous ammonia differs from that by sodium hydroxide or baryta water; from alloxazine 2-aminoquinoxaline-3-carboxylic acid is obtained and this is decarboxylated to 2-aminoquinoxaline[175,178]:



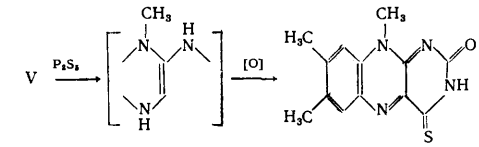
The last is also obtained directly from alloxazine by heating with concentrated sulphuric acid[175,178].

1,3-Dimethylalloxazine undergoes cleavage by sodium hydroxide in two stages[53]:

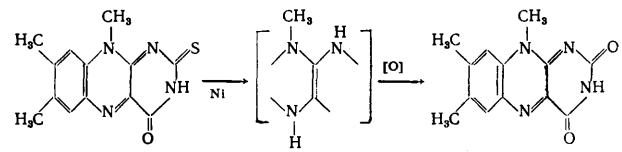


Substitution of the oxygen atom in positions 2 and 4 of the isoalloxazine molecule by a sulphur atom is evidently possible only if alloxazine is in the form of a leuco-compound[120]. 4-Thiolumiflavin is formed in good yield by the action of phosphorous pentasulphide on lumiflavin in pyridine; the lumiflavin is first reduced by the sulphide to a leuco-compound, substitution taking place only after this.

The intermediate 4-thioleucolumiflavin is then oxidised by atmospheric oxygen to 4-thiolumiflavin[120]:



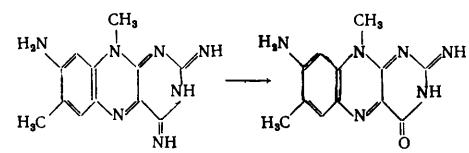
The sulphur atom in thioalloxazines is easily replaced by oxygen, alloxazines being formed. 7-Amino-2-thioalloxazine loses the sulphur atom on treatment with mercuric oxide[57]. 2- and 4-thioisoalloxazines are oxidised to isoalloxazines by atmospheric oxygen. By the action of Raney nickel on 2-thiolumiflavin its leuco-compound was first obtained; in the latter the sulphur atom is not replaced by hydrogen with Raney nickel at 20°, but on heating with access of air the sulphur is removed and lumiflavin is formed[120]:



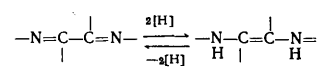
Under the action of dilute hydrogen peroxide or atmospheric oxygen, 2-thioriboflavin, 2-thio-2′-deoxyriboflavin, 6-methyl-2-thioalloxazine, and 2-thiolumiflavin are easily oxidised to riboflavin[170], 2′-deoxyriboflavin[149], 6-methylalloxazine[170], and lumiflavin[151] respectively.

An attempt to replace the oxygen in positions 2 and 4 of lumiflavin by chlorine using phosphoryl chloride or thionyl chloride led to breakdown of the isoalloxazine ring[120].

In 7-amino-2,4-diimino-6,9-dimethylisoalloxazine the 4-imino-group is selectively hydrolysed; the compound gives, on brief treatment with warm alkali, 7-amino-2-imino-6,9-dimethylisoalloxazine in which the 2-imino-group is stable towards alkali[136]:



Isoalloxazines possess characteristic redox properties because of the presence, in the molecule, of the redox system:

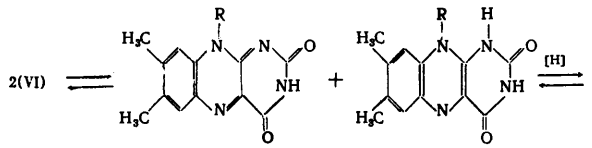


They can be easily reduced chemically or catalytically to colourless leuco-compounds which give coloured compounds again on oxidation.

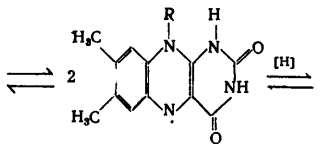
For example, riboflavin is easily reduced by two hydrogen atoms to leucoriboflavin, the yellow-orange colour of the substance and its fluorescence in solution disappearing[179]. Under the action of atmospheric oxygen or other oxidising agents the leuco-compounds is easily reconverted into riboflavin.

The reduction of riboflavin to the leuco-compound takes place through intensely coloured intermediate compounds[180], which are complexes of riboflavin or its leuco-form with

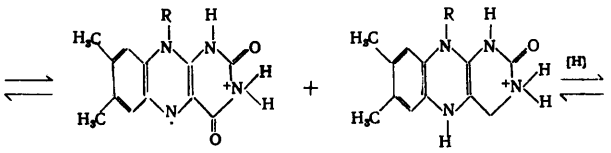
semiquinonoid radicals and which form a flavin cation on losing one electron or give leucoriboflavin on gaining a proton:



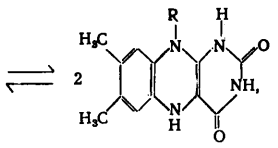
riboflavin (yellow-orange) verdoflavin (green)



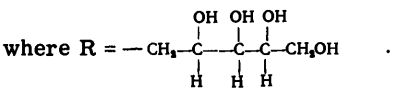
chloroflavin (green)



rhodoflavin (carmine red)



leucoriboflavin (colourless)

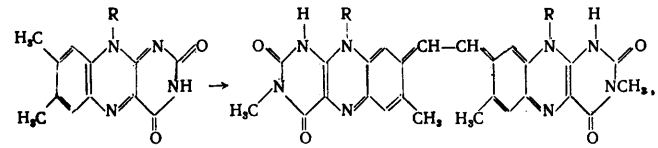


According to new evidence, flavin enzymes are involved in the transfer of an electron in the respiratory chain in the form of the intermediate flavo-semiquinonoid compound of the free radical chloroflavin[181-189]. The extremely high activity of flavin enzymes as biocatalysts can be explained by this.

When isoalloxazines are exhaustively hydrogenated in the presence of a platinum catalyst under pressure the aromatic nucleus is reduced and colourless compounds are formed; for example, octahydro-9-(1-*L*-arabityl)isoalloxazine is obtained from 9-(1-*L*-arabityl)isoalloxazine[190].

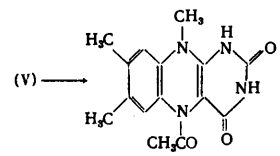
Alkylation and dealkylation reactions of alloxazines and isoalloxazines are of interest. 1,3-Dialkylalloxazines are formed rapidly and in good yield in the alkylation of alloxazines at 120°-150° with diazomethane[38] or a mixture of excess dialkyl sulphate and dimethylformamide, with potassium carbonate as a basic catalyst, for example, alloxazine gives 1,3-dimethylalloxazine[191] and lumichrome, 1,3-dimethyllumichrome[38]. In the isoalloxazine series the same reaction gives 3-alkyl derivatives — 3,9-dimethylisoalloxazine is obtained from 9-methylisoalloxazine[191]. 3-Methyllumiflavin is produced from lumiflavin under the action of dimethyl sulphate in the presence of sodium hydroxide solution[192].

7-Methylisoalloxazines, first and foremost lumiflavin and riboflavin, behave anomalously under the above methylation conditions; irreversible dimerisation occurs as well as methylation[191]:



where R = CH_3 or ribityl.

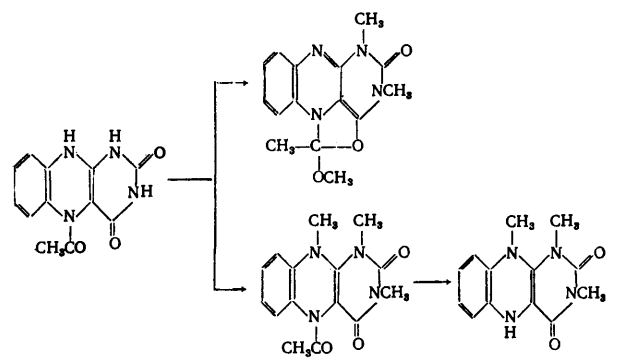
Stable 10-acetylleuco-compounds are formed on the reductive acetylation of alloxazines and isoalloxazines using zinc in a mixture of acetic anhydride and acetic acid[120], for example,



The acetyl group in position 10 inhibits the reverse oxidation of the leuco-compounds to alloxazines and isoalloxazines. It is hydrolysed by heating in dilute mineral acids[120].

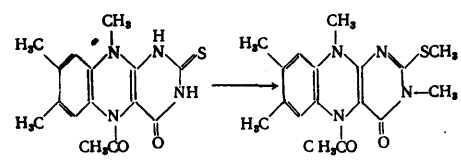
The alkylation reaction of leucoalloxazines is unusual. Methylation of 10-acetylleucoalloxazine with dimethyl sulphate and dimethylformamide plus potassium carbonate gives a complex mixture which, after acid hydrolysis and autoxidation, contains 1- and 3-methylalloxazines with 1,3-dimethylalloxazine and a small amount of 3,9-dimethylisoalloxazine[80].

Methylation of 10-acetyl-1,3-dimethylleucoalloxazine using diazomethane leads to ψ-10-acetyl-*ONN*-trimethylleucoalloxazine and 10-acetyl-1,3,9-trimethylleucoalloxazine, from which 1,3,9-trimethylleucoflavin is formed on hydrolysis in the presence of hydrochloric acid.



The last is more stable than all known leucoisoalloxazines[80].

10-Acetyl-2-thioleucolumiflavin is methylated, using dimethyl sulphate, first at the sulphur atom and then at the nitrogen in position 3:[120]



while 2-thiolumiflavin in the normal form is methylated by methyl iodide or diazomethane at position 3, forming 3-methyl-2-thiolumiflavin[120].

Isoalloxazines containing 3- and 2-hydroxyalkyl groups in position 9 undergo photolysis under the influence of light particularly direct sunlight[18,19,60,63,64,193,194] and ultraviolet light[195]. In alkaline, neutral, and even acidic, solutions the hydroxyalkyl group is split off; this reaction is more vigorous at low concentrations. Such compounds as 9-(2-hydroxyethyl)- and 9-(2,3-dihydroxypropyl)-isoalloxazine are decomposed to alloxazine[60]. Photolysis of riboflavin in neutral and acidic solutions leads to complete dealkylation and the formation of 6,7-dimethylalloxazine (lumichrome)[196] and the breakdown of the pentose residue to hydroxyethanal and glyceraldehyde[197,198].

In alkaline solutions the main photolysis of the riboflavin molecule is connected with the splitting off of the side chain between atoms $C_{(1)}$ and $C_{(2)}$, with formation of 6,7,9-trimethylisoalloxazine (lumiflavin)[18,21]; there is at the same time partial decomposition to lumichrome. The photolysis of riboflavin in alkaline solution in the presence of hydrogen peroxide gives, besides lumichrome and lumiflavin, 6,7-dimethylisoalloxazine-9-acetic acid (7%)[199]. Metals catalyse the photolysis of riboflavin[200]. The ribityl group of riboflavin, which is unstable to light, is stabilised by passing oxygen through the solution[185,186,201].

Isoalloxazines with 3-hydroxyalkyl substituents in position 9 display less photosensitivity than compounds with 2-hydroxyalkyl groups. The photolysis of 9-(3-hydroxypropyl)- and 6,7-dimethyl-9-(*D*-2-deoxyribit-1-yl)-isoalloxazine is considerably more difficult[63].

2′,3′,4′,5′-Tetraacetylriboflavin and lumiflavin, the molecules of which do not contain free hydroxyl groups, do not decompose on irradiation[60].

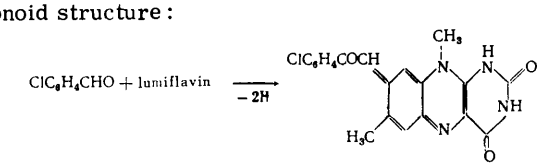
Lumiflavin is not dealkylated at 18°–20° but in hot neutral or weakly acid solution it decomposes photolytically to lumichrome[80]. The very slow reaction is accelerated by adding metal ions: Fe^{2+}, Sn^{2+}, or Co^{2+}. Decomposition does not occur if oxygen is passed through the solution.

Light is not a specific catalyst for the decomposition of 9-substituted isoalloxazines, which is catalysed by metal ions[185,186,200], and in some cases by bases[171] and by reagents for a carbonyl group[80].

9-Methylisoalloxazine, lumiflavin (9-methylflavin), and their 3-methyl derivatives were dealkylated (in good yields) to alloxazine, lumichrome, and their 3-methyl derivatives by boiling repeatedly with excess hydroxylammonium sulphate in glacial acetic acid. The same result was obtained with hydrazine and phenylhydrazine, but with lower yields[80].

Since the carbon atom in position 7 of the alloxazine molecule has a lower electron density than atoms $C_{(5)}$, $C_{(6)}$, and $C_{(8)}$,[172] a methyl group in that position must have an increased tendency to react with electrophilic reagents.

Lumiflavin reacts with *p*-chlorobenzaldehyde at 20° in concentrated sulphuric acid containing phosphorus pentoxide; the compound obtained by Hemmerich *et al*[191] is considered to be an isoalloxazine derivative possessing a quinonoid structure:

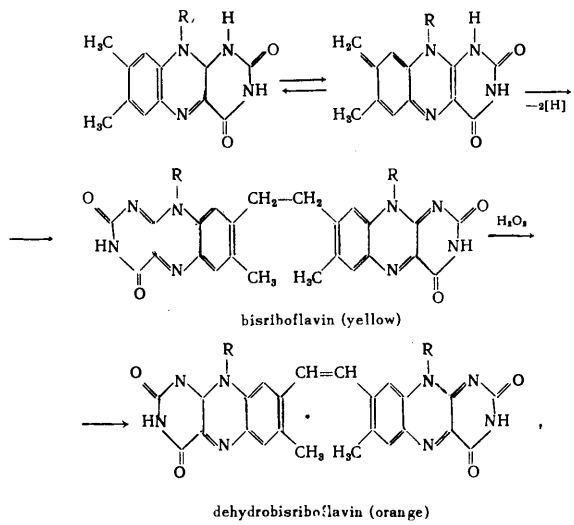


When lumiflavin is treated with excess nitrous acid in boiling acetic acid, the methyl group in position 7 is oxidised giving the hardly stable 6,9-dimethylisoalloxazine-7-carboxylic acid which is converted into 6-methylalloxazine-7-carboxylic acid under the action of alkali[191].

The particular activity of position 7 in the isoalloxazine system is shown by the chlorine in 7-chloro-6,9-dimethylisoalloxazine being rather easily replaced using such nucleophilic reagents as sodium methoxide and ethanolamine, with the formation of, respectively, 7-methoxy- and 7-(β-hydroxyethylamino)-6,9-dimethylisoalloxazine[191].

The amino-group in 7-amino-6,9-dimethylisoalloxazines is weakly basic and can, with difficulty, be acylated and diazotised[136]. However, the amino-group in 8-aminolumiflavin has aromatic character; it is diazotised in strongly acid solution, the diazonium cation takes part in azo-coupling and undergoes cleavage. Deamination results and lumiflavin is formed[108].

The ability of lumiflavin and riboflavin to dimerise through the methyl group in position 7 is also of interest. The reactions connected with the dimerisation can be represented by the following scheme[191]:



where R = $-CH_2-\overset{H}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-CH_2OH$.

The dimers bisriboflavin and bislumiflavin were obtained by treating the flavins with potassium carbonate in hot dimethylformamide in a nitrogen atmosphere.

Where isoalloxazines containing a polyhydroxyalkyl group in position 9 are treated with lead tetraacetate or periodic acid, this side chain is split off; thus 9-formylmethyl-6,7-dimethylisoalloxazine was obtained from riboflavin[202,203]. Riboflavin is oxidised by chromic acid[204] and by potassium permanganate but bromine, hydrogen peroxide, and nitric acid have no effect on it.

The hydroxyl groups of the ribityl chain in riboflavin easily form ethers and esters. The primary hydroxyl in the 5′ position is the first to undergo esterification, and then the secondary hydroxyls in the 2′, 3′, and 4′ positions.

5′-Tritylriboflavin is produced by the action of triphenylchloromethane on riboflavin in pyridine[205]. With acetic anhydride or acetyl chloride, riboflavin gives 2′,3′,4′,5′-tetraacetylriboflavin[92]. Sulphate esters are obtained by

dissolving riboflavin in concentrated sulphuric acid[206] or by the reaction of chlorosulphonic acid in chloroform with a solution of riboflavin in pyridine[207,208]. The mono-, di-, tri-, and tetra-sulphate esters are isolated as the calcium salts. Riboflavin-5′ monosulphate is an antivitamin[207].

Phosphate esters are obtained by the action on riboflavin of various phosphorylating agents, such as phosphoryl chloride, phosphorochloridic acid, dialkylphosphorochloridic acids, etc.[209-216]. A mixture of mono-, di-, and poly-5′-phosphates is obtained; they are fairly stable. The riboflavin di- and poly-phosphates are partially hydrolysed to riboflavin-5′ monophosphate by hydrochloric acid[216-218].

Albert showed, in 1950, that riboflavin forms inner complexes (chelate compounds) with bivalent metals[219]. A series of these insoluble complexes of riboflavin with iron, nickel, cobalt, copper, zinc, and manganese was isolated[220]. They contain two metal atoms to each flavin molecule but it is not clear how these atoms are bound. It is probable that the biocatalytic activity of many flavin enzymes is connected with metal ions, such as iron molybdenum, copper, or manganese, contained in them[219-228].

A peculiarity of alloxazines and isoalloxazines is their ability to fluoresce in solutions exposed to light, particularly on excitation by ultraviolet light. Weak aqueous solutions of many flavins, including riboflavin, emit an intense yellow-green light. The fluorescence spectrum of riboflavin lies between 515 and 615 mμ with a maximum[229] at 565 mμ and it is most intense at pH 6–8; [204] the intensity of colour weakens in acidic and alkaline medium and depends on the concentration of the substance in the solution[230].

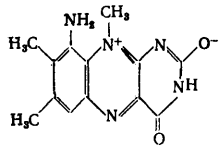
It has been shown that the ability of isoalloxazines to fluoresce is accounted for by the conjugated system $-N=C-C=N-$ and the intensity of fluorescence depends on the coplanarity of this system with the plane of the nucleus of the molecule[76]. The fluorescence is reduced to 20–23% when a methyl group is substituted in the 5-position[76].

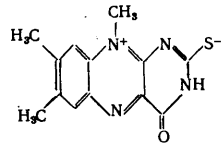
It is of considerable interest to establish how the fluorescence of alloxazines and isoalloxazines depends on different substituents and their position. However, a systematic study of the effect of substituents, under comparable conditions, on the fluorescence has not been made.

Change of the position of the methyl groups in the benzene ring of alloxazine and an increase in their number causes the fluorescence colour to deepen from violet through dark blue-violet, greenish blue, yellow to purple-yellow[40,41,186] in the following sequence: unsubstituted alloxazine < 6- or 7-mono- < 6,7-di- < 8-mono- < < 6,7,8-tri- < 5,7,8-tri- < 5,6,7,8-tetra-.

The isoalloxazine molecule with the simplest $N_{(9)}$-methyl substituent has a yellow-green fluorescence; introduction of a methyl group into positions 5, 6, and 7, a carboxy- or methoxy- group in position 7, a nitro-group in position 8, or hydroxyalkyl groups in position 9 has hardly any effect on the spectrum[58,108,191,196]. However, some substituents in position 8, such as a methyl group, cause a bathochromic effect, the colour deepening to brownish yellow[66]. An imino-group in position 2 or 4 causes a small increase of colour (a hypsochromic effect)[120,136,151].

Lumiflavin with an amino-group in position 8 (brownish red) and 2-thioflumiflavin (reddish violet) and its derivatives do not possess fluorescence[120,136]. It can be assumed that the absence of fluorescence is connected with the nitrogen atom in position 9 possessing a high positive charge, the isoalloxazine compounds being in a polar form in which evidently they mainly exist in solution[108,151]:

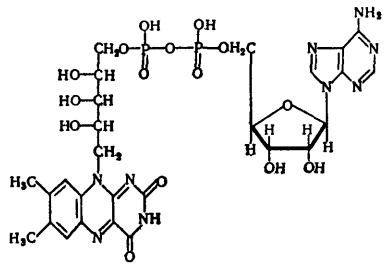




XIII. NATURALLY OCCURRING ALLOXAZINES AND ISOALLOXAZINES AND COMPOUNDS WITH ANTIMETABOLITE AND PHARMACOLOGICAL PROPERTIES

Besides riboflavin (vitamin B_2), *L*-lyxoflavin is possibly found in animal organisms; its isolation from cardiac muscle has been reported[231], but reliable confirmation of this has not been obtained[232]. Lumiflavin and lumichrome have been isolated together with riboflavin from the retina of the eye.

Riboflavin-5′ monophosphate and flavin-adenine dinucleotide



are coenzymes containing riboflavin. They represent the prosthetic group of flavin enzymes[17,18,233-237].

Of riboflavin analogues, 2-thioriboflavin possesses the full activity of vitamin B_2.[170]

In their biological action, many alloxazine and isoalloxazine compounds are antivitamins; the strongest are: araboflavin[238], galactoflavin[239], 5′-deoxyriboflavin[148], isoriboflavin[93], and riboflavin-5′sulphate[207]. 6,7-Dichloro-9-(1-*D*-ribityl)isoalloxazine[99,100], 7-chloro-6-methyl-9-(1-*D*-ribityl)isoalloxazine, and many other halogen-substituted isoalloxazines[100,102,105] are bacterial inhibitors of riboflavin. It was found that 7-chloroalloxazine possesses diuretic action[55].

6-(5-Dialuryl)-7-methyl- and 6-chloro-9-(4-diethylamino-1-methylbutyl)-isoalloxazine possess antimalarial action[106,240]. 2-Thiolumiflavin and 2-iminolumiflavin display bacteriostatic action on Gram - positive bacteria and, in experiments on animals, inhibit the growth of cancerous tissue[171]. 1,2-Dihydro-6,7-dimethyl-2-oxo-1-(1-*D*-ribityl)-quinoxaline-3-carboxylic acid, a decomposition product of riboflavin, lowers the blood pressure and depresses the activity of cardiac muscles[177].

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CATALYTIC HYDROGENATION AND HYDROGENOLYSIS OF FURAN COMPOUNDS

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INTRODUCTION

In 1897 Sabatier discovered the catalytic hydrogenation of organic compounds. Subsequently the most diverse classes of such compounds have been examined, and catalysts have been found possessing the necessary activity, stability, and specificity.

The hydrogenation of furan compounds by Sabatier's method on a nickel catalyst[1,2] did not yield satisfactory results, and therefore liquid-phase hydrogenation was employed almost exclusively in subsequent work on furan compounds. Adams platinum, Raney nickel, copper chromite, and several other catalysts were widely used for the liquid-phase hydrogenation of furan derivatives. It was soon found, however, that the furan ring can be smoothly hydrogenated to a tetrahydrofuran ring also in the vapour phase if special catalysts are employed for this purpose, such as osmium on asbestos (Zelinskii, Shuikin), palladium and foraminate Ni–Al (Shuikin and his collaborators). The hydrogenation of furan compounds is also of practical value, mainly owing to the possibility of opening the ring and passing from compounds of the furan series to those of other classes. Thus from 2-substituted homologues of furan it proved possible to obtain aliphatic ketones and alcohols, and the limits of applicability of this method were considerably extended after the discovery of "conjugate" hydrogenolysis of the furan ring.

Starting from furfuraldehyde the synthesis of furylacraldehydes and furfurylidene ketones on the one hand, and of 2-acyl-5-alkylfurans on the other, can be accomplished in an extremely simple manner. Both of these groups of furan compounds are valuable starting materials for the catalytic synthesis of aliphatic, heterocyclic, and carbocyclic compounds. 2-Acyl-5-alkylfurans can be directly converted by vapour-phase hydrogenation into 1,5-diketones and homologues of tetrahydropyran, of cyclohexanone, and of phenol. Furylacraldehydes and furfurylidene ketones are converted, on hydrogenation and reductive amination, into furan alcohols and furan amines, in which the functional groups are in position 3 with respect to the furan ring. Catalytic hydrogenation of furan alcohols and amines of this structure in the vapour phase forms di- and tri-substituted homologues of tetrahydrofuran and of pyrrolidine, which are products of the intramolecular cyclisation of the alkane-1,4-diols and 4-aminoalcohols formed as intermediates. All this shows that the problem of the catalytic hydrogenation of furan compounds has acquired fresh importance, for the development of new methods, convenient in practice, of synthesising organic compounds of the aliphatic, heterocyclic, and carbocyclic series. In several cases these methods not only supplement the old methods of organic synthesis, but are also more feasible in practice, because of their simplicity and the availability of the furan starting materials. The successful development of improved industrial methods for obtaining furfuraldehyde from raw materials containing pentosans provides the main conditions for the evolution of organic synthesis on the basis of furan compounds.

1. HYDROGENATION OF 2-ALKYL- AND 2-ALKENYL--FURANS

The first investigation of the catalytic hydrogenation of the furan ring was carried out by Padoa and Ponti in 1906,[1] and in 1908 Bourguignon[2] examined the hydrogenation of furan by Sabatier's method. When furan was passed over a nickel catalyst at 170° a mixture was formed of tetrahydrofuran (12%), butan-1-ol (8%), and lower hydrocarbons which were not investigated, while 34% of the furan remained unchanged.

In 1923 Kaufmann and Adams[3] employed a platinum catalyst for the liquid-phase hydrogenation of several functional derivatives of furan (furfuraldehyde, furfuryl alcohol, etc.), and found that under these conditions the process takes place without side reactions, and can be controlled to obtain partly or completely hydrogenated products.

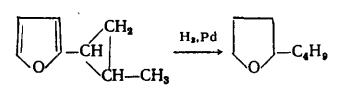
Then it was found that in the presence of Raney nickel the furan ring is hydrogenated quite satisfactorily at moderate temperatures[4]; thus an 80% yield of tetrahydrofuran was obtained from furan at 50°.[5]

Adkins and Connor[6], and then Lazier[7] used chromite catalysts (mainly copper chromite) for the liquid-phase hydrogenation of furan and several of its derivatives, obtaining either tetrahydrofuran derivatives or products of the hydrogenolysis of the furan ring.

Zelinskii and Shuikin[8] investigated the hydrogenation of sylvan [methylfuran (Ed. of Translation)] in the presence of osmium on asbestos in a flow system at 80°–82°, and obtained a quantitative yield of tetrahydrosylvan. The smooth hydrogenation of furan to tetrahydrofuran was accomplished in the presence of the same osmium catalyst at 65°–70°.[9]

An excellent catalyst for the hydrogenation of the furan ring proved to be palladium oxide mixed with palladium black. Starr and Hixon[10] obtained a quantitative yield of tetrahydrofuran by the hydrogenation of furan at a pressure of ~7 atm.

Shuikin *et al.* made a detailed study[11,12] of palladium as catalyst for the hydrogenation of the furan ring. Furan and its mono- and di-alkyl derivatives (the 2-methyl, 2-ethyl, 2-propyl, 2,5-dimethyl, and 2-ethyl-5-methyl derivatives) were hydrogenated over a palladium catalyst at 150° and ordinary pressures in a flow system. Only the corresponding mono- and di-alkyltetrahydrofurans were obtained. Shuikin and Daiber[13] found that the hydrogenation of 2-furylcyclopropane and 1-fur-2′-yl-2-methylcyclopropane by a flow method in the presence of palladium on asbestos at ordinary pressures yielded interesting results. At 140° the former gave 2-propyltetrahydrofuran, and at 150° the latter yielded 2-butyltetrahydrofuran:



Thus the cyclopropane ring underwent cleavage with extraordinary ease under conditions producing smooth hydrogenation of the double bonds in the furan ring.

Shuikin *et al.*[14] investigated the hydrogenation of 2-benzylfuran on platinum and palladium catalysts. Liquid-phase hydrogenation at room temperature in the presence of platinum on charcoal or of platinum black yielded 2-benzyltetrahydrofuran (the main reaction product) and 1-phenylpentan-2-ol. Hydrogenation of 2-benzylfuran by a flow method in the presence of platinum and palladium on asbestos at 230° resulted in the complete opening of the furan ring with the formation of 1-phenylpentan-2-ol and a small amount of n-pentylbenzene.

A palladium catalyst was extensively used by Yur'ev and his coworkers[15–17] for the hydrogenation of various furan compounds. Mixtures of 2-alkyl- and 2-alkenyl-furans,

methyl pyromucate [methyl furan-2-carboxyate (Ed. of Translation)], and 2,4-dimethylfuran were hydrogenated in the presence of palladium on asbestos at 150°–160° in a flow system. The yields of the corresponding tetrahydrofuran derivatives were not less than 70%.

Nickel catalysts prepared in various ways showed high activity in effecting hydrogenation of the furan ring. Foraminate nickel catalysts, approaching palladium and osmium in their properties, found especially wide use. Shuikin and Bunina [18] showed that a foraminate nickel catalyst prepared by the incomplete extraction of aluminium from an Ni–Al alloy can successfully replace osmium and palladium catalysts for the hydrogenation of the furan ring. In the presence of this catalyst furan and sylvan were hydrogenated at 100°–140° and 120° respectively to give high yields of the tetrahydro-derivatives. It was noted that raising the reaction temperature to 170° produced a thorough breakdown of the furan with the formation of volatile products. Burnette [19] also employed a foraminate nickel catalyst, from which only 6–8% of the aluminium had been removed, for the hydrogenation of sylvan by a flow method. At 200° the main product was tetrahydrosylvan (yield 50%), and appreciable amounts of ring-cleavage products, pentan-2-one and pentan-2-ol, were obtained. Paul [20] studied the hydrogenation of mixtures of the 2-furyl derivatives of propene and propane, butene and butane, and pentene and toluene (ω-) in the presence of Raney nickel. Hydrogenation was carried out in the liquid phase at 110°–118° under a hydrogen pressure of 65–85 atm. The yield of the corresponding tetrahydrofurans varied from 68% for 2-butyltetrahydrofuran to 91% for 2-benzyltetrahydrofuran.

Yur'ev *et al.* [21] hydrogenated furan, over nickel deposited on aluminium oxide, at 123°–160° and an initial pressure of 60 atm in an autoclave. An 86% yield of tetrahydrofuran was obtained. A 95% yield of this product was obtained in the presence of nickel on kieselguhr when this was employed by Katsuno [22] for the liquid-phase hydrogenation of furan at high pressures of hydrogen.

Boles [23] hydrogenated furan, sylvan, and dimethylfuran on catalysts containing Ni, Cu, or Mo. At 190°–200° and 60–80 atm, 90–95% yields of the corresponding tetrahydrofurans were obtained.

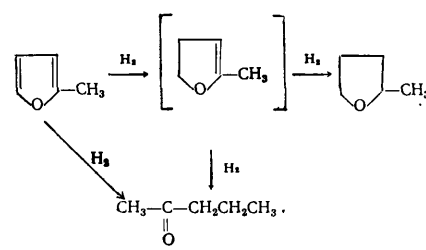
The aim of all these investigations was to discover catalysts and reaction conditions such that furan compounds would be hydrogenated to the maximum extent into their tetrahydro-derivatives. However, apart from this type of hydrogenation, the furan ring can undergo cleavage at the C–O and C–C bonds. The predominant or sole occurrence of one of these reactions depends on the conditions, mainly of temperature and on the nature of the catalysts. A rise in temperature favours ring cleavage. The use of different catalysts is even more effective than temperature for achieving selective hydrogenation of the furan ring. The properties of catalysts can be compared if the other reaction conditions are kept the same, since it has been established that the same catalyst can effect hydrogenation of the furan ring in different ways depending on whether reaction takes place in the liquid or in the gas phase. For example, various furan derivatives are smoothly hydrogenated to the corresponding tetrahydrofurans in the liquid phase over an Adams platinum catalyst. Similarly palladium also exhibits excellent catalytic properties for the liquid-phase hydrogenation of the furan ring [10]. However, these two catalysts differ markedly in their behaviour towards hydrogenation and hydrogenolysis of the furan ring in the vapour phase. Under these conditions palladium retains its property of specifically catalysing hydrogenation of the furan ring [11], whereas in the vapour phase over platinum at 275° the furan nucleus undergoes solely hydrogenolysis.

Hydrogenolysis of the furan ring results in the conversion of furan compounds into aliphatic compounds, and in this respect is of great practical value. In 1947 Bremner [24] stated in a patent that it was possible to obtain alcohols by the hydrogenation of furan and its alkyl and aryl derivatives at temperatures above 120° (preferably at 200°–300°) and hydrogen pressures exceeding 100 atm in the presence of catalysts containing silver, copper, or silver or copper chromite deposited on an inert carrier, kieselguhr or pumice. It was stated that the yields of the alcohols were increased by adding small amounts of an acid or of a salt thereof to the reaction mixture. Thus the hydrogenation of furan in the presence of $CuCr_2O_4.BaCr_2O_4$ at 220° and 100 atm in an autoclave gave tetrahydrofuran (30%) and n-butanol (70%). In the same way the homologues of furan yielded pentan-1-ol, pentan-2-ol, and hexan-2-ol.

Further investigation showed that hydrogenolysis of the furan ring could be more usefully carried out in the vapour phase. Bremner *et al.* [25] reported that hydrogenolysis of sylvan with the formation of pentan-2-one takes place when the sylvan is passed through a tube containing a Cu–ZnO catalyst at 325°. Ethylfuran gives ethyl propyl ketone under these conditions.

Wilson [26] investigated the conditions for obtaining tetrahydrosylvan and pentan-2-one by the vapour-phase hydrogenation of sylvan over a nickel catalyst. At 100° tetrahydrosylvan (yield 86%) is formed, and at 185° pentan-2-one (75%). The latter product is formed also on other catalysts, but in lower yields and at higher temperatures (340°–350°). Thus on copper chromite 52% of pentan-2-one and a little pentan-2-ol are formed, on a Co–Cu catalyst ~ 60% of pentan-2-one, and on an Fe–Cu catalyst mainly tetrahydrosylvan with only ~ 10% of the ketone.

Wilson considers that the formation of pentan-2-one from sylvan does not involve an intermediate stage of tetrahydrosylvan formation, since a mixture of the latter with hydrogen passed over a nickel catalyst at 250° yielded no ketone at all, but considerable formation of gas was observed; at 100° tetrahydrosylvan remained unchanged. On this basis Wilson suggested the following scheme of successive reactions



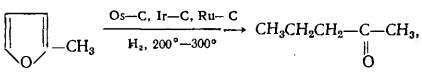
Thus he assumes that fission of the C–O bond is possible both in the sylvan ring and in that of dihydrosylvan.

Platinum deposited on carbon proved to be a good catalyst for the vapour-phase hydrogenolysis of the furan ring. Hydrogenation of 2-alkylfurans (where the alkyl group is methyl, ethyl, propyl, butyl, or pentyl) in the vapour phase at atmospheric pressure and 275° over Pt–C involves selective hydrogenolysis at the 1,5 C–O bond (not adjacent to the alkyl radical), with formation of the corresponding aliphatic ketones (pentan-2-one, hexan-3-one, heptan-4-one, octan-4-one, and nonan-4-one) in yields of 90–95%. [27]

Under the same conditions hydrogenolysis in 2-ethyl-5--methylfuran takes place in both ways, with the formation of heptan-2-one and heptan-3-one, and also a small amount of heptane[28]. A foraminate Pt–Al catalyst exhibited properties similar to those of platinised carbon. On this catalyst sylvan undergoes hydrogenolysis in the vapour phase at 275°, being smoothly converted into methyl propyl ketone[29]. The difference between palladium and platinum is also marked at this temperature. Both palladised carbon and also a foraminate Pd–Al catalyst act as specific catalysts for the hydrogenation of the double bonds in the furan ring over quite a wide temperature range. For example, sylvan and 2-ethyl-5-methylfuran are hydrogenated, in the vapour phase over palladium catalysts at 275°, to the corresponding homologues of tetrahydrofuran in yields of 75–80%.[29]

A comparative study of the catalytic properties of the Group VIII metals was made by investigating the hydrogenation of sylvan in the vapour phase over osmium, iridium, ruthenium, and rhodium precipitated on carbon[30].

The results for the hydrogenation of sylvan on Os–C, Ir–C, and Ru–C at 200°–300° show that these catalysts are completely devoid of the ability to reduce the furan ring, but effect exclusively hydrogenolysis of the ring at the 1,5 C–O bond with the formation of methyl propyl ketone, the yield of which depends on the temperature and the speed at which the substance is passed over the catalyst:



On Ir–C at 200° and with a flow velocity of 0.1 h^{-1} sylvan yields ~60% of methyl propyl ketone, but at 275° with the same flow velocity it is practically all converted into the ketone. On Os–C and Ru–C at 275° and with other conditions the same, the degree of conversion of sylvan into pentan-2-one is 40% and 85% respectively. In no case has tetrahydrosylvan been isolated at this temperature. An exception is provided by the rhodium catalyst, on which at 200° both hydrogenation of the furan ring (40%) and hydrogenolysis of the ring at the 1,5 C–O bond (60%) take place.

The results obtained enable some general conclusions to be reached. All these catalysts containing Group VIII metals deposited on carbon can be divided into two groups according to their action on the furan ring in vapour-phase hydrogenation at normal pressure:

1. Catalysts of the platinum type (Pt, Os, Ir, Ru) possess a feebly developed capacity (or practically none at all) for hydrogenating the double bonds in the furan ring. On these catalysts at 200°–300°, only hydrogenolysis of the ring at the 1,5 C–O bond takes place.

2. Catalysts of the palladium type (Pd, Rh) are able smoothly to hydrogenate the double bonds in the furan ring over quite a wide temperature range. They are able to effect hydrogenolysis of the ring, though to no great extent, only at elevated temperatures.

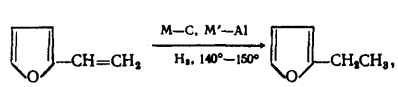
The hydrogenation of sylvan in the vapour phase has been investigated also on Ni–Zn and Cu–Al foraminate catalysts[29,31]. These showed the same activity and selectivity as platinum: in contact with them at 250°–300° sylvan is split only at the C–O bond not adjacent to the methyl group, and is quantitatively converted into methyl propyl ketone. Nickel deposited on zinc, cadmium, and beryllium oxides also has a similar effect on the furan ring on vapour-phase hydrogenation. At 250°–300° the ring undergoes hydrogenolysis solely at the ether bond remote from the alkyl side-group, the reaction going just as smoothly on Ni–ZnO as on a platinum catalyst, but not quite as well on Ni–CdO and Ni–BeO.[31]

All these catalysts, while being so very effective for the hydrogenolysis of the furan ring, show very little activity in effecting hydrogenation of the cyclic double bonds. Thus sylvan on Pt–C and foraminate Ni–Zn at 150° is hydrogenated to tetrahydrosylvan to the extent of only 20–25%, the remainder of the catalysate consisting of hydrogenolysis products of the furan ring, pentan-2-one and pentan-2-ol.[31,32]

Thus three groups of catalysts have been investigated under conditions of the vapour-phase hydrogenation of the furan nucleus at ordinary pressures: (1) metals deposited on carbon: Pt–C, Pd–C, Os–C, Ir–C, Rh–C, and Ru–C; (2) foraminate catalysts: Pt–Al, Pd–Al, Ni–Zn, and Cu–Al; (3) nickel on oxides: Ni–ZnO, Ni–CdO, and Ni–BeO.

Among all these it is only the palladium catalysts (Pd–C and foraminate Pd–Al) which exhibit a clearly marked ability to hydrogenate the furan to the tetrahydrofuran ring in the vapour phase at normal pressure; this ability is shown in lesser degree by rhodium on carbon. All the rest are typical hydrogenolysis catalysts for the furan ring, and in the case of the 2-alkylfurans they effect hydrogenolysis in only one way, at the C–O bond remote from the alkyl radical. A double bond in the side chain of various furan derivatives is hydrogenated at lower temperatures than is the furan ring. Thus there is a considerable difference in optimum temperatures for hydrogenation of a side-chain double bond in furan compounds and hydrogenolysis of the furan ring. Therefore all catalysts which are active in the hydrogenolysis of the furan ring and inactive towards hydrogenation thereof exhibit a high selectivity with respect to a side-chain olefinic bond on vapour-phase hydrogenation at atmospheric pressure. The flow velocity is also important, apart from the temperature, since a decrease in speed will favour the secondary reaction of hydrogenolysis of the furan ring.

The hydrogenation of 2-vinylfuran has been investigated in the vapour phase at normal pressure on Group VIII metals deposited on carbon[30] and over foraminate catalysts[29]. The temperature of hydrogenation was 140°–150°, and the flow velocity 0.1 h^{-1}. Under these conditions 2-vinylfuran was converted into 2-ethylfuran in 95–100% yield



where

$$M = Pt, Os, Ir, Ru, Rh;\ M' = Pt, Cu.$$

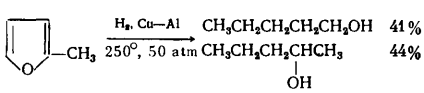
Nickel deposited on the oxides of zinc, cadmium, and beryllium has almost identical properties. At 150°–175° 2-propenylfuran was hydrogenated to 2-propylfuran in 90–95% yield[31]. Thus provided that certain temperature conditions are observed, many catalysts can be used for the selective hydrogenation of a double bond in the side chain of furan compounds.

Bremner[33] accomplished the selective hydrogenation of the double bond in the hydrogenation of 2-vinylfuran on Raney nickel or on nickel deposited on carriers in the presence of ammonia or diethylamine. At 80° and 50 atm a 90% yield of 2-ethylfuran was obtained. In the absence of ammonia, the main product of hydrogenation under the same

conditions was 2-ethyltetrahydrofuran. Bremner also found that the hydrogenation of 2-vinylfuran in the presence of nickel on kieselguhr at 65° and 250 atm gives 2-ethylfuran practically exclusively. Hydrogenation of the furan ring begins at pressures above 250 atm.

Interesting results were obtained in an investigation of the effect of the hydrogen pressure on the direction of hydrogenation of the furan ring by a flow method. Sylvan was hydrogenated at 50 atm in a flow system over platinised carbon, foraminate Ni–Zn, and foraminate Ni–Al catalysts [34].

As mentioned above, on these catalysts at atmospheric pressure and 250°–300° sylvan is completely hydrogenolysed at the C–O bond remote from the methyl group, with the smooth formation of methyl propyl ketone. In contrast, its hydrogenation on Pt–C at 275° and an increased pressure of hydrogen (50 atm) gives as the main product tetrahydrosylvan (75%) with considerably smaller amounts of pentan-2-one (20%) and pentan-2-ol (5%). The use of elevated pressures in the hydrogenation of sylvan on a foraminate Ni–Zn catalyst also favours hydrogenation of the furan nucleus and represses hydrogenolysis, but this effect is less marked than on a platinum catalyst. Over foraminate Ni–Zn at 250°–260° and 50 atm sylvan forms 35–40% of tetrahydrosylvan, 20–25% of pentan-2-one, and ~40% of pentan-2-ol. In the hydrogenation of sylvan over a foraminate Cu–Al catalyst, raising the pressure influences the course of hydrogenation of the furan nucleus in a different way from that found with Pt–C and foraminate Ni–Zn. On the Cu–Al at 50 atm the furan ring is hydrogenated to the extent of only 5–8%. Thus in this case a rise in pressure has a very slight influence towards hydrogenation of the furan ring. On the other hand, hydrogenolysis at elevated pressures and 250° takes place here in both possible ways, as a result of which sylvan is converted predominantly into pentan-1-ol and pentan-2-ol:



The relative amounts of alcohols formed depend on the pressure: at 25 atm 33% of pentan-1-ol and 54% of pentan-2-ol are formed, but at 50 atm the corresponding quantities are 41% and 44%. Thus, depending on the nature of the catalyst, raising the pressure in the hydrogenation of 2-alkylfurans in a flow system favours hydrogenation of the furan ring or increases the degree of hydrogenolysis of the furan nucleus at the ether bond adjacent to the alkyl group.

Conjugate Hydrogenolysis of the Furan Ring

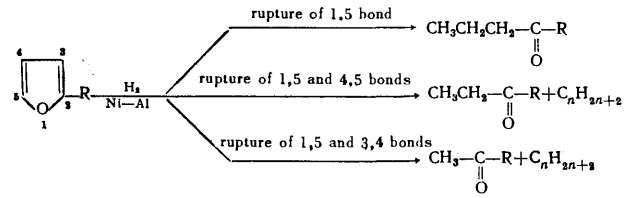
Among catalysts investigated for the hydrogenation of furan compounds, the foraminate Ni–Al catalyst occupies a special position. As already mentioned above, this catalyst hydrogenates the furan ring in both the liquid and the vapour phase. In this respect it resembles palladium catalysts, and is sharply distinguished from foraminate Ni–Zn, which exhibits very little ability to hydrogenate the furan ring. But the most important property distinguishing foraminate Ni–Al from all other catalysts and making it valuable from the point of view of synthesis is its ability to effect the so-called "conjugate" hydrogenolysis of the furan ring. An investigation [35,36] of the hydrogenation of 2-alkyl- and 2-alkenyl-furans in the vapour phase at normal pressure on a foraminate Ni–Al catalyst showed the following:

1. The hydrogenolysis products of 2-alkyl- and 2-alkenyl-furans are mainly secondary alcohols and the corresponding ketones. Primary alcohols are either almost completely absent from the reaction products, or else are present in very small amounts.

2. The hydrogenolysis of 2-alkyl- and 2-alkenyl-furans yields on the one hand alcohols and ketones containing the same number of carbon atoms as the original furan compound, and on the other alcohols and ketones in which the carbon chain is shorter by one or two C-atoms compared with the number of carbon atoms in the original alkylfuran.

3. Furan and tetrahydrofuran rings display a fundamental difference in their ability to undergo hydrogenolysis under identical conditions of hydrogenation. The latter ring is more stable than the furan ring, and undergoes hydrogenolysis in a different way.

All these experimental facts can be explained on the assumption that on a foraminate Ni–Al catalyst the furan ring undergoes hydrogenolysis both at C–O and at C–C bonds. It is obvious that separate rupture of cyclic C–C bonds does not occur (this would lead to the formation of ethers), but simultaneous, or so-called "conjugate", fission of C–O and C–C bonds takes place, as a result of which a 2-alkylfuran molecule yields a molecule of an aliphatic alcohol or ketone and a molecule of an aliphatic hydrocarbon



When homologues of furan are hydrogenated over foraminate Ni–Al, all the ketones containing a carbon chain which is one C-atom shorter are alkan-3-ones, while ketones containing two C-atoms less than the original 2-alkylfuran molecule are alkan-2-ones. In general the formation of alcohols and ketones having such a structure is possible only as a result of hydrogenolysis of carbon–carbon bonds in the furan ring.

The influence of temperature on conjugate hydrogenolysis was also examined, and it was found that a rise in temperature increases the degree of hydrogenolysis of the furan ring, substantially changing the direction of the reaction. At temperatures not exceeding 120°–130°, smooth hydrogenation of the furan to a tetrahydrofuran nucleus is possible in the vapour phase over foraminate Ni–Al. With rise in temperature conjugate hydrogenolysis of the furan ring becomes increasingly predominant, alcohols and ketones being formed at the lower temperatures, but only ketones at the higher temperatures. It was also established that a change in temperature affects the direction of conjugate hydrogenolysis of the furan ring. At 175° the ring in 2-alkylfurans is hydrogenolysed mainly in two ways, at the 1,5 C–O bond (60–75%) and at the 1,5 and 4,5 bonds (20–40%). At 235° the conjugate hydrogenolysis of these compounds takes place in these two ways (33–37% and 14–16% respectively) and also in a third way, at the 1,5 and 3,4 bonds (41–45%).

A comparative examination of the hydrogenolysis of sylvan and of tetrahydrosylvan, as well as of 2-propylfuran and tetrahydro-2-propylfuran on a foraminate Ni–Al catalyst, leads to the conclusion that the fission of C–O and

C–C bonds takes place in an adsorption complex formed by the furan ring and the catalyst surface. As a result, the alkylfuran molecule is converted on the surface either into an alkyltetrahydrofuran or into open-chain compounds, which are then desorbed from the catalyst surface.

The foraminate Ni–Al is so far the only catalyst on which conjugate hydrogenolysis of the furan ring is known to occur. Neither foraminate Ni–Zn nor other nickel catalysts are able to effect conjugate hydrogenolysis.

Conjugate hydrogenolysis of the furan ring opens up new synthetic possibilities, since the products are ketones and alcohols containing the carbonyl or hydroxyl group in positions 2, 3, or 4. On other catalysts, on which hydrogenolysis occurs only at the C–O bond, compounds are in general obtained containing the functional group in position 4.

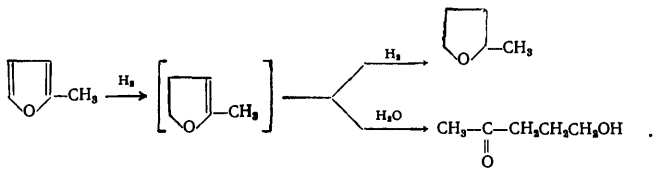
The foraminate Ni–Al catalyst has been investigated also for the hydrogenation of sylvan at a high pressure (50 atm) in a flow system. In this case, too, raising the hydrogen pressure has a very substantial effect in changing the direction of hydrogenation towards affecting mainly the cyclic multiple bonds. At 270° sylvan forms ~50% of tetrahydrosylvan, 45% of aliphatic ketones and alcohols (butan-2-ol, ethyl methyl ketone, and methyl propyl ketone), and 5% of pentane[34].

Mechanism of Hydrogenolysis of the Furan Ring

Since the hydrogenation of furan compounds yields on the one hand the corresponding tetrahydrofurans and on the other hydrogenolysis products of the furan ring, the question arises as to whether the tetrahydrofurans do not constitute an intermediate stage, from which the hydrogenolysis products are formed. The problem of the mechanism of hydrogenolysis includes the further question of whether hydrogenolysis of the C–O bond does not take place after only one C=C bond in the furan ring has been hydrogenated, *i.e.* in the dihydrofuran ring. The method used to prove the validity of one mechanism or the other consisted in a comparative study of the hydrogenation of corresponding furans, dihydrofurans, and tetrahydrofurans under identical conditions.

The behaviour of furan and tetrahydrofuran[37] and of furfuryl and tetrahydrofurfuryl alcohols[3] has been examined under the conditions of liquid-phase hydrogenation on a platinum catalyst, and that of sylvan and tetrahydrosylvan, as well as of the above alcohols[38], on copper chromite. These investigations proved that, under the conditions of liquid-phase hydrogenation, the tetrahydrofuran ring is completely devoid of that capacity for hydrogenolysis which is so highly characteristic of the furan ring. This difference in behaviour between furan and tetrahydrofuran rings under conditions of catalytic hydrogenation is exhibited also when the reaction is carried out in the vapour phase over nickel catalysts.

Shuikin and Bel'skii[39] showed that, on Pt–carbon at 250°–300°, the homologues of tetrahydrofuran isomerise into aliphatic ketones. However, this reaction occurs far more slowly than direct hydrogenolysis of the alkylfurans themselves under the same conditions, and therefore tetrahydrofurans cannot be regarded as intermediates in the hydrogenolysis of furan compounds. Thus all these investigations lead to the conclusion that hydrogenolysis of the C–O bond can take place either in the furan ring itself or in the dihydrofuran ring. Formation of the latter as an intermediate is proved by the conversion of sylvan into 5-hydroxypentan-2-one on hydrogenation over Pd in the presence of water[40]

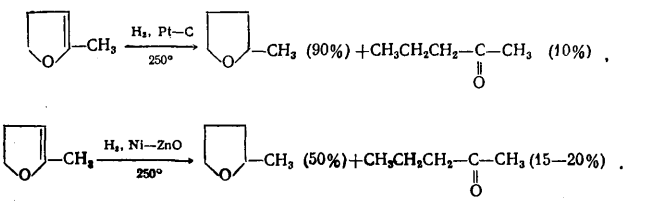


Another indirect proof of stepwise hydrogenation of the bonds in the furan ring is provided by the formation of spirans in the hydrogenation of 3-furylalkanols on nickel and copper–chromium catalysts.

On the basis of these experimental results several investigators[26] consider the formation of dihydrofurans to be an intermediate stage in hydrogenolysis of the furan ring. On the other hand, by measuring the rate of hydrogenation of furan on a platinum catalyst, Bradley[41] found that the addition of three moles of hydrogen does not take place in stages, since all the hydrogenation curves were smooth. This fact, in conjunction with what has been said above, can be interpreted on the basis that hydrogenation in the presence of water produces conditions which favour a different reaction path, and hence that the question of the mechanism of hydrogenolysis cannot be settled from a consideration of the results for hydrogenation of the furan ring in the presence of water.

A direct proof that dihydrofurans are not formed as intermediates in the hydrogenolysis of the furan ring was provided by an investigation of the hydrogenation of 4,5-dihydro-2-methylfuran in the gas phase over platinised carbon and nickel on zinc oxide at 250°–260°.[42] As has been shown above, under these conditions sylvan is completely split at the 1,5 C–O bond with the formation of methyl propyl ketone.

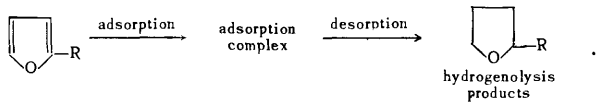
Dihydrosylvan, if it is formed as an intermediate in the hydrogenolysis of sylvan, should be converted into methyl propyl ketone just as easily and just as completely as sylvan, but experiments show[42] that the main reaction in the hydrogenation of dihydrosylvan on Pt–C and Ni–ZnO at 250°–260° is not hydrogenolysis of the C–O bond but hydrogenation of the cyclic C=C double bond:



These results confirm the conclusions of the multiplet theory, according to which hydrogenation of the first double bond in the furan ring occurs with considerably greater difficulty than that of an olefinic bond and approximately similarly to hydrogenolysis of a C–O bond in the furan ring. Hence it follows that rupture of C–O bond should be considerably more probable for furan itself.

On the basis of the above investigations it can be stated that the formation of dihydrofurans and tetrahydrofurans is not an intermediate stage in the hydrogenolysis of the furan ring, *i.e.* after a series of elementary acts in the process

of hydrogenation, either tetrahydrofurans or products of the hydrogenolysis of the furan ring are desorbed from the catalyst surface:



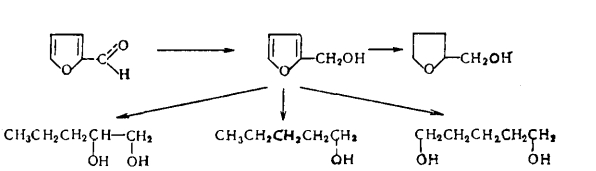
2. HYDROGENATION OF FURAN COMPOUNDS CONTAINING A CARBONYL GROUP IN THE SIDE CHAIN

The first work on the catalytic reduction of furfuraldehyde was published in 1906 by Padoa and Ponti [1], who passed its vapour mixed with hydrogen over a nickel catalyst at 190°. They found that the primary product of hydrogenation was furfuryl alcohol. However, further hydrogenation always took place, and sylvan, tetrahydrosylvan, pentan-2-one, and pentan-2-ol were isolated from the mixture of products. This shows that ring cleavage took place in the hydrogenation of furfuraldehyde. These workers also established that raising the temperature of hydrogenation to 270° results in the formation of furan and carbon monoxide.

Wienhaus [43] reduced furfuraldehyde in the presence of activated carbon impregnated with palladium chloride solution, at ordinary temperatures and a hydrogen pressure of 1 atm. The main product of hydrogenation was tetrahydrofurfuryl alcohol.

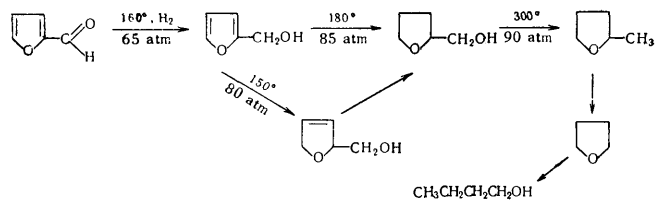
Pringsheim and Noth [44] passed a mixture of furfuraldehyde vapour and hydrogen over an iron catalyst at 200°, and observed the formation of the same products as in Padoa and Ponti's experiments together with furan and dihydrofuran. They point out that furfuraldehyde can undergo conversion in three ways: (1) the aldehyde group may be reduced to a methyl group; (2) the carbonyl may be eliminated to yield furan; and finally (3) the furan ring may be broken.

The above work was not systematic in character. A more extensive study of a wider range of problems was undertaken by Kaufmann and Adams [3], who investigated the reduction of furfuraldehyde and several of its derivatives in alcoholic solution in the presence of platinum oxide at ordinary temperatures and a hydrogen pressure of 1–2 atm. Absorption of an equivalent amount of hydrogen converts furfuraldehyde quantitatively into furfuryl alcohol. Further reduction led to the formation of a mixture of four products: tetrahydrofurfuryl alcohol (the main product), pentane-1,2-diol, pentane-1,5-diol, and n-pentyl alcohol. These workers concluded that the formation of glycols and pentan-1-ol cannot involve tetrahydrofurfuryl alcohol as an intermediate stage, since under these conditions the latter does not undergo hydrogenolysis to any appreciable extent. They represent the scheme of successive reactions in the hydrogenation of furfuraldehyde as follows:



They postulate that the C–O bond can undergo fission directly in the furan ring, with the intermediate formation of unsaturated glycols and subsequent hydrogenation of the latter to alkanediols.

A great amount of research has been devoted to finding conditions for the hydrogenation of furfuraldehyde to sylvan and to furfuryl and tetrahydrofurfuryl alcohols. We shall deal only with a few of the chief papers. Komatsu and Masumoto [45] showed that, depending on the temperature, the hydrogenation of furfuraldehyde on reduced nickel may yield various products, as can be seen from the following scheme

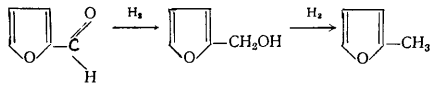


Schoeller and Jordan [46] discovered the conditions under which furfuraldehyde can either be smoothly converted into tetrahydrofurfuryl alcohol or give glycols as a result of fission of the ring. If the aldehyde is hydrogenated in the presence of reduced nickel on a carrier at 100°–150° and 40 atm hydrogen pressure, a catalysate is obtained containing 95% of tetrahydrofurfuryl alcohol and 5% of glycols. If, however, the hydrogenation is carried out at 200°–220°, the reaction products comprise only a mixture of pentane-1,2- and -1,5-diols with a small admixture of n-pentanol.

In 1931 Adkins and Connor [6] used copper chromite as catalyst for the hydrogenation of various classes of organic compounds. In their first research they investigated the liquid-phase hydrogenation of furfuraldehyde, among many other organic compounds. At 150° and a hydrogen pressure of 100–150 atm over copper chromite a quantitative yield of furfuryl alcohol was obtained. However, in the vapour-phase hydrogenation of furfuraldehyde over copper chromite, the main product will be sylvan. Schniepp *et al.* [47] obtained sylvan by hydrogenating furfuraldehyde in the vapour phase at 250° over copper chromite deposited on activated carbon. Besides sylvan (yield 92%) the products included furfuryl alcohol and unchanged aldehyde. Natta *et al.* [48] investigated the hydrogenation of furfuraldehyde and other furan derivatives on various catalysts. The aldehyde was hydrogenated in the presence of nickel, copper, cobalt, iron, silver, and mixtures thereof at various temperatures. Nickel catalysts proved to be more active for the hydrogenation of the aldehyde group and of the ring, which resulted in the formation of furfuryl and tetrahydrofurfuryl alcohols. Catalysts containing nickel and cobalt, and also nickel and iron, favoured complete reduction of the side group, and were thus most effective in the conversion of furfuraldehyde into sylvan and tetrahydrosylvan.

Copper and especially copper chromite were most active in opening the furan ring, so that glycols were obtained. When furfuryl alcohol was hydrogenated in the presence of these catalysts, pentane-1,2- and -1,4-diols were obtained; however, hydrogenation of tetrahydrofurfuryl alcohol under the same conditions gave only pentane-1,5-diol, whereas furfuraldehyde gave a mixture of all three isomers. Vigorous hydrogenation of furfuraldehyde, furfuryl and tetrahydrofurfuryl alcohols, and also tetrahydrosylvan on a copper catalyst yields pentan-1-ol, and on other catalysts pentan-2-ol.

The most detailed investigation of the conditions for the hydrogenation of furfuraldehyde to sylvan and furfuryl alcohol was made by Bremner and Keeys[49]. They established that the course of the reaction is affected by the nature of the catalyst, the temperature, and the flow velocity of the substance. Vapour-phase hydrogenation at normal pressure over copper catalysts forms mainly furfuryl alcohol and sylvan, together with a small quantity of furan and traces of n-pentanol. Hydrogenation of furfuraldehyde on a foraminate Cu–Al catalyst yields furfuryl alcohol at temperatures below 200° and sylvan at 250°. At 300° and above, however, the main product of hydrogenation becomes furfuryl alcohol, although the catalyst then loses its activity rapidly. Copper chromite possesses similar properties to a Cu–Al catalyst, but gives sylvan both at 250° and at 300°. These workers studied the effect of alkali on the selectivity of the catalysts, and found that addition of increasing quantities of alkali to the catalyst results in the formation predominantly of furfuryl alcohol. Thus a Cu–Al catalyst, after treatment of the alloy with alkali and incomplete washing with water, gave 2% of furfuryl alcohol and 88% of sylvan at 253°, whereas a Cu–Al catalyst which had been treated with 5% sodium carbonate solution with heating yielded 70% of the alcohol and 12% of sylvan. Bremner and Keeys concluded that the alcohol is an intermediate in the formation of sylvan from furfuraldehyde:



Actually, it was shown that the formation of the alcohol is favoured by carrying out the reaction with insufficient hydrogen and by a high rate of supply of the substance.

Bremner *et al.*[50] obtained sylvan from furfuraldehyde in the vapour phase at atmospheric pressure in the presence of a copper catalyst, which had been prepared from alloys of copper with metals which dissolve in acids or alkalis more readily than does copper. Satisfactory catalysts were obtained from alloys of copper with aluminium and with silicon. These workers point out that it is important to keep the temperature of the catalyst below some maximum value during the hydrogenation. On a copper–aluminium catalyst at 190°–250° furfuraldehyde was converted into sylvan with an 85% yield.

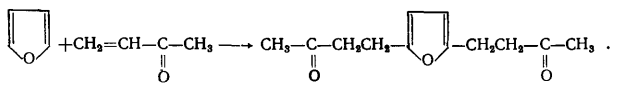
Starkey and Bremner[51] described the continuous hydrogenation of furfuraldehyde, over cobalt–aluminium and copper–aluminium catalysts, to furfuryl and tetrahydrofurfuryl alcohols, pentane-1,2- and -1,5-diols, and pentanols. Passage of the aldehyde over a Co–Al catalyst at 15° and 250 atm gave a mixture containing 40% of furfuryl alcohol and 60% of unchanged furfuraldehyde. Over a Cu–Al catalyst under the same conditions, but at 80°, the aldehyde was completely converted into furfuryl alcohol, whereas at 120° the ring was opened, the reaction products including 30% of a mixture of pentane-1,2- and -1,5-diols, and at 150° ~30% of pentanols. On a Co–Al catalyst at 50° and 250 atm furfuraldehyde was hydrogenated to tetrahydrofurfuryl alcohol, and under the above conditions a mixture of 50% of the aldehyde and 50% of tetrahydrofurfuryl alcohol was obtained.

Mizuguchi and Iwase[52] examined the relative activities of reduced copper, Raney copper, copper chromite, and reduced nickel in the hydrogenation of furfuraldehye to furfuryl alcohol. In the presence of the copper catalysts the aldehyde was quantitatively reduced to the alcohol at 140° and 100 atm; the greatest activity was shown by copper chromite, and this was attributed to the presence of chromic oxide in the catalyst. The nickel catalyst was comparatively inactive, after prolonged reaction it gave only 56% of furfuryl alcohol together with other products. Stewart[53] described the preparation of a Cu_2O catalyst which was active towards the hydrogenation of organic compounds. It could be activated by the oxides of aluminium, calcium, chromium, or vanadium. With a catalyst containing Cu_2O, CaO, and Al_2O_3 furfuraldehyde was almost quantitatively hydrogenated to furfuryl alcohol at 155°.

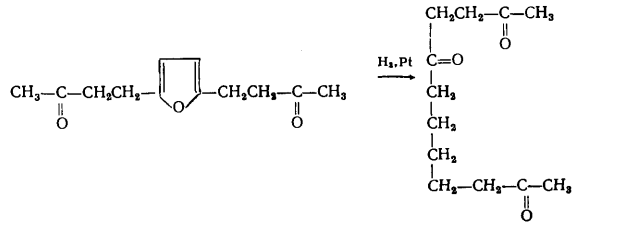
Howk[54] proposed a ruthenium catalyst for the hydrogenation of furfuraldehyde to tetrahydrofurfuryl alcohol. A 78% yield of the latter was obtained at 110° and 150 atm in the presence of RuO_2.MgO. We can confine ourselves to these papers, since they give the principal experimental results establishing the conditions for the selective hydrogenation of furfuraldehyde to furfuryl and tetrahydrofurfuryl alcohols and sylvan. Selective hydrogenation of the oxo- to a hydroxyl group without affecting the furan ring is best accomplished by hydrogenating furfuraldehyde in the liquid or the vapour phase over copper catalysts (copper chromite, foraminate copper, activated cuprous oxide) at both normal and elevated hydrogen pressures. Under the same conditions, but at higher temperatures, copper catalysts are highly effective in opening the furan ring, as a result of which furfuryl alcohol is converted into pentane-1,2- and -1,5-diols. The primary reduction product of furfuraldehyde on nickel and platinum catalysts is also furfuryl alcohol, which is obtained in quantitative yield after an equivalent amount of hydrogen has been absorbed. The complete hydrogenation of furfuraldehyde in the liquid phase over nickel, platinum, and ruthenium catalysts gives high yields of tetrahydrofurfuryl alcohol. Conversion of the aldehyde into sylvan necessitates carrying out the hydrogenation in the vapour phase, the best results being obtained on copper catalysts (copper chromite, foraminate copper).

The next most simple furan system containing a carbonyl group is formed by the furan ketones. Those containing the carbonyl group in positions 1 or 3 relative to the furan nucleus are available in practice.

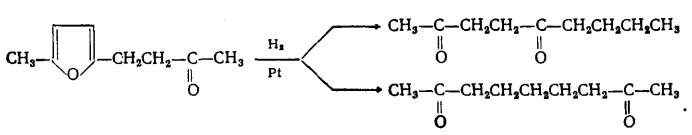
Continuing the investigations of Scherlin *et al.*, Alder and Schmidt[55] showed that the interaction of furan and sylvan with unsaturated aldehydes and ketones does not follow the pattern of diene synthesis but that of substitutive addition. Thus furan and methyl vinyl ketone yielded 2,5-bis-3′-oxobutylfuran:



In a similar manner, with methyl vinyl ketone and with phenyl vinyl ketone, sylvan gave 4-5′-methylfur-2′-ylbutan-2-one and 2-5′-methylfur-2′-ylethyl phenyl ketone respectively. These ketones were hydrogenated in ethyl acetate solution at ordinary temperatures in the presence of PtO_2. Hydrogenation of 2,5-bis-3′-oxobutylfuran yielded dodecane-2,5,11-trione:



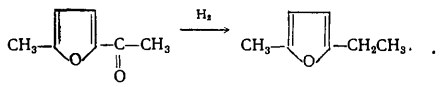
The hydrogenation products of the methylfurylbutanone were two acyclic diketones, nonane-2,5- and -2,8-diones:



These results show that, when ketones of the furan series are hydrogenated in the liquid phase over PtO_2, the primary reaction is hydrogenolysis of the ring with formation of aliphatic diketones and triketones, the carbonyl group remaining unreduced. In contrast to the above ketones, the methylfurfurylacetophenone does not undergo hydrogenolysis under analogous conditions, probably owing to the stabilising influence of the phenyl group on the furan ring.

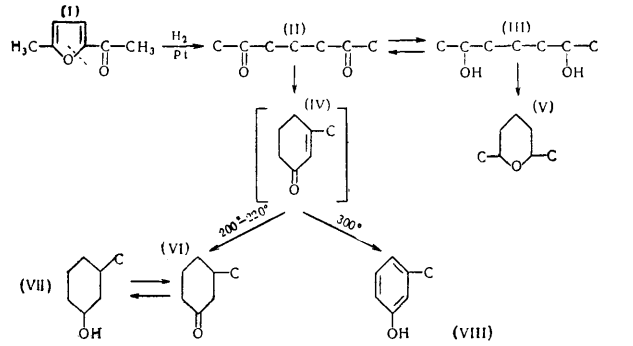
Interesting results were obtained in the vapour-phase hydrogenation of furan ketones containing the carbonyl group adjacent to the furan ring, *i.e.* 2-acyl-5-alkylfurans. Depending on the nature of the catalyst, the primary reaction was found to be either reduction of the carbonyl to a methylene group with preservation or subsequent hydrogenolysis of the furan ring[56] or else hydrogenolysis of the furan ring at the ether bond adjacent to the carbonyl group with formation of δ-diketones and the corresponding diols[57]. A more detailed investigation was made of the hydrogenation of methyl 5-methylfur-2-yl ketone on various catalysts: Pt–C, Pd–C, Ni–ZnO, Ni–CdO, and foraminate Cu–Al.

1. On Ni–ZnO, Ni–CdO, and foraminate Cu–Al catalysts the methyl methylfuryl ketone is reduced, in the vapour phase at 250°, to 2-ethyl-5-methylfuran in yields of ~60% on nickel catalysts and 90–95% on the foraminate Cu–Al catalyst:

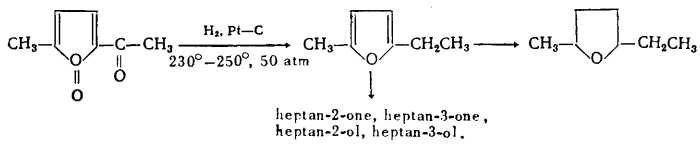


A side reaction is hydrogenolysis of the ring to form heptan-2-one, which is especially noticeable on Ni–ZnO.

2. Extremely interesting changes occur in the hydrogenation of the methyl methylfuryl ketone (I) on a platinum catalyst: among the principal products are heptane-2,6-dione, 3-methylcyclohexanone, 3-methylcyclohexanol, *m*-cresol, and tetrahydro-2,6-dimethylpyran. The formation of carbocyclic and heterocyclic compounds in the hydrogenation of the acetylsylvan is possible only if fundamental structural changes take place in the molecule of this heterocyclic ketone, and is undoubtedly the result of a series of consecutive reactions. A probable mechanism for these changes may be that hydrogenolysis of the furan ring at the 1,5 C–O bond gives heptane-2,6-dione (II), which undergoes either hydrogenation to heptane-2,6-diol (III) or cyclisation to 3-methylcyclohex-2-enone (IV), as in the treatment of δ-diketones with acids or alkalis. The heptane-2,6-diol then cyclises into tetrahydro-2,6-dimethylpyran (V), while the methylcyclohexenone is converted into either 3-methylcyclohexanone (VI) or *m*-cresol (VIII):



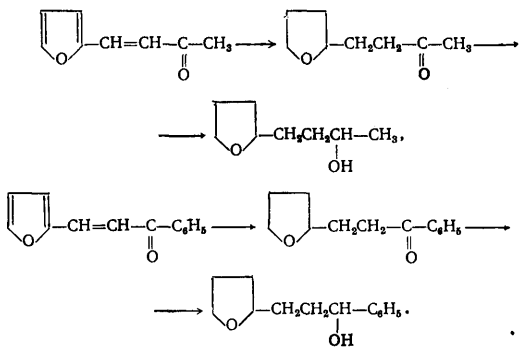
The transformation of 2-acyl-5-alkylfurans into δ-diketones, 2,6-dialkyltetrahydropyrans, alkylcyclohexanones, and alkylphenols is a general phenomenon, since it has been established that various homologues of 2-acylfurans can be transformed according to the above scheme. Variation of the reaction conditions, especially temperature, enables the course of the reaction to be controlled. δ-Diketones as the primary products of hydrogenation can be isolated in greatest quantity (~35%) from the catalysates obtained in the hydrogenation of 2-acyl-5-alkylfurans on platinised asbestos at 200°.[58] The yield of 2,6-dialkyltetrahydropyrans is especially dependent on temperature, since the hydrogenation of diketones to diols is favoured by a low temperature. On platinised carbon at 200°–220° the 2,6-dialkyltetrahydropyrans are formed in yields of 20–40%.[59] At 270°–300° the catalysate from 2-acetyl-5-methylfuran (methyl 5-methylfur-2-yl ketone) contains 50% of *m*-cresol, while 3-methylcyclohexanone is absent, but at 215°–220° some 25% of the latter compound is formed mixed with 3-methylcyclohexanol, and *m*-cresol is practically absent. Roughly similar relations are observed in the hydrogenation of other 2-acyl-5-alkylfurans[60]. The conversion of these compounds into δ-diketones, tetrahydropyrans, cyclohexanones, and phenols may prove a convenient method for the catalytic synthesis of compounds of these classes, in view of the fact that not only 2-acyl-5-alkylfurans, obtained from furfuraldehyde, but also 2-acyl-3,5-dialkylfurans, which are synthesised from alkenes and aliphatic acid chlorides *via* pyrylium salts[61], are readily available. The hydrogenation of methyl 5-methylfur-2-yl ketone on platinised carbon was further investigated at high pressures of hydrogen under flow conditions. As in the other cases considered earlier, the pressure of hydrogen has a substantial effect on the character of the hydrogenation of the 2-acetyl-5-methylfuran. The only primary reaction at 230°–250° and 50 atm of hydrogen is reduction of the carbonyl group, resulting in the formation of 2-ethyl-5-methylfuran, which is further hydrogenated to 2-ethyltetrahydro-5-methylfuran (55%) and undergoes hydrogenolysis with the formation of heptan-2- and -3-ones and the corresponding alcohols[34]:



3. HYDROGENATION OF FURAN COMPOUNDS CONTAINING AN OLEFINIC BOND AND A CARBONYL GROUP IN THE SIDE CHAIN

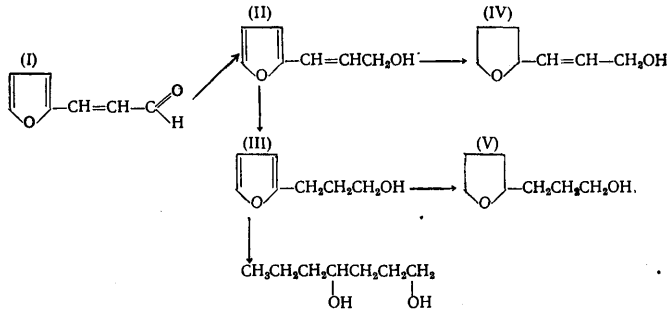
Ketones and aldehydes of the furan series, obtained by the condensation of furfuraldehyde with ketones and aldehydes, constitute the most convenient compounds for studying the possibilities of selective hydrogenation, since they contain three types of unsaturated bonds: olefinic and carbonyl in the side chain, and double bonds in the furan ring. Ketones and aldehydes of this structure have been subjected to hydrogenation in the liquid phase in the presence of various catalysts: Pt, Pd, Ni, Cu, etc.

Kaufmann and Adams[3] investigated the hydrogenation of furfurylideneacetone and furfurylideneacetophenone on a platinum catalyst at room temperature and a hydrogen pressure of 1–2 atm. These compounds were converted first into the corresponding tetrahydrofuran ketones, and then into the corresponding alcohols:



These workers studied several properties of the platinum catalyst. They showed that pure platinum oxide is not an effective hydrogenation catalyst. However, the addition of small quantities of ferric chloride exerts a promoter action, and the platinum oxide acquires excellent hydrogenating properties. With increasing content of ferric chloride in the catalyst, the rate of reduction increases to a maximum and then decreases. In the latter stage the increased content of ferric chloride in the catalyst has a greater effect in suppressing the ability to hydrogenate the ring than to reduce the aldehyde group.

Bray and Adams[62] examined the possibility of the selective hydrogenation of furylacraldehyde at ordinary temperatures and 2–3 atm pressure over a platinum catalyst. Addition to the platinum of iron salts and zinc acetate not only increased its activity but also favoured selective hydrogenation of the furylacraldehyde. By interrupting hydrogenation after the absorption of a definite quantity of hydrogen these workers obtained products of different degrees of saturation. They established that the hydrogenation of furylacraldehyde involves the following reactions: first of all the aldehyde group is reduced, and the furylacraldehyde (I) is converted into furylallyl alcohol (II), the latter undergoing change in two ways: the side-chain olefinic bond is hydrogenated to form furylpropyl alcohol (III) and the double bonds in the furan ring are hydrogenated, tetrahydrofurylallyl alcohol (IV) then being formed, but in considerably smaller amount than furylpropyl alcohol; this shows that the side-chain olefinic bond is more reducible than the cyclic double bonds. Furylpropyl alcohol on further reduction is converted mainly into tetrahydrofurylpropyl alcohol (V), and to a slight extent undergoes hydrogenolysis to heptane-1,4-diol (VI)



Thus the reactions involved in hydrogenation of the various bonds in furylacraldehyde on a platinum catalyst promoted with iron and zinc salts can be arranged in the following sequence according to their ease of occurrence: (1) hydrogenation of the C=O bond in the side chain; (2) hydrogenation of the C=C bond in the side chain; (3) hydrogenation of the C=C bonds in the furan ring; (4) rupture of a C–O bond in the furan ring.

We are now able to draw some general conclusions on the basis of the experimental results obtained for the hydrogenation of furan ketones and aldehydes on platinum catalysts.

Kaufmann and Adams showed that, in the hydrogenation of furfuraldehyde in the presence of a platinum catalyst promoted with ferric chloride, furfuryl alcohol is formed at first, and this on further hydrogenation gives a mixture of tetrahydrofurfuryl alcohol and pentane-1,2- and -1,5-diols. Since a quantitative yield of furfuryl alcohol is obtained after the absorption of one mole of hydrogen, it is obvious that the hydrogenation of furfuraldehyde first involves reduction of the carbonyl group, and then hydrogenation of the double bonds and hydrogenolysis of the cyclic C–O bonds. In the hydrogenation of furfurylideneacetone and furfurylideneacetophenone on the same catalyst, however, these workers obtained tetrahydrofuran ketones, *i.e.* compounds containing a tetrahydrofuran ring and an unchanged carbonyl group. The sequence of reactions was obviously different in this case from that observed in the hydrogenation of furfuraldehyde, since tetrahydrofuran ketones can be formed as a result of hydrogenation of the furan ring before reduction of the carbonyl group. On the other hand, Alder and Schmidt showed that, in the hydrogenation of furan ketones, for example, 5-methylfurfurylacetone, on an Adams catalyst, hydrogenolysis of the furan ring takes place before reduction of the carbonyl group. These facts show that the relative ease of hydrogenation of the carbonyl group and of the furan ring depends on the chemical structure of the compounds undergoing hydrogenation.

The role of the catalyst as the main factor governing the selectivity of hydrogenation is seen especially clearly from a comparison of the results for the hydrogenation of furfurylideneacetone and of furylacraldehyde, since these two compounds contain the same system of an olefinic and a carbonyl bond in the side chain.

Under conditions of vapour-phase hydrogenation, platinum catalysts effect hydrogenolysis of the furan ring also before reduction of the carbonyl group. For example, as

already mentioned above, 2-acetyl-5-methylfuran on vapour-phase hydrogenation over platinised carbon or asbestos gives first of all heptane-2,6-dione by hydrogenolysis of the furan ring. Since, however, the carbonyl group in the acetyl derivative is adjacent to the furan ring, another primary reaction, reduction of the C=O to a CH_2 group, takes place at the same time. A condition for the selective reduction of a carbonyl group adjacent to a furan ring is vapour-phase hydrogenation over copper catalysts (foraminate copper, copper chromite). Under these conditions furfuraldehyde is smoothly converted into sylvan[47], and 2-acetyl-5-methylfuran into 2-ethyl-5-methylfuran[56]. Selective hydrogenation of the olefinic bond in unsaturated furan ketones and aldehydes is possible on various catalysts. Thus Alder and Schmidt found that, in the 5-methylfurfurylideneacetophenone molecule in the presence of Pd at 25°, only the olefinic bond is hydrogenated, while the carbonyl group and the furan ring remain unaffected[55]. A similar effect is shown by a foraminate Cu–Al catalyst, on which various furfurylidene ketones are hydrogenated at 30°–40° to the corresponding saturated ketones with yields of 70–85%.[63] At higher temperatures (120°–140°) furylacraldehydes and furfurylidene ketones are hydrogenated on foraminate Cu–Al to the corresponding furan alcohols in yields of 75–85% and 90–95% respectively[56].

Much research has been done† on the hydrogenation of unsaturated ketone and aldehyde derivatives of furan on nickel catalysts. We shall deal only with the most important work.

Burdick and Adkins[64] made a detailed investigation of the hydrogenation of furylacraldehyde and several products of its partial reduction, on copper–chromium and nickel catalysts (nickel on kieselguhr and Raney nickel), in the liquid phase at hydrogen pressures of 100–200 atm.

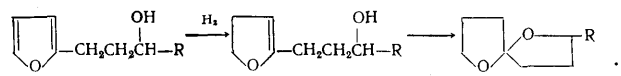
Raney nickel proved to be an active catalyst at moderate temperatures for the hydrogenation of a side-chain olefinic bond. In the presence of this catalyst at 23° furylacraldehyde was converted into furylpropionaldehyde in 46% yield. Raising the temperature of hydrogenation ot 160° resulted in the formation of tetrahydrofurylpropyl alcohol in 65% yield. Hence at elevated temperatures Raney nickel is an effective catalyst for hydrogenation of the C=C bonds in the furan ring. A copper–chromium catalyst is relatively inactive towards the hydrogenation of the furan ring, but proves extremely effective for opening the cyclic ether bond. At moderate temperatures a copper–chromium catalyst is active in hydrogenating side-chain olefinic and carbonyl bonds without affecting the ring. In the presence of copper chromite at 120°–175° furylacraldehyde gave a 72% yield of furylpropyl alcohol. Thus at this temperature the olefinic bond and the aldehyde group were hydrogenated, but the ring remained untouched. At 200° the ring was split at the C–O bonds with the formation of heptane-1,4-diol (yield 29%) and heptane-1,7-diol (20%).

Raney nickel was extremely active also in the fission of C–C bonds in primary alcohols. Tetrahydrofurylpropyl alcohol on this catalyst at 250° suffered cleavage of a side-chain C–C bond, with the formation of 2-ethyltetrahydrofuran (yield 60%) and tetrahydro-2-propylfuran (yield 1%). Under the same conditions heptane-1,4-diol was converted into hexan-3-ol (yield 66%), and heptane-1,7-diol into n-pentane (yield 21%).

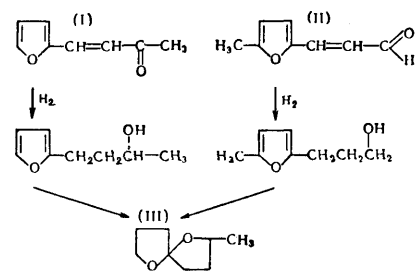
† See monograph by A.P.Dunlop and F.N.Peters, "The Furans", New York, 1953.

Nickel on kieselguhr, like Raney nickel, was a good catalyst for hydrogenation of the furan ring. It was also the most effective in converting furylacraldehyde into 2,2′-spirobitetrahydrofuran, a 33% yield of which was obtained at 160°.

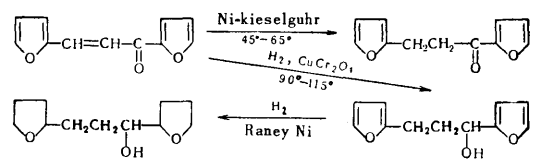
Burdick and Adkins considered that only 3-furylpropionaldehyde can be converted into a spiran, whereas 3-furylpropan-1-ol merely gives traces of this compound. However, this was not confirmed subsequently. Alexander *et al.*[65] established that 2,2′-spirobitetrahydrofuran and its 5-methyl derivative are formed by the hydrogenation of 3-furylpropan-1-ol and 3-furylbutan-1-ol respectively in the presence of nickel on kieselguhr at 70°–125°. Spiro-compounds were obtained also by the hydrogenation of furfurylideneacetone and difurfurylideneacetone [1-fur-2′-ylbut-1-en-3-one and 1,5-difur-2′-ylpenta-1,4-dien-3-one (Ed. of Translation)] on a copper–chromium catalyst[66]. From these facts Alexander *et al.* concluded that the formation of spirans is a general reaction in the hydrogenation of γ-furylalkanols on copper chromite or nickel deposited on kieselguhr. They suggested the following mechanism of spiran formation:



The structure of the spirans obtained by the hydrogenation of γ-furylalkanols was demonstrated by the work of Farlow *et al.*[67] and also of Ponomarev *et al.*[68] The latter showed that the hydrogenation of furfurylideneacetone (I) and of 5′-methylfurylacraldehyde (II) yields the same 5-methyl-2,2′-spirobitetrahydrofuran (III), as can be seen from the following scheme:



Alexander and Smith[69] investigated the hydrogenation of 1,3-difur-2′-ylprop-2-enone in the presence of Raney nickel, nickel on kieselguhr, and copper chromite. Their results support the conclusions reached earlier by Burdick and Adkins[64] from the hydrogenation of furylacraldehyde:



At moderate temperatures (20°–60°) only the side-chain olefinic bond is hydrogenated on Raney nickel and nickel deposited on kieselguhr; at temperatures above 100° (130°–160°) these catalysts effect complete reduction of the C=C and C=O bonds in the side chain and hydrogenation of the double bonds in the ring. A copper–chromium catalyst, in contrast to Raney nickel and nickel on kieselguhr, does not exhibit any appreciable activity towards hydrogenation of the cyclic double bonds.

A large number of derivatives containing one or two furan rings in the molecule together with olefinic and carbonyl bonds in the side chain have been obtained by condensing furfuraldehyde, furylacraldehyde, and acetylfuran with various aldehydes, ketones, and esters. Hydrogenation of these compounds on Raney nickel at 170°–180° and 125–250 atm gives up to 90% yields of tetrahydrofuran derivatives (esters or alcohols)[70], but in the presence of copper chromite at 110°–135° only hydrogenation of the side-chain olefinic bond and carbonyl group takes place, with formation of the corresponding furan alcohols[71]. Hydrogenation on nickel deposited on kieselguhr converts these into tetrahydrofuran alcohols (yields up to 75%) and spirans, which are homologues of 2,2′-spirobitetrahydrofuran[71].

Balandin and Ponomarev[72] employed the multiplet theory to determine the sequence of reactions in the hydrogenation of furan compounds on a nickel catalyst. They calculated the energies of formation E' of the intermediate multiplet complexes from the starting materials and the catalyst, using a doublet reaction scheme:

1.	Hydrogenation of olefinic bond	-2.9
2.	Hydrogenation of carbonyl bond	-10.1
3.	Hydrogenation of first double bond in furan ring	-10.9
4.	Hydrogenolysis of ether bond in furan ring	-11.8
5.	Formation of spiran from furan alcohol	-15.8
6.	Hydrogenolysis of carbon–oxygen bond	-16.8
7.	Hydrogenolysis of carbon–carbon bond	-48.4

Since the activation energy $E = -\frac{3}{4}E'$, the above reaction sequence obviously indicates the relative ease of occurrence of the reactions on a nickel catalyst. Those reactions for which E' has the highest numerical value will occur more readily, *i.e.* at a lower temperature; hence in the hydrogenation of furan compounds on a nickel catalyst, the reactions should take place in the order of decreasing values of E'. However, owing to the closeness of the values of E' for reactions 2–4, some of them can be expected to occur simultaneously or even in the reverse order. In fact, experiment shows[73,74] that in some cases hydrogenation of C=C bonds in the furan ring can precede, on a nickel catalyst, reduction of the side-chain carbonyl group. On the other hand, hydrogenolysis of C–O bonds in the furan ring takes place earlier, on a nickel catalyst, than hydrogenation of the cyclic double bonds. No catalyst has yet been found which would hydrogenate the furan ring before the aldehyde group is reduced, and would, for example, convert furfuraldehyde into tetrahydrofurfuraldehyde. In the case of ketones, however, hydrogenation of the ring double bonds can take place before reduction of the carbonyl group on some nickel catalysts, resulting in the formation of ketones of the tetrahydrofuran series. Thus the statement[72] that substituents have no decisive effect in the hydrogenation of furan compounds cannot be accepted unreservedly. It was shown[72] that, in the hydrogenation of furan compounds, the sequence of reactions depends on the nature of the catalyst. Thus theory explains why, over copper, hydrogenolysis of a C–O bond in the furan ring takes place more readily than hydrogenation of the cyclic C=C bonds. In general, the agreement between theoretical calculations based on the multiplet theory and experiment can be regarded as quite satisfactory (especially for the conditions of liquid-phase hydrogenation), if it is borne in mind that the conclusions of the theory relate to a nickel catalyst of average properties.

4. HYDROGENATION OF FURAN COMPOUNDS CONTAINING A HYDROXYL OR AN AMINO-GROUP IN THE SIDE CHAIN

As was shown above, the simplest representative of the furan alcohols, furfuryl alcohol, is readily obtained by hydrogenating furfuraldehyde on various catalysts. The synthesis of other furan alcohols containing the hydroxyl group adjacent to the furan ring is accomplished by hydrogenating 2-acylfurans or by the Grignard reaction from furfuraldehyde and alkyl halides. Another readily available group of furan alcohols are those containing the hydroxyl group in position 3 with respect to the furan nucleus. Furan alcohols of this type are obtained by hydrogenating furylacraldehydes and furfurylidene ketones in the liquid phase on copper catalysts (see above).

In the case of the furan alcohols the problem of hydrogenation reduces in the first instance to finding conditions under which they would be converted into tetrahydrofuran alcohols. Those catalysts which are used for the hydrogenation of homologues of furan prove suitable for this purpose. Douris[75] hydrogenated 1-furylpropanol on a nickel catalyst at 175°, and obtained the tetrahydrofuryl derivative as the main product.

Pierce and Adams[76] reduced 1-furylpropanol and 1-furylpentanol in the presence of platinum black (prepared from PtO_2) at ordinary temperature and a hydrogen pressure of 1–2 atm. The hydrogenation products of the former compound were heptan-3-ol, 1-tetrahydrofurylpropanol, and heptane-3,4-diol; from the products of the hydrogenation of the furylpentanol they isolated nonan-5-ol, 1-tetrahydrofurylpentanol, and nonane-4,5- and -1,5-diols. Thus the 1-furylalkanols investigated by Pierce and Adams gave open-chain products on hydrogenation as well as their tetrahydro-derivatives.

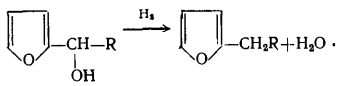
Paul[77] investigated the hydrogenation of furfuryl alcohol, 1-furylethanol, 1-furylpropanol, 1-furylbutanol, and α-furylbenzene alcohol, and found that, depending on the nature of the catalyst and the temperature, hydrogenation of these compounds yielded 1-tetrahydrofurylalkanols, 1,5- and 4,5-diols, and also other products (furans, carbinols, hydrocarbons). He examined platinum catalysts, colloidal palladium, copper chromite, reduced nickel, nickel on kieselguhr, and Raney nickel. The best catalyst for hydrogenation of the ring was Raney nickel, which is already active at moderate temperatures (50°–80°). Yields of 90–100% of tetrahydrofuran derivatives were obtained on it.

In 1932 Connor and Adkins[38] published results obtained by hydrogenating furfuryl and tetrahydrofurfuryl alcohols on copper–chromium and nickel catalysts. On copper chromite at 200°–250° the former alcohol is hydrogenated to a slight extent to the latter, but the main reaction under these conditions is hydrogenolysis of the ring at the C–O bonds, yield pentane-1,2-diol (14%) and pentane-1,5-diol (15%), as well as sylvan (20%) and pentan-1-ol (10%). On a nickel catalyst, in contrast, furfuryl alcohol was hydrogenated to tetrahydrofurfuryl alcohol in high yields. They established that, in contrast to furfuryl alcohol, tetrahydrofurfuryl alcohol is considerably more resistant to hydrogenolysis of the ring. On copper chromite the latter alcohol gave, after hydrogenation for 11 h, tetrahydrosylvan and water (5%) as well as pentane-1,5-diol, about 77% of the alcohol remaining unchanged. Undergoing hydrogenolysis to a slight extent, tetrahydrofurfuryl alcohol gave pentane-1,5-diol almost exclusively, whereas furfuryl alcohol

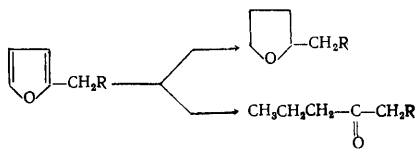
under the same conditions was converted into a mixture of almost equal quantities of pentane-1,2-diol and pentane-1,5--diol. Hence it follows that the furan ring undergoes hydrogenolysis considerably more readily than, and in a different way from, the tetrahydrofuran ring.

Let us draw some conclusions. Nickel catalysts, and especially Raney nickel, have proved extremely effective for the hydrogenation of furan alcohols to tetrahydrofuran alcohols. On a platinum catalyst promoted with iron salts, the hydrogenation of furfuryl alcohol[3] and of 1-furylalkan--1-ols[21] also results mainly in formation of the corresponding tetrahydro-derivatives. However, even at low temperatures this catalyst tends to cause hydrogenolysis of the furan ring at one or both ether bonds, with the production of alkanediols and alkanols. This last reaction takes place especially readily on copper catalysts, in particular on copper chromite. Extremely interesting peculiarities are exhibited in the hydrogenation of furan alcohols in the vapour phase. Under these conditions alcohols containing the hydroxyl group in positions 1 or 3 with respect to the furan nucleus undergo completely different changes.

1. 1-Furylalkan-1-ols on vapour-phase hydrogenation at 200°–250° over Pd–C, Ni–ZnO, and foraminate Pd–Al, Cu–Al, and Ni–Zn catalysts are reduced to 2-alkylfurans in yields of 60–95%:[56,78-80]



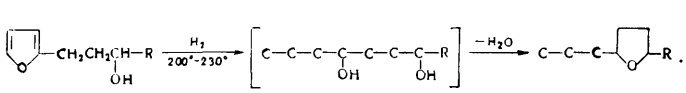
Small quantities of the corresponding 2-alkyltetrahydrofurans and aliphatic ketones are also formed. These compounds, the yields of which are increased by passing the furylalkanols more slowly through the catalyst, are obtained as secondary products of hydrogenolysis and hydrogenation of the alkylfurans which are formed:



The ready fission of the bond between the carbon atom and the hydroxyl group in 1-furylalkan-1-ols under the action of hydrogen in the presence of a catalyst is a specific property of this type of compound, depending on the presence of a furan ring adjacent to a hydroxyl group. The corresponding tetrahydrofurylalkanols are not reduced at all under the same conditions. 1-Tetrahydrofurylethanol remained unchanged[78] over palladised carbon under conditions under which the hydroxyl group in 1-furylethanol was reduced.

Thus the aromatic system formed by the furan ring has the same effect on the stability of the bond between a carbon atom and a hydroxyl group adjacent to the ring as has the benzene nucleus[81].

2. Furan alcohols containing the hydroxyl group in position 3 relative to the furan nucleus are converted into homologues of tetrahydrofuran on vapour-phase hydrogenation over a platinum catalyst at 200°–230°:[82,83]



The reaction consists of two consecutive stages: hydrogenolysis of the furan ring to form alkane-1,4-diols, and intramolecular cyclisation of the latter, with elimination of water, to yield homologues of tetrahydrofuran. The formation of alkane-1,4-diols as intermediate compounds is favoured by a low temperature. The highest yields of tetrahydrofurans are obtained at 200°–230°. The catalyst must be active in effecting hydrogenolysis of the furan ring at moderate temperatures. Therefore catalysts other than platinum can be used, for example, foraminate Cu–Al and Ni–Zn. The structure of the tetrahydrofuran homologues which are formed is ultimately determined by that of the aliphatic oxo-compounds with which furfuraldehyde condenses. With aliphatic aldehydes furfuraldehyde yields successively 2-alkyl-3-furylacraldehydes, 2-alkyl-3-furylpropanols, and finally 3-alkyltetrahydro-5-propylfurans. 2-Alkyltetrahydro-5-propylfurans are obtained by the hydrogenation of 3-furylalkanols, which are reduction products of furfurylidene ketones. The catalytic method of synthesising tetrahydrofuran homologues also enables trialkyltetrahydrofurans to be obtained if ketones of the type RCH_2COCH_2R' are condensed with furfuraldehyde. The limits of applicability of this method may be further extended by replacing furfuraldehyde by other carbonyl derivatives of furan, for example, 2 acylfurans.

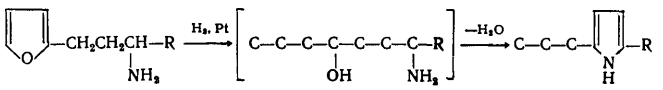
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Amines of the furan series are obtained from furan ketones either by reductive amination or by conversion of the ketones into oximes with subsequent reduction of the latter to amines. Consequently those furan amines which are accessible in practice contain the amino-group in positions 1 or 3 of the side chain with respect to the furan nucleus (corresponding in structure to the furan ketones). Among derivatives having the amino-group in position 1, the hydrogenation of furfurylamine has been investigated in some detail. Early work established[84] that platinum oxide is an effective catalyst both for hydrogenation of the furan ring in furfurylamine and for hydrogenolysis of the resulting tetrahydrofurfuran nucleus. In the presence of PtO_2 furfurylamine in the liquid phase at room temperature and a hydrogen pressure of 1.5–2 atm is smoothly hydrogenated to tetrahydrofurfurylamine. Further hydrogenation results in the tetrahydrofurfuran ring being opened mainly at the C–O bond adjacent to the substituent, with the formation of 5-aminopentanol. Under analogous conditions furylpropylamine gives an 88–89% yield of tetrahydrofurylpropylamine, and on further hydrogenation is converted into 7-aminoheptanol, a product of the hydrogenolysis of tetrahydrofurylpropylamine at the ether bond adjacent to the substituent[85,86].

Palladium deposited on carbon has proved to be a satisfactory catalyst for hydrogenation of the ring in furfurylamine, a yield of ~75% of tetrahydrofurfurylamine being obtained in glacial acetic acid solution in its presence[87]. Vil'yams found that the rate and the course of hydrogenation in nitrogen-containing furan compounds are affected by the nature of the solvent[88] as well as the catalyst. Furan amines of more complicated structure, 2,5-bis-(3-aminopropyl)furan and 2,5-bis-(3-aminobutyl)furan, were hydrogenated, in dioxan solution over Ru–C at 120°–160°, to 80–87% yields of the corresponding tetrahydrofuran amines[89]. It was pointed out in this work that the yields are lower on Raney nickel than on Ru–C, since hydrogenolysis of the furan ring occurs to a greater extent on the former catalyst. These

not entirely satisfactory properties of a nickel catalyst were noted also by Ponomarev *et al.*, who succeeded in hydrogenating quite smoothly on Raney nickel, not the furan amines themselves, but their *N*-acetyl derivatives[90].

The vapour-phase hydrogenation of furan amines has been little studied to date, but the results already obtained open up possibilities for the synthesis from these amines of heterocyclic compounds containing nitrogen. The hydrogenation of 3-furyl-1-alkylpropylamines, investigated over Pt–C in a flow system at 200°–210°, gave 70–80% yields of 2-alkyl-5-propylpyrrolidines[91]



It must be stressed that the conversion of 3-furyl-1-alkylpropylamines into homologues of pyrrolidine, and that of 3-furylalkanols into homologues of tetrahydrofuran (see above), constitute reactions of the same type, which can be represented as follows: if the side chain of a furan compound contains functional groups capable of interaction with the hydroxyl or carbonyl produced by hydrogenolysis of the furan nucleus, and if the bifunctional aliphatic compounds resulting from hydrogenolysis of the ring are of the γ-series, the vapour-phase hydrogenation of such furan compounds results in the formation of new five-membered heterocyclic rings. It is not difficult to see that the conversion of 2-acyl-5-alkylfurans into 2,6-dialkyltetrahydropyrans, discussed above, also belongs to this type of reaction. In this case the bifunctional aliphatic compounds formed as intermediates are of the δ-series, and give six-membered heterocycles by intramolecular cyclisation.

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In conclusion, let us consider the kinetics of the hydrogenation of furan compounds.

Pierce and Parks[92] examined the effect of temperature on the rate of reduction of furfuraldehyde in the presence of platinum black, and found that the rate increases with rise in temperature from 0° to 40°, passes through a maximum, and falls with further rise in temperature to 60°. The reason for this is a more rapid loss in activity by the catalyst at 60°. The only product of the hydrogenation of furfuraldehyde was furfuryl alcohol.

Smith and Fuzek[37] studied the kinetics of the hydrogenation of furan, sylvan, 2,5-dimethylfuran, furfuraldehyde, furfuryl alcohol, pyromucic acid, and dibenzofuran in acetic-acid solution over an Adams platinum catalyst. They found that: (1) the hydrogenation of furan compounds is of the first order with respect to hydrogen and of zero order with respect to the compounds undergoing hydrogenation; (2) the reaction velocity is directly proportional to the quantity of catalyst taken for the reaction; (3) the rate constants and the activation energies for the hydrogenation of furan compounds are greater than the corresponding values for hydrogenation of analogous benzene derivatives. These workers established that hydrogenolysis of the ring at the carbon–oxygen bonds was the principal reaction in the hydrogenation of furan compounds, either the 1,2 or the 1,5 C–O bond undergoing cleavage, depending on the nature of the side chain. Thus hydrogenolysis of pyromucic acid occurred at the 1,2 C–O bond with the formation of 5-hydroxyvaleric acid, while sylvan and furfuryl alcohol underwent hydrogenolysis at the 1,5 C–O bond to give respectively pentan-2-ol (yield 80–90%) and an almost quantitative yield of pentane-1,2-diol. Small quantities of tetrahydrosylvan and tetrahydropyromucic acid from the products of the hydrogenation of sylvan and pyromucic acid were isolated also.

Furan and 2,5-dimethylfuran gave only butan-1-ol and hexan-2-ol on hydrogenation. In contrast to all these compounds, the furan ring in dibenzofuran did not undergo hydrogenolysis, for the only product of its hydrogenation was perhydrodibenzofuran. An experimental proof was obtained that tetrahydrofuran derivatives are not intermediates in the formation of hydrogenolysis products. Tetrahydrofuran remained unchanged on subjection to hydrogenation under conditions under which furan was converted quantitatively into butan-1-ol. From this and also some other facts it was concluded that hydrogenation of furan compounds on a platinum catalyst involves two simultaneous reactions, hydrogenation of the ring with the formation of tetrahydro-derivatives, and hydrogenolysis of the ring with the formation of open-chain compounds.

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THE RADIOLYSIS OF FROZEN AQUEOUS SOLUTIONS

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INTRODUCTION

The great interest displayed recently in studying the action of ionising radiation on frozen aqueous solutions is due to the possibility in this case of recording and examining the primary products of the radiolysis of water, and also the possibility of elucidating the nature of the redistribution of the absorbed energy among individual components of the solutions. The present review constitutes the first attempt at a systematic survey of results published in this new branch of radiation chemistry. The first part of the paper discusses problems associated with the kinetics of the accumulation of the end-products of radiation-chemical changes in ice and solid aqueous solutions. The next two sections give data obtained from a study of the intermediate products of radiolysis by the methods of luminescence analysis and electron paramagnetic resonance. At the end of the review is a brief statement of some general conclusions which, in the writer's opinion, can be drawn at the present time from published results.

I. INVESTIGATION OF THE KINETICS OF THE ACCUMULATION OF END-PRODUCTS IN THE RADIOLYSIS OF ICE AND FROZEN AQUEOUS SOLUTIONS

The final products of the radiolysis of ice, as also of liquid water, are hydrogen, oxygen, and hydrogen peroxide. The first investigations by Duane and Scheuer in 1913 established that, when ice is exposed to α-rays at -180°, the yield of the stoichiometric mixture of oxygen and hydrogen which is formed is one-twentieth of that in the case of liquid water[1]. The yield of hydrogen peroxide on irradiation of ice with α-particles has only been halved compared with water (0.47 and 0.88†). The formation of molecular oxygen in the irradiation of ice, as also of water, is due to decomposition of hydrogen peroxide, and therefore the yield of oxygen is strongly dependent on the experimental conditions.

Investigation of the kinetics of the formation of H_2O_2, O_2, and H_2 under various conditions of exposure enabled Lefort and his coworkers[2-5] to establish the way in which the accumulation of the "molecular products" of the radiolysis of ice depended on the density of the ionising radiation‡ (α-rays and X-rays). In the case of densely ionising radiation (α-particles), raising the temperature of the ice from -196° to -40° had no effect on the yield of H_2 and H_2O_2. The absence of a temperature effect is probably due to the specimen's being warmed in the track of the particles to the liquid state (calculation shows that such "heated portions" exist for 10^{-9} sec) and to the radicals recombining (mean time of recombination of the radicals ~ 10^{-10} sec).

In the case of the radiolysis of ice by lightly ionising radiation, Bonet-Maury and Lefort[3,5] showed that the yield of hydrogen peroxide depends on the concentration of molecular oxygen dissolved in the water before it was frozen (X-rays). No H_2O_2 was detected in specimens of ice irradiated at between -192° and -116°.[3] It was established that H_2O_2 was formed at higher temperatures, its concentration increasing with rise in temperature of the specimen. Changing from the liquid to the solid phase is accompanied, as in the case of radiolysis by α-rays, by a diminished yield of hydrogen peroxide[3,5] and of molecular hydrogen[7]§. The change in the yield of hydrogen on passing to the solid phase is explained by differing conditions of diffusion of the intermediate species in water and in ice[7]. In the case of irradiation of ice with light ionising radiation at between -196° and -180°, $G(H_2)$ is of the order of 0.10-0.15.[8] The initial radiation yield of $2H_2 + O_2$ when ice is exposed to β-particles from tritium at -196° is 0.27.[9]

Ghormley and Stewart[10,11] investigated the kinetics of the formation of H_2, O_2, and H_2O_2 in the radiolysis of ice as a function of temperature and the presence of dissolved gases. Irradiation was carried out at temperatures between -269° and 0° with a cobalt source and with X-rays obtained by means of a van der Graaf accelerator (2 MeV). The products were analysed, as in the work quoted earlier, after fusion of the specimens. The initial yields of H_2O_2 and H_2 in ice containing dissolved oxygen were found to increase with rise in temperature. Molecular oxygen has no effect on the formation of H_2. In the case of the radiolysis of solutions of hydrogen peroxide, the rate of decomposition of the H_2O_2 was found to change sevenfold when the temperature was raised from -100° to -50°. It is interesting that, when specimens were irradiated at -196° with periodic interruption of the radiation and warming to 180° and above, the final concentration of hydrogen peroxide was lower than in specimens which had been continuously exposed at -196° until the same dose had been absorbed. In Ghormley and Stewart's opinion, the primary products of radiolysis (electrons, radicals, etc.[12]) "captured" at low temperatures by some kind of traps in the matrix are set free when the specimen is unfrozen, and enter into reaction with the dissolved substances, in particular with hydrogen peroxide.

Results obtained by Berger[13] indicate the possibility of the occurrence at low temperatures of chemical processes involving products of the radiolytic breakdown of components of the system, including water. According to these investigations, radiolysis with accelerated protons (energy 12 MeV, current 0.5 μA) of a mixture of methane, ammonia, and water frozen at 77°K results in the formation of urea, acetaldehyde, and acetone, the aggregate yield of the products being 1.39.

Investigations[14] on the ethyl alcohol–water system have established a definite correlation in the kinetics of the accumulation of H_2, H_2O_2, and acetaldehyde. These results indicate that the same chemically active species

† Here and subsequently the radiation yield G is given, as is customary in radiation chemistry, by the number of particles (molecules, radicals, etc.) formed calculated for 100 eV of radiated energy absorbed by the system.

‡ Günther and Holzapfel did not detect the formation of hydrogen on irradiation of ice with X-rays at -180°.[6]

§ Investigations made[7] on specimens irradiated with accelerated electrons (680–750 keV).

(probably H and OH radicals) are involved in the formation of "molecular products" of the radiolysis of water and of reaction products from the solute. A study of the dependence of the accumulated yield of these products on the concentration of the solution (the ethanol concentration was varied from 10^{-3} M to 15 M) led to the conclusion that at low temperatures (between -196° and -10°) ethanol can inhibit the recombination of H and OH radicals (at C_2H_5OH concentrations up to 5 M). This and other work[10,11,15] established that a rise in temperature of the frozen specimen is accompanied by an increase in the rate of radiolytic transformation of the dissolved substances.

As in the case of pure water and ice, the change from the liquid to the solid phase is accompanied, in the irradiation of aqueous solutions of some substances, by a decrease in their rate of conversion. Thus according to Haissinsky and Lefort[2,16] the efficiency of oxidation of the arsenite ion on exposure of its aqueous solutions (0.01 M, pH 7) to α-rays at -196° is half its value at ordinary temperatures. In the case of exposure to X-rays $G(AsO_2^-)$ at the temperature of liquid nitrogen is one-thirtieth of its value at room temperature (pH 10.5). A similar diminution in the efficiency of conversion of NO_3^- is observed in the radiolysis of the nitrate ion-water system[17,18].

The presence of molecular oxygen in frozen solutions greatly affects the yield of the accumulated final products[16-18]. In the nitrate ion-water system, for example, the inhibiting effect of O_2 has been shown to be due to its reaction with an intermediate product of the radiolytic transformation of the nitrate[19]. It has been suggested that the decrease in efficiency of radiolysis of the solutes on passing from liquid to frozen aqueous solutions should be used to estimate the direct effect of radiation on the solutes[20], on the hypothesis that the diffusion of intermediate products of radiolysis is a minimum in the case of frozen solutions, and that all the main effects of radiolysis are caused by the direct action of radiation (for example, see Cottin[21]).

However, the method of freezing the solutions cannot be regarded as acceptable for this type of estimate, since firstly the structure of the solution, and hence the conditions of radiolysis¶, change on passing from the liquid to the solid phase, and secondly it must be remembered that radiolytic changes in the specimen are recorded on the basis of an analysis of the specimen after fusion. In the course of fusion, however, intermediate products of radiolysis trapped in the lattice may undergo various reactions[2,22], and as a result the picture of the direct effect of radiation is confused.

Research in the 1960s has shown that radical involving H and OH may take place in frozen solutions even at very low temperatures (below -160°). It may be supposed, for example, that under these conditions H and OH migrate by a mechanism of relay transfer along hydrogen bonds. (The more "unwieldy" radicals formed from solutes react at temperatures in the vicinity of -90° to -100°[23].)

¶ Even in the case of frozen solutions, the peculiarities of the phase constitution must be taken into account in estimating the radiolytic effects. Thus Livingston and coworkers have shown (see Section III. 2) that the yield of atomic and molecular hydrogen in solutions of acids may vary by an order of magnitude depending on whether amorphous (vitreous) or crystalline specimens are subjected to radiolysis.

In spite of the great difference between the conditions of radiolysis of liquid and frozen solutions (resembling one another perhaps only in the initial distribution of ions and excited molecules) the laws governing the formation of the end-products of radiolysis in several cases, surprisingly, are identical. We have spoken earlier of the inhibiting effect of molecular oxygen on the reduction of the NO_3^- ion in liquid and frozen solutions of sodium nitrate[18]. We may also mention a definite correspondence in the yields of accumulated OH radicals[19].

When frozen concentrated solutions of a nitrate are irradiated in the presence of alkali, a lack of balance in the conversion products is observed, as in the case of liquid solutions, with respect to the oxidising (OH) and reducing (H) components of radiolysis, which is greater the higher the concentration of sodium nitrate. This phenomenon is explained by stabilisation of the OH radicals by the anion and formation of a compound which is not recorded by the usual methods (electron paramagnetic resonance and analysis for H_2O_2). Acidification of the solution to pH 2–3 was accompanied by a loss of nitrite, which was explained by interaction of this compound with the nitrite ion. The balance of conversion products of oxidising and reducing components of radiolysis then converges[19].

Work in which the kinetics of the formation of radical (H, OH, HO_2) and molecular (H_2, H_2O_2, O_2) products of the radiolysis of water were compared provided results[24-26] of considerable interest for an understanding of the mechanism of radiation-chemical reactions. They indicate that the final products of the radiolysis both of pure ice and frozen aqueous solutions result mainly from recombination of radical products†, but also from interaction of these radicals with solute molecules.

II. INVESTIGATION OF RADIOLYTIC EFFECTS IN FROZEN AQUEOUS SOLUTIONS BY THE LUMINESCENCE METHOD

Fluorescence

The first investigations of the luminescence of ice and water under the influence of ionising radiations were made during the late 1940s and early 1950s. In 1952 Grossweiner and Matheson[28] succeeded in observing, during the exposure of ice to X-rays (50 kV), a steady luminescence in the ultraviolet at temperatures between -170° and -100°. They established that the intensity of the steady luminescence varies linearly with the radiation dose (at rates of the latter of 400–100 000 r h^{-1}) and diminishes with rise in temperature. These workers also studied the luminescence of tritium ice at -196°; in this case the luminescence is due to absorption by the specimen of β-rays from the tritium. The efficiency of conversion into light of the energy absorbed by the specimen was found to be 3×10^{-5} quanta per ion pair[28].

Experiments on the luminescence of irradiated water and ice had also been made earlier[29-31], but then the possibility of estimating the luminescence effect in the visible region had been denied[30] on the grounds of the masking action of Čerenkov radiation.

† Glasel, for example, reaches the same conclusion from a study of the kinetics of the formation of D_2 in D_2O-ice by the action of electrons (of energy 2 keV)[27].

The most detailed data on the luminescence of tritium ice were obtained by Jones[32], who found that the spectrum contains two maxima, near 400 and 550 mμ. At 77°K the specimens were found to have a colour, which disappeared on heating to 190°K.

When ice is irradiated at -196° with γ-rays from ^{60}Co, examination of the luminescence spectrum is prevented by the intense Čerenkov radiation[12,33]. When ice is exposed to 50 kV X-rays, *i.e.* under conditions such that Čerenkov radiation is absent, a luminescence band can be observed with a maximum at 395 mμ and a width of 75–90 mμ at half-height as well as an unresolved band with a maximum at 550 mμ. The intensity of the latter band is about one-quarter of the maximum intensity at 385 mμ[33]. When the specimen is heated, the intensity of the peak corresponding to 385 mμ decreases, and at -120° this peak completely disappears. The emission band in the region of 550 mμ remains roughly constant over this temperature range (between -196° and -120°)[33,34]. The luminescence completely vanishes at -100°.[34] Observations show[32,34] that, from the instant of exposure of the ice, there is a slow initiation of fluorescence, which follows a first-order law with rate constants of 0.086 and 0.31 min^{-1} at -196° and -145° respectively[34]. Over the range of rates of radiation dosage investigated (0–10^{17} eV g^{-1} min^{-1}) the intensity of fluorescence varies linearly with this rate over a wide temperature range[24,34].

With rise in temperature of the irradiated specimens from -196° to -70°, the intensity of fluorescence passes through a maximum at -180°.[33,34] With specimens irradiated for the first time, the curve relating intensity of luminescence with temperature shows a second peak in the region of -150°. After repeated cooling (to -196°) and irradiation of the specimen, the peak at -150° becomes smaller or disappears altogether. This effect is associated with radiolytic changes in the specimen.

Work on the effect of impurities on the fluorescence of ice is of interest for an understanding of the nature of the active fluorescence centres. The type of spectrum and also its intensity have found to depend on the nature of the cation[34].

Results on the effect of hydrogen peroxide and molecular oxygen on the luminescence of ice indicate that the chemical effects of radiolysis have a definite correlation with fluorescence and thermoluminescence. A hydrogen peroxide concentration of 2×10^{-5} M in a frozen solution appreciably diminishes the fluorescence when the specimen is first irradiated[34]. During subsequent exposures the intensity of the luminescence is restored to the values observed in pure ice. Hydrogen peroxide does not affect the temperature variation of the luminescence. Molecular oxygen, in contrast to H_2O_2, does not influence the intensity of the fluorescence[34].

Grossweiner and Matheson conclude that the species responsible for the steady fluorescence of ice are atoms formed by the capture of electrons by cations, the atoms then having undergone reionisation with subsequent capture of other electrons and emission of light.

Thermoluminescence

It has been found several times[10,33,34] that, when a specimen of ice is subsequently heated after being irradiated at the temperature of liquid nitrogen, it begins to emit light. The intensity of the luminescence passes through a series of maxima as the specimen is heated. The principal maxima occur at temperatures around -115° and -155°. In the first temperature range the emission band is almost entirely located in the visible region of the spectrum, but in the second range 90% of it is located in the ultraviolet[33]. The absorption spectrum at -196° is a broad line with a maximum at 2800 Å.[10] Ghormley[10,33] points out a correlation between the temperature characteristics of the thermoluminescence of ice (the appearance of an emission peak at -155°), the disappearance of the absorption band with a peak at 2800 Å, and also the decomposition of hydrogen peroxide in aqueous solutions of H_2O_2 which have first been irradiated at -196°. In his opinion the same stage of the process develops on heating the specimen in these three cases, and this can be represented either as the liberation of captured electrons or of positive holes, or else, finally, as the diffusion of free radicals. However, this last phenomenon, *i.e.* luminescence due to the "liberation" of radicals[10], is improbable in the opinion of other workers[12].

When the radiation dose is changed from 10^{18} to 10^{21} eV g^{-1} the intensity of the luminescence peak at -155° increases about hundredfold compared with that at -115° (rate of heating of specimen 10° min^{-1}). Grossweiner and Matheson found that the intensity of the main peak (at -118° according to them) at a rate of heating of 3° min^{-1} increases linearly with the dose[34]. The depth of the electron trap responsible for the glow has been estimated[34,35] as ~0.25–0.32 eV. A fairly intense luminescence peak is observed at -165°. Apart from the main peak at -118° and that at -165°, maxima have also been recorded[34] at -95° and -180°. Storing the specimens in air makes their luminescence more intense. The appearance and the intensity of the latter peaks are associated with the presence of molecular oxygen in the ice. When irradiated ice, prepared at 150 mm O_2 pressure, is heated, no distinct thermoluminescence peaks are observed over a wide range of temperature. Hydrogen peroxide also suppresses all the luminescence peaks. NaCl and HCl (0.05 M) appreciably depress the thermoluminescence.

Grossweiner and Matheson's information on thermoluminescence enabled them to suggest a model according to which an electron, originally captured by a "trap" and set free in the ice on heating, migrates to impurity centres, where radiation capture takes place. The nature of the trap was not established. Two main processes are postulated: (*a*) the electron is separated from the ion on activation, *i.e.* a process of the type $R^- \xrightarrow{h\nu} R + e$; (*b*) reaction takes place in the ice between neighbouring particles of the type: (1) $H + OH^- = H_2O + e$; (2) $OH + H^- = H_2O + e$, a process of type (2*b*) being regarded as the more probable. Apart from these schemes another possibility is, in the opinion of these workers, the capture of the electron by two protons with the formation of an ionised hydrogen molecule. However, they assume that the correctness of this or the other model should be carefully verified by magnetic measurements. In order to check the hypothesis that the fluorescing species may be an alkali metal ion, Matheson and Smaller[36] investigated the magnetic properties of irradiated samples of ice containing NaCl (concentration 0.01 M), on the assumption that in this case it is possible to record the presence of Na atoms, having a nuclear spin of $\frac{3}{2}$. Even in this case, however, only the species recorded in pure ice were detected.

Data on the magnetic properties (obtained by the electron paramagnetic resonance method) of irradiated frozen solutions and of ice have not confirmed the above schemes.

According to recent experimental results the paramagnetic species, which have been identified with great reliability as H atoms and OH radicals, have different temperature parameters for their existence from those species which could have explained the thermoluminescence effects. Moreover, calculation shows that the yield of light quanta per 100 eV of absorbed energy is $\sim 10^{-4}$ in the case of the fluorescence of tritium ice at -196°,[28] and on irradiation with Co γ-rays it is $\sim 10^{-3}$ [33] (*i.e.* it has values differing by 2–3 orders magnitude from the yields of H and OH radicals[24,25]).

In the case of thermoluminescence the quantum yield is four orders of magnitude lower[33]. Comparison of the yields of photons and radicals shows that, in any case, not all the H and OH radicals can be involved in the formation of electrons which subsequently recombine with the active luminescence centres.

III. STUDY OF INTERMEDIATE RADICAL PRODUCTS OF RADIOLYSIS

The most important results, which are of great value for an understanding of the mechanism of the radiolytic transformation of dissolved substances and the nature of the intermediate products, have been obtained by examining the radiolysis of ice and of frozen solutions by the electron paramagnetic resonance (EPR) method. This is a very reliable method for investigating the nature and the kinetics of the accumulation of radical products of radiolysis, both primary and those resulting from secondary processes.

Research on the radical products of radiolysis can be divided into three groups. The first group of investigations relate to the identification and study of the properties of radical products of the radiolysis of ice, and also the kinetics of their accumulation. The second group comprises investigations on the effect of various additions on the behaviour of radicals formed from water. The third group deals with the study of radical products of the radiolysis of dissolved substances.

1. Identification and Properties of the Radical Products from the Radiolysis of Ice

The first work on the EPR spectra of irradiated frozen water was done by Livingston *et al.*[37] during 1953–1954. Their aim was to verify the hypothesis that H and OH radicals are formed by the action of radiation on water.

Identification and properties of H. This group of workers were able to detect atomic hydrogen in irradiated frozen solutions of acids ($HClO_4$, H_2SO_4, H_3PO_4). The spectrum of atomic hydrogen is a symmetrical doublet with a splitting of ~500 G and a g-factor close to that of a free electron (*i.e.* the spectrum is analogous to that of the free H atom in the gas phase)[38]. Such characteristics show that in this case the unpaired electron is well represented by the 1s wave function of atomic hydrogen. It was established that the intensity of the lines does not change when irradiated specimens are kept at 77°K.

When frozen solutions of H_2SO_4 in D_2O were irradiated, a triplet was observed caused by the presence of D atoms in the specimen.

Atomic hydrogen exists in frozen acids right up to -170° (H_2SO_4)[39] and -160° ($HClO_4$).[40] Kinetic investigations involving a comparison of the accumulation of atomic and molecular hydrogen on irradiation of an acid[8,24,29], and also an examination of the effect of ionisation density on the yields of radical and molecular products[40], showed that molecular hydrogen is formed in frozen acids mainly as a result of the recombination of hydrogen atoms.

Paramagnetic resonance in solutions of oxygen-containing acids irradiated with ^{60}Co γ-rays and tritium β-particles (βT), due to the presence of atomic hydrogen ($\Delta H \simeq 500$ Oe), has been observed also in other work[36,41–43]. The yield of H formed was found to depend on the nature of the anion of the acid and its concentration, as well as on the type of ionising radiation[40] (linear energy transfer, LET). There are indications in the literature that the EPR spectrum of atomic hydrogen has been recorded also in irradiated frozen solutions of hydrogen halides (HCl, HF)[39,40], fluorine derivatives of acids, and solutions of hydroxides of the alkali and alkaline earth metals (see Table 1).

Attempts to detect atomic hydrogen by the EPR method in pure ice irradiated at 77°K were unsuccessful. In 1958 a report appeared that the EPR spectrum of the hydrogen atom had been recorded when ice was irradiated at 4.2°K.[44] Subsequent investigations showed the initial radiation yield of H formed to reach values of ~0.5 (40-MeV electrons[45]) and 0.9 (^{60}Co γ-rays)[46]. The formation of atomic hydrogen in ice irradiated at 4.2°K has been regarded[47] as resulting from the capture of a "dislodged" electron by H^+ ions present in the matrix.

As ice irradiated at the temperature of liquid helium warms up[46,48,49], some of the hydrogen atoms disappear rapidly at 15°K, and the remainder more slowly at 60°K. The energy of "escape" of H atoms from the trap is less than 1.0 kcal mole^{-1} in the first temperature region, and rather more thane 2.5 kcal mole^{-1} in the second region[49]. These results were explained[46,48,49] on the basis of a model involving a postulated non-uniform initial distribution of H atoms in the irradiated ice.

TABLE 1. Properties of atomic hydrogen formed by the irradiation of frozen aqueous solutions.

Material irradiated	Type of radiation and max. yield G, H atoms/100 eV	Temp. range of existence, °K	Ref.
Sulphuric acid (0.25 mole fraction), 77°K (glass)	1.62 (γ-rays)	up to 104°	24
Perchloric acid (0.125 mole fraction), 77°K	2.2 (γ) 1 ($T\beta$-rays)	up to 104° up to 119°	24 40
Phosphoric acid (0.45 mole fraction), 77°K (glass)	1.1 (γ)	up to 104°	24
$NaNO_3$ soln. (0.1 – 1 M) + CO_2, 84°–89°K	accelerated electrons (1.6 MeV)	up to 94°	42
Ice, 4.2°K	0.5 (e, 40 MeV)	disappears up to 77°	45
Ice, 4.2°K	0.9 (γ)	partly disappears at 15°, completely disappears at 60°	46
HF (16%), 77°K	0.06 (βT)	–	40
HCl (24%), 77°K	~0.006 (βT)	–	40
HF (48%), 77°K	"moderate" (γ)	–	39
NaOH, KOH, LiOH, Ba(OH), (0.1 – 0.5 M), 77°K	"low" (γ)	–	40
Fluorosilicic and fluoroboric acids, 77°K	"high" (γ)	–	40

The "dislodged" electron may be stabilised [50,71] in frozen solutions containing alkali ($\geqslant 2$ M) and irradiated at 77°K. The g-factor of the singlet absorption line of this stabilised electron is close to that of a free electron.

In concluding this subsection we note that the nature of the traps which stabilise the H atoms is still unknown. The suggestion that hydrogen atoms are stabilised by their ability to form hydrogen bonds with the surrounding molecules of the matrix [39], is worthy of serious consideration.

Identification and properties of other radicals formed in the radiolysis of ice. The spectrum due to the presence of OH radicals in irradiated ice at 77°K was first observed by Smaller and Matheson during 1953–1954 [41]. However, they erroneously attributed the recorded paramagnetic resonance lines to atomic hydrogen [20,51–53]. The observed EPR spectrum [41] of the OH radical is a doublet with components of different intensities and a g-factor of ~2.0; the hyperfine splitting is approximately 30 Oe. D_2O–ice irradiated under the same conditions [41] gave a triplet spectrum with a line width of 2 Oe and a separation of ~5 Oe between the components of the triplet. The intensities of the lines were in the proportions 1:2:1. Further work on the radiolysis of ice and frozen aqueous solutions of hydrogen peroxide [25,36,40,41,43,45,46,54–61] and on the photolysis of these systems [62,63] (the latter work is not specially considered in this review) enabled the spectral and kinetic characteristics of OH radicals to be obtained with greater precision (see Table 2). The investigations of McMillan *et al* [52,54] on single crystals of ice irradiated at 77°K established that the OH radical in the matrix of ice possesses cylindrical symmetry and has a minimum hyperfine splitting of 35.5 Oe with $g_{\parallel} = 2.0127$ and $g_{\perp} = 2.0077$.

It was established that OH radicals exist in irradiated ice right up to -170° to -175° [36,40,55]. They disappear rapidly in the vicinity of -163°, according to the law [25,57,58]

$$-\frac{d(OH)}{dt} = k(OH)^{3/2} .$$

TABLE 2. Characteristics of OH and HO_2 radicals formed in the radiolysis of ice and of frozen aqueous solutions.

Irradiated material	g-Factor	Separation between components of hyperfine structure, Oe	Max. yield of radicals formed	Max. temperature of existence, °K	Suggested radical	Ref.
Ice, 4.2°K	2.008	~40	0.8	119°	OH	46
Ice, 77°K	2.008	~40	0.6 (γ)	119°	OH	25, 46, 55, 58
	2.01	~40	0.32 (β?)	119°	OH	40, 56
	2.0	~10	0.14 (γ)	146°	HO_2	25, 36, 41, 55
Ice, 77°K	—	41.5	(overall) (220-kV X-rays)			61
Ice, single crystal, 77°K	2.0127 ($g_{\parallel}$)	35.5		—	OH	
	2.0077 ($g_{\perp}$)			—	OH	52
	2.00 ($g_{\parallel}$)				$H_3O^+ \cdot HO_2$	52
	2.04 ($g_{\perp}$)			—		59
H_2O_2 (60–70%) 77°K	2.039 ($g_{\parallel}$)	13.5	10.3 (250-kV X-rays)	—		
	2.0055 ($g_{\perp}$)					
$NaNO_3$ soln. (neutral), 129°K	2.015	—	—	184°	$[OH \cdot NO_3^-]$ $[HOONO_2^-]$	19
$NaNO_3$ soln. (alkaline), 129°K	2.04	—		184°	$[O^- \cdot H_2O]$ $[O_3^-]$	19

Examination of the initial stages in the radiolysis of ice at 4.2° and 77°K showed that the radiation yields of accumulated OH radicals [25,46] and of atomic hydrogen are equal (0.8 and 0.9, ^{60}Co γ-rays) within the limits of experimental error. A close analogy has been noted [40] between these two species (and also between OD and D) in the kinetics of their accumulation and in their thermal stability. Analysis of the experimental results [25,26,58] shows that the destruction of OH radicals in irradiated ice is due mainly to their recombination with H atoms. A change in the density of the ionising radiation affects the accumulated yield and the steady-state concentration of OH radicals in the irradiated ice [59]. When β-particles from the tritium are used to irradiate ice, G(OH) is reduced to half compared with irradiation with γ-rays [40] (see Table 2).

Several papers on the thermal properties of radicals [36,40,55] report the appearance, in irradiated specimens of ice and in frozen solutions of H_2O_2 between -160° and -145°, *i.e.* after the spectrum of the OH radical has disappeared, of a fresh absorption line (an unsymmetrical spectrum, with a doublet hyperfine structure and a splitting of ~13.5 Oe), which disappears only in the vicinity of -130°. [55,63]. Like the spectrum of the OH radical, this absorption line exhibits anisotropy of the g-factor, with $g_{\parallel} = 2.039$ and $g_{\perp} = 2.0055$. Its structure is similar [25] to that of the EPR spectrum of O_2^-, observed in crystals of NaO_2. [64] The radical responsible for this spectrum was identified as HO_2. [59]

McMillan and coworkers examined the EPR spectra of an irradiated single crystal of ice [52,53], and found that the broad absorption line usually observed in polycrystalline specimens is split into at least two lines. Analysis of the results gave the spectral characteristics ($g_{\parallel} = 2.00$ and $g_{\perp} = 2.04$) and led to the conclusion that the observed paramagnetic species is symmetrical along the hydrogen bond of the crystal lattice. It was suggested that this species is the H_2O^+ radical.

Thus the EPR method has provided an experimental proof of the formation of H and OH radicals in the radiolysis of aqueous solutions, which had been postulated by chemists 16–18 years previously. These primary radical products of the radiolysis of water give rise to the formation of the molecular products of radiolysis, H_2 and H_2O_2, and produce various changes in the dissolved substances, as will be seen from the subsequent account.

2. Effect of Additions on the Behaviour of Radicals Formed in the Radiolysis of Ice.

The influence of additives on the behaviour of radicals formed by the irradiation of water is important in connection with the possible direct control of radiolytic reactions by varying the paths for the redistribution of the absorbed energy among the components of the irradiated system. Most such information has been obtained by examining systems containing hydrogen peroxide and an acid in addition to water.

Matheson and Smaller [36,41] noted an increase in the intensity of the spectral lines due to the OH radical in solutions of hydrogen peroxide. They also observed that the distance between the peaks in this spectrum as well as the intensity of the latter increase with increasing concentration of H_2O_2. At the same time the distance between the components in the spectrum of the OH radical increases, and its lines diminish in intensity. The change in the distances between doublet peaks is linked, in the opinion of

these workers, with changes in the environment of the radicals, which become increasingly noticeable as the hydrogen peroxide concentration is raised. The antibathic changes in the peaks of the two doublets can probably be attributed to the conversion of one type of radical into another by the reaction $HO + H_2O_2 = HO_2 + H_2O$. These workers found that the yield of radicals is 2–3 times greater in the presence of 0.02 M hydrogen peroxide (or D_2O_2), and becomes still higher in more concentrated solutions. An investigation[59] of the decomposition of H_2O_2 (250 keV X-rays, 90°K) showed that the yield of radical products (mainly HO_2) formed increases by a factor of 10 with increase in the H_2O_2 concentration from 0 to ~45 wt.%, then remains constant over the range 45–85%, and diminishes to about half its value on passing to still more concentrated solutions. This work established also that the linear energy transfer (LET) greatly influences the yield of radicals formed in H_2O_2 solutions (see Table 3), which falls appreciably with growth in density of ionisation in the track.

This indicates that the diffusion and the recombination of radicals play an important part at low temperatures too.

The literature contains many facts on the effects of additions on the kinetics of the formation of the reducing component, H radicals, in radiolysis. The work of Livingston and his coworkers (for example, Ref. 24) has established that such compounds as acids tend to extend the temperature range of existence of atomic hydrogen in ice (Table 1). The yield of H atoms formed depends, as already noted, on the nature of the anion and also on the structure of the specimen[24].

The nature of the anion in the acid influences also the maximum steady-rate concentration of H atoms. Thus the latter is an order of magnitude greater in $HClO_4$ than in H_2SO_4 solution (2.9×10^{19} atoms g^{-1}). A study of the width of the lines due to atomic hydrogen yields interesting results. Thus when the concentration of $HClO_4$ is increased from 0.02 to 0.25 mole fraction, the line width (the distance between the heights of semi-maximum intensity) first increases from 2 to 4.2 G (at a mole fraction of 0.15), then increases to a still greater extent on passing to 0.16 mole fraction (to 5.0 G) and to 0.18 (to 5.8 G), and decreases to 4.8 G (at the mole fraction 0.25). With specimens containing sulphuric acid, a change in concentration from 0.02 to 0.8 mole fraction is accompanied by a continuous decrease in line width (from 4.8 to 3.6 G), but in the case of H_3PO_4 there is only a slight change in the lines. These data may be useful in elucidating the nature of the traps in frozen specimens and the character of the interaction between them.

Examination of the effects of such additions as O_2, H_2O_2, etc. on $G(H)$ under the stabilising influence of acids makes it possible to study the interaction of the radicals with acceptors and the capture of radicals in traps. Whereas molecular oxygen has no effect on the kinetics of H formation in irradiated frozen solutions of acids, hydrogen peroxide lowers the value of $G(H)$ on irradiation at the temperature of liquid nitrogen‡. For example, the value of $G(H)$ in sulphuric-acid solution is diminished by 80% and more at a hydrogen peroxide concentration of ~0.7 wt.%. The yield of molecular hydrogen then drops sharply over the range of H_2O_2 concentrations up to 0.15 wt.%. These data indicate that hydrogen peroxide successfully "intercepts" H atoms even before the stage of H capture by a trap.

TABLE 3. Yields of radicals in H_2O_2 solutions (~ 65 wt.%) with different types of radiation.

Type of radiation	Mean LET, keV μ^{-1}	Yield of radicals, spins/100 eV
250 kV X-rays	0.6	10.3
15 MeV deuterons	14	6.3
5.7 MeV α-particles	86	2.1

As already noted, increasing the acid concentration (sulphuric, perchloric, and phosporic) first involves a growth in the accumulated yield of atomic hydrogen, after which it passes through a maximum and then falls. This phenomenon is easily explained if it is supposed that the increased content of the anion in the solution changes the conditions under which recombination of H and OH radicals and their capture by traps (or stabilisation by anions) take place[19]. In the radiolysis of concentrated solutions (>0.15–0.3 mole fraction) of the acids $HClO_4$, H_2SO_4, and H_3PO_4, the recombination of H atoms obviously becomes less probable — this follows from a comparison of the curves for the variation of the changes in $G(H)$ and $G(H_2)$ with the acid concentration§. It must again be stressed that this concentration dependence of the yields of H and H_2 is general in character, and extends to the anions of oxo-acids (SO_4^{2-}, ClO_4^-, PO_4^{3-}, NO_3^-, CO_3^{2-}).

3. Study of Intermediate Radical Products of the Radiolysis of Dissolved Substances

In spite of the ever increasing use of the EPR method in studying intermediate products of radiolysis, only two or three papers have yet appeared reporting more or less detailed investigations of intermediates formed from dissolved substances. The EPR spectra of many irradiated frozen aqueous solutions are characterised by extreme complexity owing to the superposition of absorption lines due to several radicals. Difficulties also arise in the identification of radical products from their spectra because no data are yet available on the influence of intracrystalline fields on the structure of these spectra. The first papers on the complicated EPR spectra recorded in irradiated frozen acids (H_2SO_4, H_3PO_4, $HClO_4$) date from 1954.[36,39] It was noted that the EPR spectrum of irradiated sulphuric acid clearly shows two absorption lines, narrow and broad, in the vicinity of $g = 2$. Their intensities depend on the acid concentration, dilution weakening the narrow line, which completely disappears at the ratio H_2O : acid = 2 : 1. The central lines of the

‡ An analogy suggests itself between the mechanism of the inhibiting action of H_2O_2 on the yield of H formed and its effect on the luminescence of irradiated specimens (Section II). It is reasonable to assume that the same process — interception of the electrons from the traps by the hydrogen peroxide — develops in these cases. Hence it can also be concluded that the H atoms are formed as a result of the addition of the electron to H^+.

§ It is interesting that, in pure water at 77°K, $G(H) = 0$, whereas $G(H)_2 \simeq 0.1$. It may be supposed that molecular hydrogen is formed by the interaction of species which are not recorded by the EPR method. The yield of the molecular end-products of radiolysis was also found to exceed that of the intermediate radical products in a study of the kinetics of the radiolysis of dissolved substances[19].

EPR spectra for the acids H_3PO_4 and $HClO_4$ differ considerably from one another and from the lines for sulphuric acid. The H_3PO_4 spectrum contains two broad lines, whereas that of irradiated perchloric acid consists of several lines of varying intensity and width. All the lines become wider on dilution of the acids. In sulphuric acid the central line remains at temperatures of the specimen right up to -110°. It is stressed[8] that the complicated line spectrum is an obstacle to identification of the radicals. Livingston and Weinberger[24] point out that the concentration of these paramagnetic species far exceeds that of hydrogen atoms. Although the latter disappear at lower temperatures, they are relatively inert towards the radical products under consideration here. Later in this paper a curious experimental fact is reported. As an acid-containing specimen is irradiated, the concentration of atoms increases, and reaches a limiting value when a certain dose has been received. With further irradiation of the specimen, however, the width of the lines due to H atoms again increases. Livingston and Weinberger link this phenomenon with dipole – dipole interaction between H atoms and other paramagnetic species having an unpaired electron. When it is remembered that in several cases $G(H) > 2G(H_2)$ (in the acids $HClO_4$ and H_3PO_4), the conclusion suggests itself that under these conditions (at the temperature of liquid nitrogen) some of the H atoms can probably react with components of the solution to form radical products. The addition of such radical-acceptors as hydrogen peroxide and nitric acid can be used to control reactions involving H atoms (for example, the formation of H_2). Unfortunately, no further details are given.

As a possible mode of formation of a paramagnetic species in irradiated solutions of sulphuric acid[65] Livingston and Weinberger suggested a scheme analogous to Allen's scheme for the liquid phase, according to which OH radicals form with the acid a complex which is also a radical but less reactive than the OH radical.

Investigations on the radiolysis of frozen solutions of sodium nitrate by Molin, Buben, and the present writer[42] showed, apart from the identified main products of the radiolysis of a nitrate (the radicals NO_2, HNO_3^-), the presence of a radical to which was assigned the structure $OH.NO_3^-$. It was suggested (as a possibility) that the nitrate ion stabilises the oxidising component in the radiolysis of water, *i.e.* the OH radical (narrow absorption line, $g = 2.015$), by forming the complex radical¶. Such a radical disappears at temperatures close to -100° to -90°. This radical was not detected in alkaline solutions; instead, a paramagnetic species was formed, whose spectrum was a wider line having $g = 2.04$. This spectrum could be due to the presence of a radical of the type $O^-.H_2O$, formed under the influence of alkali: $OH + OH^- = O^-.H_2O$.

An absorption line with analogous spectral characteristics (g, ΔH) was recorded also in irradiated frozen alkali solutions at 77°K, and was attributed to the radical $O^-(nH_2O)$.[50]

The possible existence of compounds of the type "OH.acid" has also been deduced[40] in the radiolysis of the $HClO_4$–H_2O system. It is assumed that OH radicals form a complex with an acid by hydrogen bond formation. The present writer and Yanova[60] were able to observe that the position of the absorption line in the EPR spectrum due to the OH radical stabilised by the anions ClO_4^-, SO_4^{2-}, and NO_3^- depends on the nature of the anion. They suggested that the g-factor of the absorption line may emerge as an indirect measure of the stability shown by the OH ... anion bond in the series of oxygen-containing anions examined.

In a study of the thermal stability of radical products of the radiolysis of frozen perchloric acid, it has been established[40] that the disappearance of both atomic hydrogen and stabilised OH radicals is accompanied by the accumulation in the system of other, as yet unidentified radicals.

Henriksen studied the radiolysis of frozen aqueous solutions of glycine[61] (220 kV X-rays), and traced the conversion of the primary radical product of radiolysis, OH, into secondary radicals. The type of spectrum characteristic of the OH radical, recorded at the temperature of liquid nitrogen, changed considerably when the specimen was annealed at about -90° for 15 sec. On further annealing at the same temperature the spectrum of the species recorded became of the type observed in irradiated polycrystalline glycine, and this spectrum did not disappear right up to temperatures close to the melting-point of the solution. This spectrum, characterised by a triplet hyperfine structure, was attributed to radicals of the type $^{\cdot}CH_2COO^-$, $^{+}NH_3\dot{C}HCOO^-$.

As can be seen from the above results, the EPR method in combination with other physicochemical methods of investigation, opens up great opportunities for the study both of the formation of the primary products of radiolysis and of the further processes which they undergo, and will thus provide direct information on the mechanism of radiochemical reactions in frozen aqueous solutions.

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As an analysis of data on the kinetics of the accumulation of radical products of radiolysis shows, the mechanism of the reactions undergone by the products of radiolysis cannot yet be regarded as entirely clear. Although a certain analogy is observed between the laws governing the formation of the end-products of radiolysis in liquid and in solid (frozen) aqueous solutions (for example, accumulation of reaction products of oxidising component as function of pH, effect of O_2 on accumulated yield of end-products, etc.), account must be taken of the changes occurring in the medium on passing from one phase to the other (quite apart from the effect of temperature on the reaction velocity). In the frozen phase itself, moreover, a change in temperature results in substantial changes both in the structure of the specimen and in the kinetics of the accumulation of radical and molecular products, as is shown by data obtained by different methods of investigation. It has already been noted that the degree of crystallinity of the

¶ It was established that the formation of this radical is in fact linked with the fate of the OH radicals. This was proved by the absence of its spectrum in $NaNO_3$ solutions (1 M) to which had been added small quantities (0.1 M) of an active acceptor for OH radicals, glycerol, or ethanol[19].

specimen (the size of the crystals) influences the radiolysis, perhaps because the principal reactions, which depend on the diffusion of active species, take place on the surfaces of these crystals. Further difficulties in considering the radiolytic effects result from the necessity for taking into account the peculiarities of energy transfer between crystallites in polycrystalline specimens. For these reasons it is not yet possible to describe quantitatively radiolytic processes in frozen aqueous solutions (and still less to transfer the results to the liquid phase), and opportunities for their elucidation must be sought from data obtained by various methods of investigation. Some information has already been obtained[23,66] from a simultaneous examination of changes in several properties of frozen solutions. Thus the disappearance of radicals varying in nature (EPR method)[23] at temperatures between -100° and -90° and changes in the structure of ice (X-ray method of investigation)[67] at these temperatures, together with a study of the dielectric properties[68], indicate, it is assumed[23], that these phenomena are interrelated. The EPR data and X-ray examination show that a similiar phenomenon occurs at lower temperatures: the disappearance of radicals formed by the irradiation of ice and a change in the structure of the latter at -160° to -150°.[23,40] A study of products formed by an electric discharge in the vapours of H_2O_2 and H_2O and frozen at various temperatures led to the conclusion[69] that the transition from amorphous to crystalline ice creates conditions which facilitate the recombination of HO and HO_2 radicals frozen out at lower temperatures. It must be emphasised, however, that X-ray examination reveals differences in the structure of ice (which probably determine which radical traps are involved, and in which temperature ranges, in the setting free of active products), not only associated with its temperature but also depending on its mode of formation (by rapid cooling of water or by condensation of the vapour)[23,67]. The results obtained by different methods of investigating radiochemical reactions in frozen specimens must therefore be compared on samples of ice obtained under identical conditions. Nevertheless, it must again be stressed that a definite link exists between several properties of these systems, although ice and frozen solutions are formed under different conditions. Thus there is obviously[66,70] a connection between phase transformations in ice and in frozen aqueous solutions of hydrogen peroxide: the regions of destruction of frozen radicals formed from H_2O and H_2O_2 practically coincide with the phase transformation points (-116° for the start of the endothermic transformation, and -53° for the exothermic transformation). The suggestion made by several workers[69,70] can be accepted that in both cases, independently of the mode of preparation of the ice, a change in temperature produces reorientation of the water molecules and an associated redistribution of hydrogen bonds; as a consequence of this, the conditions of interaction of active products of radiolysis, in particular radical products, are changed.

In conclusion we may underline some fundamental generalisations which have now been established experimentally, and on which future research may be based: (1) at low temperatures there is a movement of active species, which affects the yield of radiolysis products in frozen solutions; (2) the formation of H and OH radicals in the radiolysis of aqueous solutions has been demonstrated, and the reactions of these species with dissolved substances determine the nature of the changes undergone by the latter; (3) it has been established that the radicals formed from water are stabilised by solute anions, and the influence of various radical-acceptors on the yield of radical products has been examined.

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ANALYSIS OF TRACE IMPURITIES BY GAS CHROMATOGRAPHY

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1. INTRODUCTION

The extensive and varied advances made in gas chromatography range from analytical studies on mixtures of several constituents on the one hand to trace analysis of minor constituents in various systems on the other hand. The latter type of problem is of great importance in the polymer industry, where high-purity monomers are often required. In some cases, even very small traces of certain impurities in the monomer can alter the course of the polymerisation reaction and mar the final product.

Whereas high precision is the foremost requirement in the analysis of complex mixtures, trace analysis relies primarily on high-sensitivity methods. Present-day gas chromatography techniques in their conventional, unmodified form can detect components present at a level of a few hundredths of one per cent. We shall therefore apply the term "trace constituent" to substances whose concentration in the sample is of the order of 0.001% or less.

Chromatographic methods of trace analysis are reviewed in the present article. The chromatographic analysis of complex organic systems has been previously discussed[1] by one of us.

2. FEATURES OF CHROMATOGRAPHIC TRACE IMPURITY ANALYSIS

Separation Criteria

The criterion most commonly employed to characterise the degree of separation (*i.e.* the resolution) of chromatographic peaks is the quantity

$$K = \frac{l_{(2)} - l_{(1)}}{\mu_{(1)} + \mu_{(2)}}, \quad (1)$$

where $l_{(1)} - l_{(2)}$ is the difference between the ordinates of the peaks on the chromatogram, and μ is the peak width, measured[2] at some chosen fraction of the maximum peak height, h. Thus, the half-width $\mu_{0.5}$, is measured at a height of 0.5 h, the width μ_e at a height of $(1/e)h$.

This criterion has been shown[3] to be satisfactory only when the peaks are well resolved, and when the substances are present at comparable concentrations ($\varphi \simeq 1$, where φ is the ratio of the corresponding peak heights). When the constituents are present in widely different concentrations, it has been suggested that the width of the larger peak should be measured at the same height as that of the smaller peak:

$$K = \frac{l_{(2)} - l_{(1)}}{\mu_{(1)}\sqrt{\ln\varphi + 1} + \mu_{(2)}}, \quad (2)$$

where the subscripts (1) and (2) refer to the main and the trace constituent respectively. Thus modified, the formula represents the degree of separation far more realistically, since Eqn. (1) can give $K = 1$ (for very large φ) even at very modest peak resolutions.

It can be shown that complete separation ($K = 1$) of two nearly equal peaks requires a minimum length of column given by the expression

$$L = 44.36\,\frac{\left(\frac{\varkappa}{\varkappa_1} + \Gamma\right)^2}{\Delta\Gamma^2}\,\frac{D\varkappa}{\alpha}, \quad (3)$$

where $\Delta\Gamma$ is the difference between the Henry coefficients of the first (Γ_1) and the second (Γ_2) constituent, Γ the mean of the two coefficients, $\varkappa$ the fractional free volume of the column, $\varkappa_1$ the fractional volume occupied by the liquid phase, α the linear velocity of the carrier gas, D the effective coefficient of longitudinal diffusion, and the numerical factor 44.36 indicates that peak half-widths are used in the calculation.

In trace analysis, complete separation of the peaks requires a length of column

$$L = 11.09\left[\frac{\left(\frac{\varkappa}{\varkappa_1} + \Gamma_2\right) + \left(\frac{\varkappa}{\varkappa_1} + \Gamma_1\right)\sqrt{1 + \ln\varphi}}{\Delta\Gamma}\right]^2 \frac{D\varkappa}{\alpha}. \quad (4)$$

It follows that longer columns, or more selective adsorbents, are needed to improve the separation of trace impurities.

In many cases complete separation cannot be achieved, and neither $\mu_{(2)_{0.5}}$ nor $\mu_{(2)_e}$ are measurable. Some subsidiary criteria have been proposed to characterise the resolution of overlapping peaks: the quantity θ, for example, is defined[4] as

$$\theta = \frac{f}{g} \times 100, \quad (5)$$

where f and g are the distances indicated in Fig. 1: f is the distance, measured normal to the base-line, between

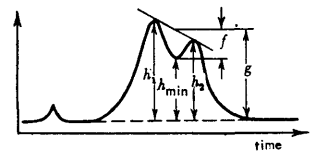


Fig. 1. Parameters of incompletely resolved chromatographic peaks.

the minimum and the tangent to the two maxima, $g = f + h_{\min}$.

In trace analysis, however, the maximum of the main peak is often inaccessible, and the extent of resolution cannot be calculated in this way. One must then turn to the criterion

$$\psi = \frac{h_2 - h_{\min}}{h_2}, \quad (6)$$

which defines the degree of resolution in systems where the main peak is very much larger than the impurity peak, and cannot be plotted on the chromatogram even if full use is made of the sensitivity control (Fig. 2).

However, since fairly large samples are used in the separation of trace impurities, the separation criterion is a function of sample size as well as of experimental conditions. With variable sample sizes, therefore, the most rational criterion is obtained by multiplying ψ by some function of the sample volume.

Sample Size

Samples used in gas chromatography are mostly between 0.5 μl and 0.1 ml (liquids) or 0.1 ml and 20 ml (gases). The use of still larger samples results in wider (as well as higher) peaks, so that neighbouring peaks tend to overlap. Van Deemter *et al.*[5] determined the permissible sample volume v_p for which the peak width is independent of the volume of material under test, and showed that v_p is equal to one-half the product of the effective volume of a theoretical plate and the square root of the number of plates in the column. In our terminology, the definition is

$$v_n \leqslant 0.5\,\frac{Lxs}{\sqrt{n}}(\varkappa + \Gamma\varkappa_1), \quad (7)$$

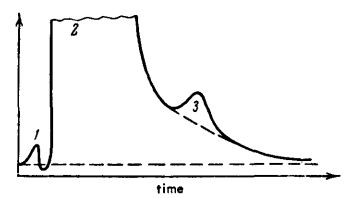


Fig. 2. Measurement of the area of an incompletely resolved impurity peak:
1) air; 2) main component; 3) impurity.

where s is the cross-sectional area of the column and n is the number of theoretical plates. Some simple manipulation gives

$$v_p \ll \frac{\omega_{0.5}}{4.7} \quad (8)$$

and

$$c_{max} \leqslant \frac{c_p}{5}, \quad (9)$$

where $\omega_{0.5}$ is the half-width of the peak, measure in millilitres of carrier gas, c_p the concentration of the desired constituent in the sample, and c_{max} the concentration of the same constituent at the maximum of the eluted peak.

These considerations show that a larger sample is permissible when the substance being analysed is strongly adsorbed. The size of the sample can also be increased in direct proportion to the cross-section of the column and to the square root of the column length.

Klinkenberg[6] has shown that the column can be overloaded by the volume of sample in the vapour phase (excluding the carrier gas) in addition to the type of overloading described by Eqn. (7), in which the volume of sample in the vapour phase includes the volume of the carrier gas. In the former case the permissible sample size can be calculated by replacing the factor 0.5 in Eqn. (7) by the factor 0.02.

Slight overloading of the column is sometimes beneficial, since it raises the sensitivity without appreciably degrading the resolution. A fourfold increase in the length of the column doubles the permissible sample size, the peak widths, and the peak separation, but leaves unchanged the concentrations of the constituents at the peak maxima. An amount of overloading which lowers the separation criterion to 1 whilst raising the concentration of the constituents at the peak maximum is therefore entirely acceptable.

Zhukhovitskii and Turkel'taub[7] have recently propounded the technique of step chromatography, in which large samples are used to give a stepped elution curve. The height of each step measures the concentration of the appropriate constituent.

If the time allowed for the separation is fixed, and the rate of mass-transfer is limited by internal diffusion, the peak width becomes proportional to the velocity of the carrier gas. Since

$$\mu_{0.5} = 3.33(\varkappa + \Gamma\varkappa_1)\sqrt{\frac{DL\varkappa}{\alpha}}, \quad (10)$$

it follows that $\mu \simeq \alpha$ if $2D\varkappa/\alpha$ is replaced by $C\alpha$ and L is replaced by $t\alpha/(\varkappa + \Gamma\varkappa_1)$, where t is the analysis time and C is a term which characterises mass transfer by internal diffusion. Hence a larger sample can be used if the gas velocity and the length of the column are increased. If the sample size is also increased in proportion to the flow rate the concentration at the peak maximum remains unchanged, because the diffuseness of the peak is proportional to the flow rate. Since the width of the chromatographic peak is proportional to time, the peak areas and the peak separation criterion also remain the same. It follows that the degree of separation can be adversely affected by column overload if the time of analysis is fixed.

Impurity Accumulation

Sorption on the stationary phase decreases the volume of an injected sample (concentration of desired constituent = c_p) by a factor of $\Gamma_0 = \varkappa + \Gamma\varkappa_1$, and raises the concentration correspondingly. During the subsequent elution on account of the diffuseness of the chromatographic band the concentration at the peak maximum, c_{max}, is inversely proportional to the square root of the column length (assuming no overloading), and at the column outlet the peak concentration is given by

$$c_{max} = p\frac{c_p\Gamma_0}{\sqrt{L}}, \quad (11)$$

where p is a proportionality coefficient. Desorption widens the peak by a factor Γ_0, and correspondingly lowers the concentration:

$$c_{max} = p\frac{c_p}{\sqrt{L}}. \quad (12)$$

In trace analysis these concentrations are frequently too low to be measured even if the column is overloaded with sample, when the value of c_{max} decreases slowly with L. Various methods of concentrating the impurity have therefore been devised. Thus, it is important to choose a packing on which the major constituent is adsorbed much more strongly than the impurity ($\Gamma_0^1 > \Gamma_0$). This compresses the injected sample by a factor Γ_0^1 and increases the concentration of both the main constituent and the impurity by the same factor. After elution, therefore, the latter concentration takes the value

$$c_{max} = p\frac{c_p}{\sqrt{L}}\frac{\Gamma_0^1}{\Gamma_0}. \quad (13)$$

This method has been used by one of us[8] in the analysis of volatile impurities in ethylene.

In the case of impurities of low volatility, adsorption is allowed to occur at some low temperature, T_1. This compresses the band by a factor $\Gamma_0(T_1)$. After removal of the major constituent, chromatography is carried out at a higher temperature T_2, resulting in an increase in the eluate concentration by a factor $\Gamma_0(T_1)/\Gamma_0(T_2)$. The low-temperature sorption can be carried out in a separate tube or on the column itself.

It is frequently possible to concentrate the impurity by partially or completely condensing out the main constituent in a suitable cold trap. This can be empty, or filled with a solid packing or with a liquid. As a result, the impurity concentration rises by a factor of $1/(1 + mC)$, where C is the initial fractional concentration of the main constituent and m is the fraction condensed. Removal of the main constituent improves the separation (by decreasing φ) as well as raising the concentration of the trace constituent.

Chromatograms free from the major peak have also been obtained by chemically removing the main constituent before the column, within the column itself, or beyond the column, by using the main constituent as carrier gas, or by choosing a detector insensitive to the main constituent.

All these techniques are effectively single-stage methods of enrichment of the impurity in the sample. Multi-stage enrichment is achieved in chromathermography[9-11], a technique which offers practically limitless possibilities in many problems of trace analysis. The programmed-temperature method[12] is suitable for continuously monitoring industrial processes, and enables low-volatility impurities to be detected in such a way that the main constituents do not give peaks on the chromatogram.

Clearly, the procedures discussed above have to be combined with analytical techniques suitable for multicomponent systems when it is desired to estimate trace impurities in complex mixtures.

Quantitative Interpretation of the Chromatograms

The main requirement on a method for the quantitative interpretation of trace-impurity chromatograms is that it should be capable of absolute calibration (carried out by calculations based on some experimentally found relationship between the concentration of the impurity and the response of the detector).

Internal standards are hardly ever applicable owing to the difficulty of preparing a series of standard mixtures with a very low concentration of one constituent. The internal normalisation method is likewise unsuitable because of its low precision, even in cases where the main peak can be fully plotted on the chromatogram.

When the peaks are sufficiently well resolved, the peak height h is the parameter normally used. In cases of partial resolution it is better to use the peak area as a measure of concentration, taking the precaution[13] of using the extrapolation of the main peak as a corrected base line (see Fig. 2).

3. TRACE IMPURITY ANALYSIS WITH LARGE SAMPLES

Isothermal Separation of Large Samples

As stated above, the sensitivity of the method can often be raised by overloading the column with sample. Many authors have analysed trace impurities simply by using rather large samples, which they eluted under isothermal conditions. Pietsch[14,15] was among the first to use this approach in his work on the determination of oxygen, carbon monoxide, nitrogen, and light hydrocarbon impurities in commercial and in pure ethylene. A conventional

TABLE 1. Trace impurity analysis by isothermal separation of large samples.

Desired impurity	Main constituent	Length of column. Sorbent	Detector	Carrier gas	Temperature, °C	Sample size	Sensitivity, %	References
Propane, propylene, C_4 hydrocarbons	ethylene	8 m. Triisobutylene on Celite	katharometer	hydrogen	25	5 ml gas	5×10^{-3} wt. 5×10^{-3} wt. $5 \cdot 10^{-2}$ wt.	16
Hydrogen, oxygen, nitrogen, methane, carbon monoxide	ethylene	2 m. Molecular sieve 13X	katharometer	helium	25	25 ml gas	5×10^{-4} vol. 4×10^{-4} wt. 7×10^{-4} wt. 7×10^{-4} wt. 10^{-3} wt.	16
$C_2 - C_4$ hydrocarbons, carbon dioxide	methane	mixture of triisobutylene and transformer oil on C-22 support	thermistor katharometer	hydrogen	0	–	$10^{-3} - 5 \times 10^{-3}$	17
Methylacetylene, vinylacetylene	acetylene	1 – 3.5 m. Dibutyl phthalate on fire brick	thermistor katharometer (thermochemical)	hydrogen, air	20 – 50	50 – 100 ml gas	$< 10^{-2}$	18
Propadiene	propylene	2 m. Glycol solution of silver nitrate on C-22	katharometer	helium	25	25 ml gas	5×10^{-4}	19
Isopropanol	benzene	1.2 – 2 m. "Nujol"* on "Celite"**	thermistor katharometer	helium	64	10 μl liquid	$< 10^{-4}$ wt.	20
Benzene	toluene	1.2 – 2 m. Tetraethylene glycol dimethyl ether on "Celite"	thermistor katharometer	helium	64	20 μl liquid	$< 10^{-3}$ wt.	20
Cyclohexanol	toluene	1.2 – 2 m. "Carbowax"*** and sorbitol on Celite	thermistor katharometer	helium	155	10 μl liquid	4×10^{-4} wt.	20
Methanol	water	1.2 – 2 m. "Carbowax" on "Celite"	thermistor katharometer	helium	80	10 μl liquid	2×10^{-4} wt.	20
Methane, ethane	air	carbon	interferometer and volumetric gas analyser	air	20 – 30	–	6×10^{-8} vol. calculated as CO_2	21
Carbon oxide sulphide	natural gas	3.6 m. *N,N*-Dibutylacetamide on a special support	katharometer	helium	28	50 ml gas	2.5×10^{-3}	22
Hydrogen, nitrogen, carbon monoxide, $C_2 - C_4$ hydrocarbons	ethylene	two columns, 0.6 and 3 m long. KSM silica gel. Crossover of gas flow	katharometer thermistor katharometer	air	room temperature for volatile constituents, programmed to 250° for heavier constituents	1 litre gas	2×10^{-4} 5×10^{-2} 1.5×10^{-3} 1.5×10^{-3}	23

* Petroleum jelly (Ed. of Translation).

** Preformed catalyst carrier made by Johns-Manville USA (Ed. of Translation).

*** Polyethylene glycols and methoxypolyethylene glycols made by Union Carbide Corp. (Ed. of Translation).

katharometer, and sometimes even a nitrometer filled with alkali, proved adequate as detectors in this work.

The most significant results obtained by isothermal separation of large samples are summarised in Table 1. It seems clear that, with a large enough sample and a katharometer detector, the sensitivity can reach 10^{-4}%. This level of sensitivity is adequate in many practical problems, but it represents the ultimate limit of katharometer response and cannot be further improved by increasing the sample size.

Since the loss of separation efficiency is one of the factors which set an upper limit to the permissible sample size in chromatographic trace analysis — particularly at high values of φ, *vide* Eqn. (2) — the advantage of using the main constituent as carrier gas is obvious: the major peak disappears, and the impurity peak becomes unmistakable. This device was used by Turkel'taub[21] in what appears to be the first application of chromatography to trace impurity analysis, and enabled him to determine methane and ethane in air with a sensitivity of approximately 10^{-5}%.

Wilkins and Wilson[24] achieved a sensitivity of 5×10^{-4}% in their estimation of oxygen, nitrogen, and other gaseous impurities in helium by using pure helium as carrier gas.

Obviously, when using a katharometer, the main peak can be eliminated by choosing a carrier (a single gas or a mixture of gases) of very nearly the same thermal conductivity as the main constituent.

Elimination of the Main Constituent

The techniques discussed so far offer a slight improvement in the sharpness of separation of the peak. However, if the main constituent is physically removed from the sample to be analysed, the sample volume can be drastically decreased, with a corresponding enrichment of the trace impurity. This raises the sensitivity of the method by compressing the peaks as well as by lowering the value of φ.

Ray[25,26] achieved a remarkable concentration of non-olefinic impurities in ethylene by passing the gas over

TABLE 2. Trace impurity analysis after elimination of the major constituent.

Desired impurity	Main constituent	Method of separation	Length of column. Sorbent	Detector	Carrier gas	Condensation temperature, °C	Analysis temperature, °C	Sample size	Sensitivity, %	References
Methane	air	99% of the air vented to atmosphere after first section	0.6 m + 1.2 m. Carbon with 1.5% dinonyl phthalate	katharometer	helium	–	room	20 ml gas	5×10^{-4}	32
Carbon dioxide, hydrocarbons up to C_4	liquid oxygen	impurities frozen out	benzyl benzoate and silicone oil on a support	katharometer	–	liquid oxygen	room	–	10^{-7} – 10^{-8}	33
Hydrocarbons up to C_4	synthetic gas	impurities frozen out in a carbon trap	1.5 m. Triisobutylene on "Meka" support. Solution of silver nitrate in benzyl cyanide on "Meka" support	nitrometer, katharometer	carbon dioxide	75. Desorption at 150°	room	up to 10 litres gas	10^{-3}	34
Hydrogen, oxygen, methane, carbon monoxide	carbon dioxide	main constituent frozen out	molecular sieves 5A and 13X	katharometer	argon, helium	– 196	50	–	10^{-4}	35
$C_5 - C_{10}$ hydrocarbons	cracking gas	circulating system. Liquid samples taken from condensation trap	3.5 m. Silicone elastomer on "Celite"	katharometer	hydrogen	dry ice	86	6.6 litres gas	0.1 mg × × litre^{-1}	38
$C_1 - C_4$ aldehydes, $C_3 - C_4$ ketones, $C_2 - C_6$ hydrocarbons	white medicinal paraffin	impurities distilled into a cold trap from sample at 60°	2 m. Mixture of silicone and dicyandiethyl oxide on a support	flame ionisation	nitrogen	liquid air	20	10 g	10^{-7} wt.	43
Ethyl methyl ketone, toluene	waxes, lubricating oils	sample heated to 200° in a stream of helium and impurities frozen out	3 m. "Carbowax" on C-22	katharometer	helium	– 50. Desorption at 125°	100	10 g	5×10^{-2} – 10^{-3}	44
Hydocyanic acid	water	water equilibrated with air and impurity condensed out	5.4 m. Dinonyl phthalate on "Chromosorb"*	thermistor katharometer	helium	acetone – dry ice mixtures	57	up to 10 litres gas	10^{-4} – 10^{-6} mole	45
Carbon dioxide, in sodium carbonate	water	carbon dioxide evolved with hydrochloric acid	30 cm. Silica gel	thermistor katharometer	helium	–	room	30 g	2×10^{-5}	46
Carbon	iron	combustion in a stream of oxygen	silica gel, "Alusil"	photometric cell	oxygen	–	room	0.01 g	10^{-6}	47

* Graded, calcined diatomite aggregates made by Johns-Manville, USA (Ed. of Translation).

carbon, saturated with bromine, in the inlet section of his chromatographic column.

Various classes of compounds can be eliminated by using methods developed for the chromatographic analysis of complex mixtures. Thus, unsaturated compounds can be removed by elution through a section containing silica gel saturated with sulphuric acid[27], normal hydrocarbons[28-30] by 5 Å molecular sieves, alcohols by a polyester column[31]. All these methods can obviously be applied in trace analysis.

Cold traps have been widely used for separating impurities from the major constituent. According to their relative volatilities, either the impurities[32-34] or the main constituents[35] can be frozen out.

West *et al.* have developed a technique for concentrating impurities in air[36], using a charcoal trap, which gives a sensitivity of 10^{-3}–10^{-4}% with samples of the order of 20 litres. The concentrated impurities are vaporised and injected into the chromatographic column by rapidly raising the temperature of the cooled trap.

Mackay[37] has investigated the condensation of impurities in a specially designed apparatus.

Vigdergauz and Gol'bert[38,39] estimated high molecular weight impurities in cracking gas by absorbing them in a cold trap containing n-octane (which they used as an internal standard). The gas was circulated through the cold trap, from which a liquid sample was then extracted and analysed. Hydrocarbons in the range C_6–C_{10} were determined with a sensitivity of approximately 0.1 mg litre^{-1}.

Serpinet[40], and also Vyakhirev *et al.*[41], used preparative gas chromatography techniques to isolate the impurities before identifying and estimating them.

TABLE 3. Trace impurity analysis with thermal enrichment in the column.

Desired impurity	Main constituent	Length of column. Sorbent	Detector	Sorption temperature, °C	Analysis temperature, °C	Sample size	Sensitivity, %	Carrier gas	References
Methane	air	1st section 0.6 m, 2nd section 1.2 m. Carbon with 1.5% dinonyl phthalate	katharometer	– 78	room	10 ml gas	$< 10^{-4}$	helium	32
C_4 and higher hydrocarbons, halogen derivatives	chloroethylene	3 m. "Nujol" on C-22	katharometer	liquid nitrogen	30	1 ml liquid	$< 10^{-4}$	nitrogen, helium	48
C_2 – C_5 hydrocarbons	liquid air	7.6 m. Dimethylsulpholane on C-22	katharometer	liquid nitrogen	0	up to 10 litres gas	up to 10^{-6}	helium	49
C_2 – C_5 hydrocarbons	air, exhaust gases	0.3 m + 7.6 m. Dimethylsulpholane on brick	katharometer	liquid nitrogen	0	up to 10 litres gas	5×10^{-6}	helium	50
Carbon monoxide, hydrogen, C_1 – C_4 hydrocarbons	ethylene	5 m alumina, 1 m dibutyl phthalate on diatomite	thermochemical	room, increasing to 130°	2nd section at room temperature	20 ml gas	5×10^{-3}	air	51
Light gases and C_2 – C_5 hydrocarbons	–	7.5 m carbon, 15 m dimethylsulpholane on brick	katharometer	liquid nitrogen	20	10 ml gas	9×10^{-3}	helium	53
Carbon dioxide	air	2 m silica gel	katharometer	– 80	–	500 ml gas	2×10^{-3}	helium	54
Acetylene	air, oxygen	2 m silica gel	katharometer	– 80	50	10 litres gas	1.3×10^{-8}	helium	54
Nitrogen, oxygen, methane, carbon monoxide	hydrogen	silica gel (50 cm³). 2 m molecular sieve 5A	katharometer	– 80	50	1 litre gas	10^{-4}	helium	54
Methane, ethane, carbon dioxide, ethylene, C_3 hydrocarbons	hydrogen	2 m silica gel	katharometer	– 80	50	20 litres gas	5×10^{-6} – 10^{-5}	helium	54
C_3 – C_5 hydrocarbons	hydrogen	polyethylene glycol on "Chromosorb" (50 cm³). 4 m dimethylsulpholane	katharometer	– 80	50	–	10^{-4}	helium	54
Acetylene	ethylene	polyethylene glycol on "Chromosorb" (50 cm³). 4 m dimethylsulpholane	katharometer	– 80	– 25	40 litres gas	10^{-4}	helium	54
C_1 – C_2 and higher hydrocarbons	air, methane	"Alusil"	colorimetric	50	60 – 120	200 ml gas	10^{-6} – 10^{-7}	oxygen	56
Carbon monoxide	hydrogen	0.35 m carbon, 0.3 m silica gel	katharometer, with conversion into CO_2 between columns	– 75 – 45	50	7 litres gas	10^{-7}	nitrogen	55

Light impurities in substances of low volatility (such as lubricating oils) are usually determined by evaporating them from the sample, concentrating them in a trap, and introducing them into the column after a second evaporation.

Impurities which lower the flash-point of lubricating oils can be estimated by an interesting chromatographic method[42] which is far more general and precise than the conventional flash-point measurements.

Typical results of various methods of trace analysis (involving elimination of the main constituent) are summarised in Table 2.

Enrichment as a Result of Thermal Effects on the Column

In the opening section it was pointed out that thermal effects can be very significant since they enable the impurities to be concentrated, thus raising the sensitivity of the analytical method.

Several workers have used methods involving low-temperature adsorption of the sample on the column itself or on to an auxiliary section, followed by chromatographic separation at a higher temperature. The main results, set out in Table 3, show that a sensitivity of the order of 10^{-7}% can be achieved with large enough samples (several litres). In another paper[57] the separation of impurities in air at low temperatures is discussed.

Many publications dealing with the chromathermographic method of trace impurity analysis have appeared. Thus, Vagin *et al.*[58] have described a chromatographic method of analysis of carbon dioxide in oxygen, in amounts of 2.5×10^{-5} vol.%, using sample volumes of up to 50 litres and a low-sensitivity detector (a GEUK-21 gauge).

Zhukhovitskii and Turkel'taub[59] constructed a recirculating chromathermographic apparatus, consisting of two columns and a detector, in which sample volume and degree of enrichment can both be increased at will.

Petukhov and Vagin[60] determined heavy noble gases and methane impurities on a continuous basis in their programmed-temperature apparatus. The chromathermographic KhTD apparatus, now commercially available, can make continuous analyses of complex mixtures and of trace impurities in various materials.

4. TRACE IMPURITY ANALYSIS WITH HIGH-SENSITIVITY DETECTORS

High-sensitivity detectors, based on the measurement of ionisation currents in the material under investigation, have become very popular in the last five years. Lovelock[61-66] has described several forms of a detector in which a radioactive source is used to ionise the gas. McWilliam and Dewar[67,68] made a detector in which the various constituents are ionised by being burned in a hydrogen flame. Detectors of this type offer a sensitivity of the order of $10^{-12}-10^{-14}$ mole.

These modern detectors, with their impressive performance, offer obvious advantages in the development of analytical methods for trace amounts of various substances. Chromatographic apparatus incorporating ionisation detectors are now available from a number of firms in the USA, England, West Germany, and other countries.

Table 4 summarises the main analytical results for trace impurities obtained with ionisation detectors. The most striking feature of this work is the achievement of sensitivities of the order of $10^{-4}-10^{-5}$% with relatively small samples.

Still higher sensitivities are possible if a high-sensitivity detector is used in conjunction with one of the enrichment methods discussed above. Thus, Theer has shown[78] that the detection for sensitivity hydrocarbon impurities in air with a flame-ionisation detector can be improved from 5×10^{-6} (1 ml sample) to 10^{-8}% by increasing the sample volume to 50–100 ml and carrying out a preliminary enrichment on a silica gel column at -78°.

Since ionisation detectors are insensitive (or only slightly sensitive) towards certain substances, it is possible to lower the value of φ [see Eqn. (2)] and obtain a sharper separation by working under conditions where the detector does not respond to the major constituent. Turkel'taub *et al.*[79] took advantage of this phenomenon in their work on the analysis of traces of benzene in silicon tetrachloride, using an apparatus with a flame-ionisation detector. Shima[80], and Emery and Koerner[81], who estimated phenols and fatty acids, respectively, in aqueous solutions, resorted to the same stratagem.

Various procedures for increasing the sensitivity of ionisation detectors towards permanent gases have been suggested. In one of these[82] helium is used instead of argon as the carrier gas: this enables oxygen, argon, and other gases to be ionised in the detector and to be estimated with a sensitivity of approximately 10^{-4}%. Other methods[83-85] rely on the introduction into the argon stream of quite small amounts of organic substances, able to increase greatly the ionisation of various molecules.

Some selective, high-sensitivity detectors have also been described: the emissivity detector and the electron affinity detector[86,87]. These react very strongly towards certain classes of compounds (aromatic hydrocarbons, in particular), but have only a moderate sensitivity towards other substances. They are thus eminently suited to the detection of impurities (*e.g.* aromatic substances in aliphatic hydrocarbons), since they give a low value of φ as well as a high sensitivity.

5. DETERMINATION OF TRACE IMPURITIES IN COMPLEX MIXTURES

The analysis of trace impurities in multicomponent systems is complicated by the serious overlapping of the peaks due to impurities with those due to the main constituents. Trace-impurity techniques therefore have to be modified, and combined with methods of analysis worked out for complex mixtures.

Heuschkel *et al.*[88], for example, have developed a chromatographic method of analysis of very small amounts (approximately 5×10^{-4}%) of propadiene and methylacetylene in a propane–propylene fraction containing up to 0.5% of C_4 hydrocarbons. A two-stage separation was used, with a silicone oil column and a diethylformamide column (both stationary phases were supported on "Sterchamol" brick). The fractions obtained after the first stage were collected in a cold trap, which was used as a sample injector for the second stage.

Vigdergauz, Gol'bert, and their coworkers[89,90] developed a method of analysis of acetylene, methylacetylene, ethyl-

TABLE 4. Trace impurity analysis with high-sensitivity detectors.

Desired impurity	Main constituent	Length of column. Sorbent	Detector	Carrier gas	Temperature, °C	Sample size	Sensitivity, %	References
Acetylene	nitrogen, ethane, propylene	6 or 12 m. Dimethylsulpholane on brick	argon ionisation	argon	10 – 20	10 – 20 ml	5×10^{-4}	69
Hydrocarbons	exhaust gases	0.2 m. Silica gel	flame ionisation	hydrogen	room	1 – 10 ml	10^{-7}	70
$C_1 - C_6$ hydrocarbons	air	2 columns in parallel, up to 4 m long, with dimethylsulpholane and diisodecyl phthalate on brick	flame ionisation	nitrogen – hydrogen mixture	25	1 ml	10^{-4}	71
Acetylene	ethylene	1.6 m. Hexamethylphosphoramide on brick	flame ionisation	–	27	5 ml	3×10^{-6}	72
Acetylene	ethylene	2.7 m. Dekalin on "Sterchamol" brick	flame ionisation	nitrogen	0	25 ml	10^{-6}	73
Carbon dioxide, carbon monoxide	ethylene	1 m. Carbon	flame ionisation (following conversion into methane)	hydrogen	room	25 ml	10^{-4}	74
Propylene	ethylene	mixture of ethanolamine, ammonium nitrate, and copper oxide on "Sterchamol" brick	flame ionisation	hydrogen	room	10 ml	3×10^{-3}	74
$C_8 - C_{10}$ aromatic hydrocarbons	styrene	capillaries: 61 m with "Apiezon" and 78 m with "Ucon"	argon triode	argon	70 – 100	0.005 μl	5×10^{-4}	75
Carbon oxide sulphide	carbon dioxide	1.2 m. Silica gel	argon ionisation	argon	25	115 ml	3×10^{-5}	76
Acenaphthene in onion root tips	–	0.15 m. Silicone oil on brick	flame ionisation	hydrogen	183	20 μl of tetralin solution	0.2γ	77
$C_2 - C_6$ hydrocarbons	air and oxygen	2 m. "Alusil" or silica gel	flame ionisation	hydrogen	room	1 ml	5×10^{-6}	78
Benzene	silicon tetrachloride	2 m. Liquid paraffin on engineering brick	flame ionisation	hydrogen	25	–	3×10^{-4}	79
Oxygen, hydrogen, nitrogen, methane	–	molecular sieve MA	argon ionisation	argon + $+ 10^{-4}$ % ethylene or acetylene	room	–	$10^{-4} - 5 \times 10^{-6}$	83
Oxygen, hydrogen, methane, argon, carbon monoxide	–	0.3 m. Molecular sieve 5 Å	argon ionisation	helium	room, but oxygen and argon separated at – 80°	–	10^{-12} mole per 1 ml carrier gas	82
Oxygen, hydrogen, nitrogen, methane, carbon monoxide	–	molecular sieve 5 Å	argon ionisation	argon + + trichloroethylene	room	–	10^{-5} ml	84

acetylene, propadiene, and divinyl in cracking gas and its fractions. A two-stage separation was again necessary, using columns packed with diisobutyl phthalate and sulpholane† (or dimethylsulpholane) respectively, supported on crushed brick. Narrow fractions were taken from the first column and injected into the second column without being first condensed out.

In conclusion we should point out that gas chromatography is not confined to the laboratory-scale analysis of trace impurities: some existing assemblies can be inserted in the control loop of technological processes[91].

† Tetrahydrothiophene 1,1-dioxide (Ed. of Translation).

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HOT SYNTHESIS OF COMPOUNDS LABELLED WITH RADIOACTIVE TRITIUM

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1. ENERGY AND CHARGE OF TRITIUM ATOMS PRODUCED BY NUCLEAR REACTIONS†

Tritium is obtained by the reactions $^6Li(n, \alpha)T$ and $^3He(n, p)T$, the former being of practical interest. The capture cross-section of ^6Li for thermal neutrons is 945 barns, and ^6Li makes up 7.5% of the mixture of lithium isotopes. The yield of tritium is calculated from the formula:

$$A = \Phi_0 (1 - e^{-n\sigma x}) \lambda t,$$

where Φ_0 is the neutron flux, σ is the cross-section of the nuclear reaction, n is the number of atoms per cm^3, x is the thickness of sample, t is the period of irradiation, and λ is the decay constant. The recoil tritium atoms obtained by the reaction $^6Li(n, \alpha)T$ have energy 2.73 MeV and free path in the condensed phase of $\sim 50\ \mu$ (5 mg cm^{-2}). The recoil tritium atoms produced by the reaction $^3He(n,p)T$ only have energy 0.192 MeV.

Chemical reactions become possible when the recoil atoms have sufficient kinetic energy so that after collision with a molecule they can form a stable bond with an atom of this molecule. With comparatively low energies the reaction between the recoil atoms and the molecule passes through a transition complex in which the excess energy is evenly distributed among all the degrees of freedom, and which as a result of concentration of the necessary energy at one of the bonds decomposes to form the reaction products. As the energy of the recoil atom increases, the probability of forming the transition complex will decrease. Kinetics are normally concerned with the minimum energy required for a reaction and with the direction of the reaction at a given energy. A feature of the kinetics of the reactions of recoil atoms is that they relate to chemical reactions of large energies.

Collisions which can produce chemical reactions will occur when the recoil atom has the maximum possible energy to allow for stabilisation of the tritium bond in the molecule. If the tritium atom has a greater energy, then on collision it will not enter into the reaction, and if after

† These atoms will subsequently be called recoil tritium atoms.

subsequent collisions it has energy less than the bond energy, then it may reach thermal energies and react as a thermal atom. The latter will only occur if the probability of reaction on collision and the number of collisions in the high-energy region are sufficiently low.

The conditions for reactions to proceed at the maximum permissible energy are greatly different from the conditions for low energies. Limitations associated with the energy of activation become less important, since normally there is always an excess of energy; moreover the direction of reaction is no longer controlled by the path of minimum energy, and the reaction can proceed much more rapidly and in several directions. As the excess of energy increases, the assumed equilibrium distribution of energy throughout the whole molecule becomes less and less probable. At very high energies, although the tritium atom forms a "complex" when it collides with a molecule, there may not be any equilibrium distribution of energy throughout the whole molecule, and it is possible that only part of the molecule will participate in substitution or other reactions, independently of the remainder of the "complex", the time required for the reaction being of the same order as, or less than, the period of vibration of a single bond. There is apparently also an intermediate region of energies where part of the excess energy is distributed throughout the whole molecule; in this case the energy of activation will have only a partial influence on the direction of reaction.

If we had accurate information on the reactions of particles of high kinetic energy, we could construct a graph of probability of reaction against energy of particle, and calculate the total probability of formation of any molecule as a function of particle energy. Fig. 1 shows such a hypothetical curve for recoil tritium atoms. The probability of any reaction is zero at energies below the energy of activation, and also at high energies when the tritium atom cannot form a stable bond on collision with a molecule. The maximum probability of reaction, the width of the high-energy sector, and the shape of the curves are generally unknown. It can be qualitatively deduced from Fig. 1 that reaction *I* will have a much greater velocity for thermal atoms than reaction *II*, because of the low energy of activation. At high recoil atom energies the rates of these reactions will be approximately the same.

According to some data, however[3,10], the initial energy of the recoil atoms has no effect on the distribution of tritium among the reaction products. Thus the yields of active products obtained from methane and recoil tritium atoms produced by the reactions $^6Li(n, \alpha)T$ and $^3He(n, p)T$ are almost the same, 49.0% and 50.0% for HT and 30.5% and 31.8% for CH_3T respectively[1-3]. Consequently the chemical reactions of recoil atoms commence after they have cooled to energies of the order of a few electron-volts.



Fig. 1. Efficiency of collisions of recoil tritium atoms with organic molecules as a function of the kinetic energy of the tritium atoms (hypothetical curve).

At the time of its formation the recoil tritium atom has a positive charge; as it is then slowed down in the medium there is repeated rearrangement of charge, and most of the recoil tritium atoms of energy of a few electron volts are neutralised[3-6]. Hence it is mainly uncharged tritium atoms which take part in reactions.

To obtain organic compounds labelled with tritium a mixture of a finely-ground solid insoluble lithium salt with solid or liquid organic compounds is irradiated; or the lithium salt may be dissolved in the organic substance. On irradiation of a mixture of organic compound and lithium carbonate the specific gravity of the parent compound is calculated from the formula[7]:

$$\beta = 10^3 KRPnt,$$

where R is the percentage introduction of tritium into the irradiated compound, P the percentage of lithium carbonate in the mixture, n the neutron flux per cm^2 per sec, t the duration of irradiation in sec, and K a constant.

With $n = 10^{12}$, irradiation for 24 h can give a specific activity of the order of 10^5–10^6 disintegrations per sec, per mg. The chemical nature of the lithium compounds used to obtain the recoil tritium atoms has no influence on the distribution or yield of the tritium reaction products[11].

2. REACTIONS OF RECOIL TRITIUM ATOMS

Tables 1, 2, and 3 show published data on the distribution of tritium when the recoil atoms react with various compounds.

TABLE 1. Products of the reaction of recoil tritium atoms, obtained by the reaction $^3He(n,p)T$, with gaseous organic compounds. In cases marked* the tritium is obtained by the reaction $^6Li(n,\alpha)T$ in the liquid phase.

System irradiated	Flux, neutrons per cm^2 per sec	Period of irradiation	Active reaction products, %							Ref.
			H_2	CH_4	C_2H_6	C_2H_4 + C_2H_2	C_3H_8	C_3H_6	C_4H_{10} and higher	
CH_4	$5\cdot10^{12}$	10 min	50.0	31.8	7.7	—		10.4		3
	$2\cdot10^9$	96 h	61.7	29.8	2.6	—		5.4		
	$3\cdot10^{13}$	1 h	46.0	31.0	6.8	—		14.2		4
	$1.2\cdot10^{13}$	2 min	53.5	32.5	—	14.0				7
	$3\cdot10^{12}$	1 h	51	33	7.4	—		8.9		10
	$5\cdot10^{12}$	—	49.0	30.5	11.2	—		9.3		10
CH_4*	$5\cdot10^{12}$	30 sec	39.1	48.6	5.5	0.3		6.5		9
CH_4+I_2	$4\cdot10^{12}$	20 min	28.2	27.5	0.1	—		0.4		3
	$3\cdot10^{13}$	1 h	40	50	trace	—		trace		2
CH_4+NO	$1\cdot10^{13}$	2 min	31.5	36.5		<1				2
$CH_4+C_2H_4$	$3\cdot10^{12}$	1 h	28	24	6.3	3.2	14	—	24.1	10
CH_4+H_2(13%)	$3\cdot10^{12}$	1 h	75	20	3.0	—		2.3		10
C_2H_6	$5\cdot10^{13}$	20 min	43.4	3.8	27.5	—	9.7	—	15.3	3
C_2H_6	$3\cdot10^{13}$	1 h	43	5	28	—	9.0	—	14.0	2
	$3\cdot10^{12}$	1 h	60	3.2	25	—	5.1	—	7.1	10
C_2H_6*	$5\cdot10^{13}$	30 sec	41.7	5.4	37.5	4	5.3	—	6.2	2
$C_2H_6+I_2$	$4\cdot10^{13}$	20 min	40.0	3.6	22.3	—	0.8	—	3.8	3
$C_2H_6+Br_2$	$3\cdot10^{13}$	1 h	42	2.0	37.0	—	—	—	—	2
$C_2H_6+C_2H_4$(10%)	$3\cdot10^{12}$	1 h	36	2.4	26	3.7	7.7	—	23.1	10
$C_2H_6+^4He$	$4\cdot10^{12}$	1 h	58.8	2.8	11.8	—	7.8	—	18.5	3
C_2H_4	$3\cdot10^{13}$	1 h	16	0.2	2.3	53	1.8	—	26.3	10
$C_2H_4+O_2$	$1\cdot10^9$	—	18	trace	79.0	3.9	—	trace	—	10
C_3H_8	$3\cdot10^{13}$	1 h	61	2.5	2.4	—	26	—	8.2	10
	$3\cdot10^{12}$	1 h	43	4	2.5	—	36.0	—	14.5	2
	$5\cdot10^{13}$	5 min	66.2	3.2	2	1.4	23.0	0.5	3.2	2
	$1\cdot10^{13}$	12 h	62.1	5.7	4.4	0.4	21.1	0.4	5.9	11
$C_3H_8+Br_2$	$3\cdot10^{13}$	1 h	50.0	3.0	1.5	—	39.0	0.5	—	11
$C_3H_8+C_2H_4$	$3\cdot10^{12}$	1 h	41	3.0	5.2	2.5	25		23.6	10
C_3H_8	$2\cdot10^9$	40 h	31.2	1.2	—	13	4.5	41	8.2	11
	$3\cdot10^9$	144 h	29.6	1.3	—	13.8	3.7	41.7	8.6	11
	$1\cdot10^{13}$	12 h	50	3.5	0.5	1.3 11.5	4.6	25.7	3.6	11
$C_3H_8+O_2$	$1\cdot10^9$	—	36.0	2.0	—	1.5 15.0 2.0	1.0	44.0	—	10

TABLE 2. Products of the reaction of recoil tritium atoms, obtained by the reaction $^3He(n,p)T$ with gaseous organic compounds.

System irradiated	Flux, neutrons per cm^2 per sec	Time, h	Active products, %												
			H_2	CH_4	C_2H_6	$C_2H_4 + C_3H_8$									
	$1 \cdot 10^9$	138	31.2	2.5	6.2	1.5	12.0	22.1	2.1	3.0	8.6				
+NO	$1 \cdot 10^9$	138	52	1	—	2.3	—	37.5	6	3.5	. . .				
+He^4	$1 \cdot 10^9$	138	31.0	1.9	8	2.3	13	11.4	1.8	—	27.9	....			
	—	—	62.3	4	4	1.3	1.6	—	0.3	—	26.5				
	$1 \cdot 10^{12}$	12	47	3.4	0.3	3.5	0.9	—	11.9	8.3		2.6	11.9	6.4	
+He^4	$2 \cdot 10^9$	48	42.6	1.5	2		—	—	14.7	7.2		2.5	21.2	1.7	
+NO	$2 \cdot 10^9$	48	43	2.1	1.2		—	—	17.1	—	—	12	22.6	3.8	
	$1 \cdot 10^{12}$	12	55.6	1.2	5.5		1.1	—	11.2	—	—	2.9	2.6	11.3	
+O_2	$1 \cdot 10^9$	168	47	2.1	2.3		—	—	17.6	—	—	2.4	1.6	26.8	
	—	—	37.3	3.4	0.8	10.4	—	—	10.4	7.8		26	1.8	1	
+O_2	—	—	39.2	2	12.5	0.6	—	—	13.4	—	—	29.1	1.1	0.9	
	$1 \cdot 10^9$	168	45	3.5	trace		—	—	8.2	3.9	—	—	—	—	39
	$1 \cdot 10^9$	168	43.7	2.2	1.5	8.1	0.7	—	10.3	—	—	1.0	—	—	—
	$1 \cdot 10^9$	168	47.5	3.3	0.5	1.5	—	—	6.0	—	—	6.0	0.5	trace	—
	$1 \cdot 10^9$	168	44.0	3.0	—	1.0 1.0	trace	—	5.0	—	—	2.0	trace		10.0
	$1 \cdot 10^9$	168	34.0	5.5	0.2	9.0	0.5	—	0.7	—	—	0.9	5.4	3.5	trace
	$1 \cdot 10^9$	168	49.0	3.6	trace	0.4	—	—	0.4	—	—	0.4	3.6	2.1	7.2
	$1 \cdot 10^9$	168	61.0	3.6	—	trace	—	—	0.9	—	—	—	—		
	$1 \cdot 10^9$	168	55.4	2.0	0.7	8.8	1.0	—	10.5	—	0.6	1.2	—		—
	$1 \cdot 10^9$	168	56.4	2.4	1.2	1.8	0.3	—	6.3	—		4.5	0.3	trace	—

TABLE 2 (contd).

System irradiated	Flux, neutrons per cm^2 per sec	Time, h	Active products, %												Ref.
															
	$1 \cdot 10^9$	138	7.5	.....											12
+NO	$1 \cdot 10^9$	138													12
+He^4	$1 \cdot 10^9$	138													12
	—	—													13
	$1 \cdot 10^{12}$	12	1.2	.....											11
+He^4	$2 \cdot 10^9$	48													10
+NO	$2 \cdot 10^9$	48													11
	$1 \cdot 10^{12}$	12	9.3	.....											11
+O_2	$1 \cdot 10^9$	168													10
	—	—													13
+O_2	—	—													10
	$1 \cdot 10^9$	168													10
	$1 \cdot 10^9$	168	5.9	24.8	2.0										10
	$1 \cdot 10^9$	168	7.7	1.5	25.8										10
	$1 \cdot 10^9$	168	4.0	—	—	28.0	2.0								10
	$1 \cdot 10^9$	168	16.0	—	—	—	0.5	24.0							10
	$1 \cdot 10^9$	168	7.6*	—	—	3.2	21.0	1.0							10
	$1 \cdot 10^9$	168	—	—	—	—	8.0	—	8.0	14.5	4.0				10
	$1 \cdot 10^9$	168	—	0.9	—	—	—	—	2.1	—	—	1.8	1.5		10
	$1 \cdot 10^9$	168	—	0.4	0.3	—	—	—	4.5	—	—	15.0	1.8	1.8	10

TABLE 3. Products of the reaction of recoil tritium atoms obtained by the reaction $^6Li(n,\alpha)T$ with solid and liquid organic compounds.

Compound irradiated	Flux, neutrons per cm^2 per sec	Period of irradiation	Active products	Radiochemical yield, %	Specific activity, $\mu c/g$	Ref.
Benzene + Li_2CO_3	$3–4\cdot10^{12}$	30 min	benzene	26	28	16
			cyclohexa-1,4-diene	2.5		
			cyclohexa-1,3-diene	1.2		
			linear C_6	0.3		
Benzene-d_6 + Li_2CO_3	$3–4\cdot10^{12}$	30 min	benzene-d_6	24.2	26	16
			cyclohexa-1,4-diene	2.6		
			cyclohexa-1,3-diene	1.1		
			linear C_6	0.2		
Benzene + LiC_2H_5	$3–4\cdot10^{12}$	30 min	benzene	52	1.7	16
			cyclohexa-1,4-diene	5.2		
			cyclohexa-1,3-diene	2.6		
			linear C_6	1		
Benzene clathrate	$3–4\cdot10^{12}$	30 min	benzene	42.5	100	16
			cyclohexa-1,4-diene	trace		
			cyclohexa-1,3-diene	trace		
Cyclohexane	$3–4\cdot10^{12}$	30 min	cyclohexane	10	8	17
Cyclohexene	$3–4\cdot10^{12}$	30 min	cyclohexene	11	10	17
			cyclohexane	9	90	17
Cyclohexa-1,4-diene	$3–4\cdot10^{12}$	2 h	cyclohexa-1,4-diene	17	60	17
			cyclohexa-1,3-diene	5	65	17
			cyclohexene	15	330	17
			benzene	29	60	17
Cyclohexa-1,3-diene	$3–4\cdot10^{12}$	2 h	cyclohexa-1,3-diene	3.3		17
			cyclohexa-1,4-diene	2.6		
			cyclohexene	14.1		
			benzene	29.0		
Methylcyclohexane(liq.) $C_6H_{11}CH_3$	$4\cdot10^{12}$	5 h	$H_2 + CH_4$	60.9		17
			C_6H_{12}	3.9		
			$C_6H_{11}CH_3$	35.2		
Cyclohexanol(liq.) $C_6H_{11}OH$	$4\cdot10^{12}$	5 h	$H_2 + CH_4$	66.3		17
			C_6H_{12}	3.9		
			$C_6H_{11}OH$	29.8		
Cyclohexylamine $C_6H_{11}NH_2$	$4\cdot10^{12}$	5 h	$H_2 + CH_4$	61.9		
			C_6H_{12}	5.3		
			$C_6H_{11}NH_2$	32.8		
$C_6H_5CH_3$	$9\cdot10^{11}$	97 h	$C_6H_5CH_3$	40	220	18
CH_3OH(liq.)	$1.8\cdot10^{12}$	1 h	CH_3OH	23	1.3	19
C_2H_5OH(liq.)	$1.8\cdot10^{12}$	2 h	H_2	51.4		19
			CH_4	3.5		
			$C_2H_4 + C_2H_6$	1.7		
			$C_3H_8 + C_4H_{10}$	0.4		
			C_2H_5OH and other liquid products	20	2.2	
				23		
CH_3COCH_3(liq.)	$1.8\cdot10^{12}$	2 h	CH_3COCH_3	24	2.9	19
			CH_3CHO	9.1		
CH_3COCH_3(solid)	$4\cdot10^{12}$	1 h	CH_3COCH_3	24	3.6	19
			CH_3CHO	5		
			iso-C_3H_7OH	1.7		
CH_3COCH_3(liq.) + 30% H_2O	$1.8\cdot10^{12}$	1 h	CH_3COCH_3	25	1.2	19
			CH_3CHO	7.5		
L(+)-$CH_3CH(NH_2)COOH$, 14% aq. soln.	$1.8\cdot10^{11}$	24 h	*dl*-$CH_3CH(NH_2)COOH$	$\geqslant 0.5$		20
L(+)-$CH_3CH(NH_2)COOH$ (solid)	$1.8\cdot10^{12}$	24 h	*dl*-$CH_3CH(NH_2)COOH$	$\geqslant 12$		20
dl-Threonine	$2.5\cdot10^{11}$	17 h	*dl*-threonine	–	82	42
			allothreonine	–	108	
			glycine	–	11	
Glucose(solid)	$6\cdot10^{9}$	65 h	glucose	10	3	21
Glucose(solid)	$1.8\cdot10^{12}$	24 h	glucose	22	266	22
Glucose, 48% aq. soln.	$1.8\cdot10^{12}$	24 h	glucose	1	1.7	22
Galactose(solid)	$1.8\cdot10^{12}$	27 h	galactose	12	11.3	21
$C_6H_5COOC_3H_7$	$1\cdot10^{12}$	118 h	$C_6H_5COOC_3H_7$	16.8	0.188	23
$C_6H_5COOC_3H_7$	$1\cdot10^{12}$	153 h	$C_6H_5COOC_3H_7$	10.2	0.217	23
C_6H_5COOH	$1\cdot10^{12}$	72 h	C_6H_5COOH	25	90	24
C_6H_5COOH	$1\cdot10^{12}$	168 h	C_6H_5COOH	16	150	25
o-, *m*-, *p*-$NH_2C_6H_4COOH$	$5\cdot10^{12}$	2 h	$NH_2C_6H_4COOH$	32–35	21.7	26
o-, *m*-, *p*-$NO_2C_6H_4COOH$	$5\cdot10^{12}$	2 h	$NO_2C_6H_4COOH$	27–29	1.6	26
o-, *m*-, *p*-HOC_6H_4COOH	$5\cdot10^{12}$	2 h	HOC_6H_4COOH	43–31	26.7	26
o-, *m*-, *p*-$C_6H_4(COOH)_2$	$5\cdot10^{12}$	2 h	$C_6H_4(COOH)_2$	32	20	26
o-, *m*-, *p*-BrC_6H_4COOH	$5\cdot10^{12}$	2 h	BrC_6H_4COOH	36–42	26.7	26
o-, *m*-IC_6H_4COOH	$5\cdot10^{12}$	2 h	IC_6H_4COOH	33–36	23.3	26
o-, *m*-FC_6H_4COOH	$5\cdot10^{12}$	2 h	FC_6H_4COOH	44–57	36.7	26
o-, *p*-ClC_6H_4COOH	$5\cdot10^{12}$	2 h	ClC_6H_4COOH	42–49	31.7	26
Phenylpropionic acid	$5\cdot10^{12}$	2 h	phenylpropionic acid	35	23.3	25
Maleic acid	$5\cdot10^{12}$	2 h	maleic acid	10	6.7	25
Fumaric acid	$5\cdot10^{12}$	2 h	fumaric acid	12	8.3	25
cis-Cinnamic acid	$5\cdot10^{12}$	2 h	*cis*-cinnamic acid	15	10	25
trans-Cinnamic acid	$5\cdot10^{12}$	2 h	*trans*-cinnamic acid	30	18.3	25
trans-Cinnamic acid Na salt	$1.3\cdot10^{12}$	8 h	*trans*-cinnamic acid Na salt + *trans*-cinnamic acid	27	20	25
Acetic acid	$1.7\cdot10^{12}$	1 h	acetic acid	18	1.7	27
			H_2	33		
			CH_4	13		

TABLE 3 (contd).

Compound irradiated	Flux, neutrons per cm^2 per sec	Period of irradiation	Active products	Radiochemical yield, %	Specific activity, $\mu c/g$	Ref.
Propionic acid	$2–4\cdot10^{12}$	1 h	propionic acid	22		27
			H_2	43		
			CH_4	2.1		
			C_2H_6	7.5		
n-Butyric acid	$2–4\cdot10^{12}$	1 h	n-butyric acid	27		
			H_2	49		
			CH_4	2.6		
			C_3H_8	3.7		
Isobutyric acid	$2–4\cdot10^{12}$	1 h	isobutyric acid	26		27
			H_2	47		
			CH_4	4.7		
			C_3H_8	3.3		
n-Valeric acid	$2–4\cdot10^{12}$	1 h	n-valeric acid	20		27
			H_2	65		
			CH_4	2.0		
			C_4H_{10}	2.2		
Isovaleric acid	$2–4\cdot10^{12}$	1 h	isovaleric acid	33		27
			H_2	48		
			CH_4	4.5		
			iso-C_4H_{10}	2.1		
t-Valeric acid	$2–4\cdot10^{12}$	1 h	t-valeric acid	20		27
			H_2	43		
			CH_4	9.6		
			s-C_4H_{10}	6.8		
n-Caproic acid	$2–4\cdot10^{12}$	1 h	n-caproic acid	27		27
			H_2	46		
			CH_4	1.3		
			C_5H_{12}	0.9		
t-Caproic acid	$2–4\cdot10^{12}$	1 h	t-caproic acid	33		27
			H_2	34		
			CH_4	2.8		
			s-C_5H_{12}	0.8		
Phenylacetic acid	$7\cdot10^{13}$	2 h	$C_6H_5CH_2COOH$	30	33	28
Nicotinic acid	$2\cdot10^{13}$	48 h	nicotinic acid	6	150	29
Nicotinic acid	$1\cdot10^{13}$	72 h	nicotinic acid	23	100	30
o-Toluidinic acid	$1\cdot10^{13}$	72 h	*o*-toluidinic acid	25	100	30
Salicylic acid	$1\cdot10^{13}$	72 h	salicylic acid	31	100	30
Dimethyl ether	$3\cdot10^{13}$	48 h	H_2	77		31
			CH_4	4		
			CH_3OCH_3	16		
			$C_2H_5OCH_3$	3.2		
H_2O(liq.)	$2\cdot10^{9}$	144 h	H_2	10		35, 38
			H_2O	90		
H_2O(gas)	$2\cdot10^{9}$	144 h	H_2	4		35, 38
			H_2O	96		
H_2O(gas) + ^4He	$2\cdot10^{9}$	144 h	H_2	2		35, 38
			H_2O	98		
H_2O(gas) + NO	$2\cdot10^{9}$	144 h	H_2	4		35, 38
			H_2O	96		
H_2O(gas) + O_2	$2\cdot10^{9}$	144 h	H_2	1.5		35, 38
			H_2O	98.5		
Methyl α-glucoside	$2\cdot10^{12}$	24 h	methyl α-glucoside		100	7
2-Methyl-2-n-propyl-propyne-1,3-diol dicarbonate	$2\cdot10^{12}$	72 h	2-methyl-2-n-propyl-propyne-1,3-diol carbonate	6	50	7
Glucose diacetone	$2\cdot10^{12}$	24 h	glucose diacetone		100	7
Glucose diethyl-mercaptal	$2\cdot10^{12}$	24 h	glucose diethyl-mercaptal		100	7

Table 1 shows that 10–50% of the tritium forms a labelled parent molecule, 30–50% is obtained as HT molecules, and 5–25% appears as organic compounds more complex or simpler than the mother compound.

The gaseous reaction products from hot tritium atoms are qualitatively similar for most substances, while the liquid products depend on the structure of the parent molecule, the composition of the irradiated mixture, and the irradiation conditions.

The reactions of various classes of organic compound with recoil tritium atoms have been studied: saturated, unsaturated, and aromatic hydrocarbons[10,12,16], alcohols[19], ketones[19], esters[23], carboxylic acids[27], and other compounds[7,22,25,26]. The same types of reaction were observed with all these compounds. Data on the influence of radical

acceptors indicate that for most of the systems studied more than half of the recoil tritium atoms enter into reaction even in the high-energy region.

We shall now consider the types of reaction of recoil tritium atoms with organic compounds, using butane as an example, in decreasing order of probability.

Hydrogen Abstraction

This reaction proceeds mainly in the high-energy region, since the yield does not greatly depend on the presence of a radical acceptor; it also partly proceeds with thermal tritium atoms.

$$T^* + CH_3CH_2CH_2CH_3 \rightarrow \begin{matrix} CH_3CH_2\dot{C}HCH_3 \\ CH_3CH_2CH_2\dot{C}H_2 \end{matrix} + HT.$$

The formation of HT is also possible as a result of intramolecular elimination of hydrogen from an excited molecule.

Hydrogen Replacement

This reaction is insensitive to the presence of a radical acceptor, so that the parent molecule, as a rule, retains its configuration.

$$T^* + CH_3CH_2CH_2CH_3 \rightarrow \begin{matrix} CH_3CH_2CHTCH_3 \\ CH_3CH_2CH_2CH_2T \end{matrix} + H$$

The substitution reaction does not depend on the phase in which the recoil hydrogen atoms are stabilised. The determination of the intramolecular and intermolecular distribution of tritium in a system having hydrogen atoms in various positions shows that substitution occurs at all types of carbon–hydrogen bond in saturated, unsaturated, and aromatic compounds, etc. The substitution of hydrogen proceeds in random fashion in all positions; any variation in the specific activity of a given position is the result of the particular properties of the given molecule, for example, the *ortho*-position of *cis*-cinnamic acid has a lower activity than the same position in *trans*-cinnamic acid[25].

Where the tritium atom can react with hydrogen adjacent to either saturated or an unsaturated carbon–carbon bond, it reacts with about the same probability in each position[42], whereas for thermal hydrogen atoms there is a large difference in the rates of these reactions. The substitution of hydrogen atoms in organic molecules by tritium has high probability. The efficiency of a collision, as evaluated by Wolfgang, is several orders greater than than of collisions in thermal reactions which also demonstrates that these reactions occur in the high-energy region. However, the substitution reactions involving recoil tritium atoms do not take place by elastic collisions[48], as is seen by the relative amounts of tritiated methane obtained from CH_4 and CD_4.[32]

The substitution by recoil tritium atoms is a fast step in the reaction (10^{-14} sec), taking place in a time comparable with the period of vibration of the bond, and there is not always time for the excitation to be spread throughout the molecule; consequently there is local bond rupture only, and in most cases the configuration of the molecule is retained[20,22,23,45,46]. The attack by a recoil tritium atom on a hydrocarbon molecule, as already stated, may produce excitation of only part of the molecule; if the attack is along the line of a C–H bond or at a small angle to it and produces rupture of the C–H bond, the tritium atom combines with the hydrogen to form HT; if the direction of attack forms a large angle to the line of the C–H bond, the product after bond rupture will be RT.[32]

An empirical formula has recently been derived[32,34] for calculating the relative proportions of products obtained by reactions of types *I* and *II* involving aliphatic hydrocarbons.

Substitution of a Group of Atoms

This reaction produces degradation products from the original substance in yields which also do not depend on the presence of a radical acceptor:

$$T^* + CH_3CH_2CH_2CH_3 \rightarrow \begin{matrix} CH_3T \\ CH_3CH_2T \\ CH_3CH_2CH_2T \end{matrix}.$$

The replacement of a radical is less probable than replacement of hydrogen. After rupture of the C–C bond the tritium is more likely to combine with the simpler radical; a possible explanation of this has been given[47]. The yield of RT depends on the number of R groups in the irradiated compound; thus the yield of CH_3T is greater with neopentane than with isopentane, greater with the latter than with n-pentane, and least with cyclopentane.

The recoil tritium atoms can replace other atoms and groups in addition to H and CH_3; thus they readily replace $-NO_2$, $-NH_2$, $-COOH$, and $-OH$ groups and halogen atoms in corresponding benzoic acid derivatives[26].

Sometimes, it can be assumed that the substitution of a group of atoms is a secondary process. The replacement of hydrogen in the parent molecule by a recoil tritium atom produces an excited molecule, which decomposes with elimination of a group of atoms; for example, in the reaction of recoil tritium atoms with carboxylic acids an excited molecule is formed as an intermediate and then decomposes:

$$T^* + CH_3COOH \rightarrow \begin{matrix} CH_2TCOOH^* + H \\ \downarrow \\ CH_3T + CO_2 \end{matrix}.$$

The yield of decomposition products decreases as the carbon chain length is increased, because the excitation is extinguished within the molecule[8,27,37].

It has been shown[26,49,56] that in some cases the yield of labelled substitution products depends on the energy of the C–X bond, increasing with decreasing stability of the bond.

Substitution of Two Groups of Atoms

This reaction produces a labelled radical:

$$T^* + CH_3CH_2CH_2CH_3 \rightarrow \begin{matrix} CH_3CH_2CH_2\dot{C}HT + H_2 \\ CH_3CH_2\dot{C}HT + CH_3 + H \end{matrix},$$

and can give either two hydrogen atoms or one hydrogen atom and an alkyl group by elimination from the parent molecule. The radical produced may be captured by a radical acceptor, or in the absence of the latter it may decompose to a smaller radical and an alkene, by rupture of a C–C bond.

Low yields of products are usually obtained in this reaction[34,35].

TABLE 4. Introduction of recoil tritium atoms into cyclic hydrocarbons (flux: 4×10^{12} neutrons per cm^2 per sec); activity of parent compound taken as 100. Period of irradiation 5–10 h in the presence of Li_2CO_3.

Substance irradiated	Activity of reaction products, %							
	cyclohexane	cyclohexene	cyclohexa-1,4-diene	cyclohexa-1,3-diene	benzene	methylcyclohexane	methylcyclopentane	hexenes and hexanes
Cyclohexane	100	5	—	—	2	5	6	25
Cyclohexene	71	100	—	—	5	—	19	24
Cyclohexa-1,4-diene	39	92	100	32	175	—	—	—
Cyclohexa-1,3-diene	30	425	80	100	875	—	—	—
Benzene	—	1	11	5	100	0	0	0

TABLE 5. The fractions of recoil tritium atoms reacting with alcohols and acetone by the various types of reaction.

Type of reaction	Activity, %, as:		
	C_2H_5OH	CH_3OH	$(CH_3)_2O$
Replacement of inactive hydrogen by tritium	22	23	25
Replacement of labile hydrogen by tritium	20	29	12
Replacement of a methyl group by tritium	1	—	9
Formation of aldehyde from alcohol	2	1	—
Formation of aldehyde from acetone	—	—	1

TABLE 6. Yield of labelled products in the reaction of recoil tritium atoms with alkanes (yield of labelled parent compound taken as unity).

Labelled compound	Type of reaction	Starting compound								
		methane	ethane	propane	n-butane	isobutane	n-pentane	isopentane	neopentane	n-hexane
HT	H abstraction	1.0	1.82	1.97	1.99	1.92	2.37	2.03	1.40	3.28
Parent compound	H replacement	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Lower alkanes	replacement of alkyl group	—	0.12	0.15	0.15	0.17	0.19	0.21	0.23	0.31
Methyl iodide (initially CH_2T) in the presence of iodine	replacement of an alkyl group + H or + 2H	0.12	0.14	0.06	0.09	0.05	0.08	0.09	0.09	0.07
Alkene (initially a radical)	replacement of an alkyl group + H	—	0.11	0.08	0.08	0.09	0.10	0.09	0.05	0.12
Isomerisation and other products	–	—	0.03	0.00	0.01	0.01	0.00	0.00	0.01	0.02

Addition Reactions

A labelled radical is also produced in the reaction of recoil tritium atoms with unsaturated hydrocarbons:

$$T^* + R{-}CH_2{-}CH{=}CH{-}CH_2{-}R' \rightarrow R{-}CH_2{-}\dot{C}HT{-}CH{-}CH_2{-}R'^*.$$

The resulting radicals are excited, and decompose to form two or three fragments containing less carbon atoms than the parent molecule [12,34] and which retain the structure of the parent molecule, being produced by the rupture of a single bond. The yields of all products obtained in the reaction of recoil tritium atoms with alkenes are given in Table 2; these yields confirm the mechanism postulated by Rice [51] and McNesby [52] for the decomposition of hot radicals. The yield of HT increases and the yield of parent compound decreases as the molecular weight of the alkene increases, as with the alkanes.

In the reaction of hot tritium atoms with unsaturated cyclic compounds (cyclohexene and cyclohexadienes) the main products, besides the parent compound and hydrogen, are hydrogenation products: cyclohexene gives cyclohexane, and cyclohexadienes give mainly cyclohexene.

The probability of rupture of a C–C bond by addition of a recoil tritium atom to a double bond is lower in the case of cyclohexene and cyclohexadienes than with open-chain alkene (Table 4) [17].

Cyclohexadienes also give labelled benzene in large amount, a large quantity of benzene being obtained by radiolysis of the cyclohexadienes.

Recoil tritium atoms can also add to aromatic bonds [16], benzene producing a labelled cyclohexadiene radical which is subsequently converted into cyclohexa-1,4- or cyclohexa-1,3-diene. Since these compounds are formed without radiolytic carriers, they have a high specific activity and their production is of considerable interest. Compounds produced by opening of the benzene ring are obtained in very low yield (Table 4).

The relative yields of products obtained from alkanes, alcohols, and acetone by the various types of reaction are shown in Tables 5 and 6.

3. INFLUENCE OF VARIOUS FACTORS ON THE YIELD OF LABELLED COMPOUNDS

Influence of Radical Acceptors

Radical acceptors normally used in the gas phase are iodine vapour, bromine vapour, nitric oxide, oxygen, etc. Table 7 relates to the reaction of methane with recoil tritium atoms, and shows that these radical acceptors have the same efficiency [9].

It is seen from Table 7 that even small amounts of the radical acceptors have a large effect on the yields of the individual products. In the presence of radical acceptors at pressure above 1 mm the yield of labelled hydrocarbons of higher molecular weight than methane (*e.g.* ethane, propane, and butane) falls sharply, while the yield of labelled methyl halide remains constant. The presence of radical acceptors has no marked influence on the yield of labelled methane. The yield of HT first falls sharply, then with a pressure of radical acceptors > 1 mm falls very slowly. Similar effects are given by oxygen in the reaction of recoil tritium atoms with dimethyl ether [4].

The influence of iodine concentration on the yield of labelled products when liquid acetic acid is irradiated has been studied [27]. The tritium distribution in the gaseous products is almost independent of the iodine concentration when the latter is below 10^{-4}; with high iodine concentrations, the yield of hydrocarbons other than methane is markedly less, but does not fall to zero. Even with an iodine concentration as high as 10^{-2} M, when the iodine

TABLE 7. Reaction of recoil tritium atoms with methane in the presence of radical acceptors.

Radical acceptor	Temperature, °C	Pressure of radical acceptor	Yield of labelled products, %			
			HT	CH_3T	CH_2TX	$>C_1$
	above room temp.	0	0.535	0.325	0	0.14
Br_2	~ −100	~0.01	0.42	0.32	0.018	0.11
Br_2	~ −60	~0.6	0.37	0.345	0.042	0.015
I_2	above room temp.	~1	0.35	0.32	0.020	<0.01
Br_2	~ −45	2—2	0.32	0.36	0.037	<0.01
NO	above room temp.	~9	0.315	0.365	...	<0.01
Br_2	~ −15	~20	0.29	0.33	0.045	<0.01
Br_2	above room temp.	>20	0.23	0.30	0.042	<0.01

remains in the free state even after the irradiation, a considerable amount of ethane is formed, apparently because some of the radicals leave the liquid phase for the gaseous phase, where they are stabilised by the addition of hydrogen atoms to form stable chemical compounds. The yield of labelled parent compound is independent of the iodine concentration.

When liquid benzene is irradiated together with lithium carbonate in the presence of diphenylpicrylhydrazide, the yield of labelled benzene hydrogenation products decreases with increasing concentration of the diphenylpicrylhdrazide [16].

All these examples show that the presence of radical acceptors does not as a rule affect the yield of products obtained by substitution of tritium for hydrogen or a group of atoms. However, substances of the radical acceptor type do not always decrease the yield of labelled products; for example, the yield of labelled benzene in the reaction of recoil tritium atoms with benzene is increased by about 50% in the presence of iodine [40]. The explanation given is the formation of an intermolecular benzene–iodine complex, which promotes removal of energy from the excited labelled benzene molecule. The yield of labelled benzene is shown in Fig. 2 as a function of the iodine concentration.

Sauer [10] used ethylene as radical acceptor in the reaction of recoil tritium atoms with methane, ethane, and propane; as with halogens as radical acceptors, the yield of labelled hydrogen falls. It may be assumed that the reaction of thermal tritium atoms with ethylene:

$$C_2H_4+T \rightarrow C_2H_4T,$$

will compete successfully with the hydrogen abstraction reaction:

$$T+CH_4 \rightarrow CH_3+HT.$$

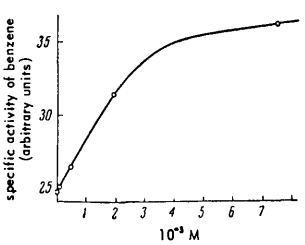


Fig. 2. Specific activity of benzene as a function of the iodine concentration.

The fact that the yield of labelled ethane from ethane and that of labelled propane from propane is unaffected by the presence of ethylene again confirms that these products are produced wholly by substitution of hydrogen in the initial molecule by a hot tritium atom. It might be expected that the presence of 8% of ethylene in the irradiation of ethane and propane would lower the yield of labelled molecules of these compounds, if only by a simple dilution effect, but in fact the yield remains constant. In this case it may be assumed that the radical C_2H_4T produced can form labelled molecules of the parent compounds, *e.g.* by the reactions:

$$C_2H_4T+C_2H_6 \rightarrow C_2H_5T+C_2H_4,$$

$$C_2H_4T+C_2H_6 \rightarrow C_2H_5T+C_2H_5,$$

and $$C_2H_4T+CH_3 \rightarrow C_3H_7T.$$

There is no reaction by which labelled methane could be produced from the ethyl radical, and therefore its yield decreases in the presence of ethylene.

Unlike halogen radical acceptors, which combine with tritium atoms to form hydrogen halides which are not detected when the irradiated mixture is analysed by gas chromatography, ethylene combines with tritium to form the radical C_2H_4T, the reaction products of which are readily detected by gas chromatography. Unlike halogens, ethylene only slightly reduces the yield of higher hydrocarbons.

Hydrogen readily enters into certain ionic-molecular reactions, and so to a certain extent can act as an ion acceptor and so hinders the formation of "higher" products. Since hydrogen is always produced in the irradiation of organic compounds, its influence must be investigated, and the system $^3He + CH_4 + H_2$ has been studied for this purpose [10]. Table 8 shows that there is no great change in the yield of labelled compounds when 20% of hydrogen is added to the methane. The cause of the reduced yield of CH_3T may be the formation of HT by reaction between hot tritium atoms and H_2, the greater retarding efficiency of H_2 as composed to CH_4, and exchange between thermal T atoms and H_2. All these factors increase the yield of labelled hydrogen. The reduction of the yield of synthesis products by half may be due to the decreased specific activity of the HT, if it is assumed that HT molecules participate in the production of more complex molecules.

TABLE 8. Influence of hydrogen on the yield of labelled products produced by irradiation of the system $^3He + CH_4 + H_2$ (yields reported as percentage of the total observed activity); partial pressure of CH_4 = 500–600 mm, partial pressure of ^3He = 6 mm.

Labelled products	Partial pressure of H_2, yield, %					Labelled products	Partial pressure of H_2, yield, %				
	0.3	0.9	5.3	9.3	12.3		0.3	0.9	5.3	9.3	12.3
H_2	50	52	65	75	74	C_5	0.3	0.5	0.2	0.2	0.2
CH_4	34	32	26	20	20	C_6	1.0	1.1	0.6	0.3	0.4
C_2H_6	7.5	7.4	4.1	3.0	2.8	C_6	—	0.5	0.2	—	0.2
C_3H_8	3.3	2.0	1.7	1.0	0.9	C_6	—	0.7	0.2	—	0.3
iso-C_4H_{10}	1.0	1.0	0.5	0.4	0.3	C_7	—	1.0	1.1	—	0.3
n-C_4H_{10}	1.0	1.1	0.7	0.4	0.4						

If radical acceptors are added to the system after the irradiation the yield of labelled products remains unchanged[3].

Influence of Inert Diluents

The introduction of inert substances into the organic compound–recoil tritium atom system, *e.g.* ^{4}He, Ne, Ar, Kr, etc. in the gaseous phase, suppresses the hot reactions and the only products are those of thermal processes, *i.e.* in the first instance the yield of parent compound is reduced[3,22]. The efficiency of retardation of the hot tritium atoms by the inert gases decreases on passing in the series from helium to xenon. These facts confirm that the recoil tritium atoms react with methane by "hot" reactions. The inert gases do not affect the yield of labelled products solely by the dilution effect, since with specimens containing the same molar fraction of different inert gases the yields are different, and decrease in the series Xe to He. The retarding capacity of the inert gases increases in the same series. In the reaction between recoil tritium atoms and a gaseous mixture of acetylene and propane the ratio of the specific activity of acetylene to that of propane increases linearly with the relative concentration of helium, because of thermal processes by which tritium is introduced into acetylene.

If a radical acceptor is present in addition to the retarding agent, the yield of labelled organic products is still further reduced: the yield of labelled methane from methane and recoil tritium atoms in the presence of helium and bromine is only 1%, the yield of HT is ~ 5± 5%, and higher hydrocarbons are absent[3]. The yield of higher hydrocarbons in the absence of a radical acceptor increases with decreasing molar fraction of the parent compound.

Hot tritium atoms may be slowed down by the sides of the ampoule in which the mixture is irradiated, and the dimensions of the ampoule may therefore affect the yield of labelled products. This effect was investigated by reacting recoil tritium atoms with methane in an ampoule containing quartz powder: however, the yield of labelled methane increased only to 37%,[3] which is within the limits of the experimental error (see Table 1).

The presence of quartz powder may appreciably affect the yield of labelled products in other reactions; thus the yields of individual products are greatly increased in the radiolysis of n-pentane in the presence of silica[30].

Influence of Temperature and Phase State of the Initial Compound on the Yield of Labelled Compounds

The yield of labelled products was not found to depend substantially on temperature in the range 0°–200°.[3] Further increase of temperature should affect the distribution of tritium among the labelled products, particularly when molecules larger than methane are irradiated. Thus it is known that in the radiolysis of gaseous pentane above 230° cracking occurs by chain reactions; for example, at 400° the yield of low hydrocarbons (up to C_5) is ~ 2000 moles per eV, which is ~ 10^3 times the yield at room temperature[31].

Change of the phase of the irradiated substance has no effect on the qualitative composition of the reaction products with recoil tritium atoms, but has a marked effect on their yield, as is demonstrated in the irradiation of liquid and gaseous methane and ethane (Table 1).

In the reaction of recoil tritium atoms with *trans*-but-2-ene and *trans*-hex-2-ene there is a considerable reduction in the yields of the alkene on passing from the gaseous to the liquid phase[54,55]. The yield of labelled parent molecules is also increased when cyclic hydrocarbons react with recoil tritium atoms in the liquid and solid phases[50].

In the reaction of recoil tritium atoms with gaseous, liquid, and solid acetone, the distribution of tritium among the products is independent of the phase of the acetone; however, with water the yield of labelled products is markedly different in the gaseous and liquid phases.

Substitution by hot and superthermal processes is thus the main reaction of hot tritium atoms, irrespective of the phase state of the system. In a condensed phase, however, the closer packing of the atoms and molecules enables the medium to absorb the excess of energy and motion from the activated complex obtained by collision. Moreover the radicals and atoms obtained by dissociation of the intermediate complex, which has too high an internal energy to form a stable compound directly, may be held together within a shell of surrounding molecules and so can recombine to produce the labelled compound. These effects explain the higher activity of the parent compound in the liquid phase as compared with the gaseous phase.

Passing from the liquid to the solid phase also has substantially no effect on the distribution of tritium in the products. Although the reaction mechanism in both condensed media is the same, the study of relatively more complex systems discloses some new and interesting effects. Studies of the irradiation by tritium of glucose and many larger molecules shows that about 20% of the tritium replaces hydrogen in C–H bonds of the parent molecule; hence the reactions of recoil tritium atoms in condensed systems can be considered as specific substitution or addition reactions which are more probable than random combination with radicals formed at the end of the free path. If the recoil energy at the end of the path were greater than required for hot substitution, it is difficult to see how a large molecule such as glucose would remain unchanged when the tritium atoms were introduced. These phenomena are in agreement with the calculations of Rowland and Wolfgang, who showed that recoil tritium atoms have a relatively long mean free path, and are not captured by the solvent until their energy is very low. This means that a very small number of radicals will be formed at the end of the path.

Influence of Radiolysis

Radiolysis produces decomposition of the parent material, forming radicals and molecules of new substances, which take part in chemical reactions by which the recoil atoms are stabilised. The yield of tritium-containing products and the distribution of tritium in the molecules will thus depend greatly on the radiolysis which accompanies the stabilisation of the recoil atoms. The labelled molecules will in their turn undergo radiolytic conversions.

The source of the radiolytic action is the γ-radiation from the nuclear reactor and the recoil nuclei of hydrogen, helium, and tritium. In most cases the recoil nuclei make the most contribution; when recoil nuclei are obtained from ^{3}He each act liberates 0.765 MeV. While the accompanying γ-radiation can be varied, it is difficult to vary the effect of the recoil nuclei. The influence of radiolysis on the labelled compounds will increase with the period of

exposure to the radiation, and can be shown by varying the period of irradiation or the intensity of the neutron flux. Specimens in which the parent compound is 10–20% decomposed will have a considerable proportion of radiolytic impurities, and the tritium distribution may differ greatly from that obtained when the parent compound is only little decomposed.

In some cases this effect is particularly marked, for example with alkanes, which are fairly inert to reactions with excited atoms and radicals; the impurities formed by radiolysis will play an important part in the final tritium distribution.

Table 9 shows the variation in the distribution of activity with the period of irradiation of cyclopropane. The labelled unsaturated compounds produced by the reactions with hot tritium atoms are rapidly saturated by reaction with hydrogen atoms, and the thermal tritium atoms react preferentially with the alkenes obtained by the radiolysis of the cyclopropane. In the initial stages of irradiation the main reactions will be hydrogen abstraction reactions:

$$H^{\cdot} + H_2C\!\!<\!\!\begin{matrix}CH_2\\ CH_2\end{matrix} \xrightarrow{K_1} H_2 + C_3H_5, \qquad (1)$$

$$R^{\cdot} + H_2C\!\!<\!\!\begin{matrix}CH_2\\ CH_2\end{matrix} \xrightarrow{K_2} RH + C_3H_5. \qquad (2)$$

but as time progresses the reaction products begin to build up, and can themselves react with the atoms and radicals:

$$H^{\cdot} + C_nH_{2n} \xrightarrow{K_3} C_nH_{2n+1}, \qquad (3)$$

$$R^{\cdot} + C_nH_{2n} \xrightarrow{K_4} R{-}C_nH_{2n}. \qquad (4)$$

The actual direction of the reaction will depend on the relative rates of the individual reactions (1)–(4) for the various radicals.

It is seen from Table 9 that the sum of the relative yields of propylene and propane remains approximately constant when the period of irradiation is varied by a factor of 70, although the individual yields are markedly different. This supports the suggestion that propylene reacts with hydrogen to form a propyl radical by reaction (3), *i.e.* saturated compounds are produced from unsaturated compounds. The total yield of ethane and ethylene is also approximately constant with different periods of irradiation.

TABLE 9. Influence of duration of irradiation on the yield of labelled products in the reaction of recoil tritium atoms with cyclopropane. The specimens contained 750 mm cyclopropane and 2 mm ^{3}He and were irradiated with a neutron flux of ~ 10^9 neutrons per cm^2 per sec. The activity of cyclopropane is taken as 100.

Period of irradiation, h	138	48	24	8	4	2	Period of irradiation, h	138	48	24	8	4	2
Percentage decomposition of initial compound	0.2	0.07	0.03	0.01	0.007	0.003	Percentage decomposition of initial compound	0.2	0.07	0.03	0.01	0.007	0.003
Labelled products	activity, %						Labelled products	activity, %					
△	100	100	100	100	100	100	C C–C	13	14	16	21	7	29
HT	141	138	147	140	153	150	C						
CH_3T	11	9	—	—	—	—	C–C–C–C	39	30	25	15	7	9
C–C	28	22	22	16	11		C_6	30	28	26	22	—	—
C=C	7	10	10	10	12	33	C						
C≡C	2	2	2	—	—	—	△	3	4	4	3	2	—
C–C–C	54	48	44	37	20	23							
C–C=C	9	15	22	31	49	54							

Starting from the assumptions that: (*i*) hydrogen atoms and alkenes are continuously produced in the irradiation of cyclopropane; (*ii*) the alkenes disappear only by reaction with hydrogen atoms according to reaction (3) with subsequent abstraction of hydrogen atoms; and (*iii*) the hydrogen atoms are removed only by reactions (1) and (3) and rapidly reach a stationary concentration, it is possible to obtain an approximate picture of the kinetic behaviour of the atoms and radicals produced in the irradiation of cyclopropane. Using the above assumptions as a basis, it is possible to construct a curve showing the variation of the alkene concentration with the period of irradiation. The shape of this curve will depend firstly on the G-values for hydrogen and the alkenes, and secondly on the ratio K_1/K_3. The alkene concentration becomes stationary after a certain time, and since the total activity increases linearly with the period of irradiation, the fraction of the total activity contributed by the alkenes continuously decreases.

Table 10 gives the data obtained[10] on the influence of the neutron flux on the yield of labelled products in the irradiation of ^{3}He in methane, ethane, and propane. Comparison of columns A and B shows that there is no marked change in the distribution of tritium in the labelled products with a tenfold change of neutron flux at a constant total dose of irradiation. Column C gives the results of experiments in which the pressure of ^{3}He (0.1 mm) was 60 times less than in A, with the period of irradiation correspondingly 60 times more. It can be estimated that the energy distributed in the reaction vessels in unit time by recoil nuclei of tritium and hydrogen in experiments A is 30 times the energy of the γ-radiation, while in experiments C the fraction of the total energy introduced by the γ-radiation is twice that introduced by the recoil nuclei.

The intensity of the ionising radiation in experiments C was thus 20 times less than in experiments A, but the total energy absorbed in C was 3 times that absorbed in A. Under these conditions the yield of HT in the reaction of recoil tritium atoms with methane increased from 51% to 61%, while the yield of higher compounds decreased to

TABLE 10. Influence of the dose intensity and total energy absorbed from recoil nuclei and γ-rays on the yield of labelled products obtained from carrying out the nuclear reaction ^{3}He(n,p)T in methane, ethane, and propane.

Radiation conditions	Methane				Ethane				Propane		
	A	B	C	D	A	B	C	D	A	C	D
Flux, 10^{12} neutrons per cm^2 per sec	2–3	20–30	2–3	2–3	2–3	20–30	2–3	2–3	2–3	2–3	2–3
Pressure of ^{3}He, mm	6	6	0.1	6	6	6	0.1	6	6	0.1	6
Period of irradiation	1 h	10 min	60 h	3 min	1 h	10 min	60 h	3 min	1 h	60 h	3 min
Labelled products	%				%				%		
H_2	51	51	61	65	60	57	63	70	61	62	75
CH_4	33	32	36	29	3.2	3.9	3.7	3.5	2.5	3.0	2.0
C–C	7.4	6.9	2.3	5.5	25	26	25	19	2.4	2.9	2.0
C–C–C	3.1	3.2	0.3	0.7	5.1	5.3	4.9	3.0	26	25	18
C C–C C	1.0	0.9	0.1	0.3	0.2	0.3	0.2	2.0	1.0	1.7	1.6
C–C–C–C	1.1	1.2	0.2	—	3.6	4.2	2.2	—	1.1	1.0	—
C_5	0.4	0.3	0.3	—	1.0	1.1	0.3	0.7	2.5	2.3	0.6
C_6	1.1	1.3	—	—	—	—	—	—	—	—	—
C_6	1.2	1.1	0.3	—	1.2	1.4	0.3	—	2.0	1.4	—
C_7	1.0	1.1	—	—	0.5	0.5	0.2	—	0.3	0.0	—
C_8	—	0.7	—		0.6	0.8	—	—	0.3	—	—

one-third its former value. Similar changes were observed by El-Sayed and Wolfgang[3] when the intensity of the neutron flux was varied by a factor of 2000. With ethane and propane, however, there is no such sharp difference between experiments A and C, apparently because while the radiolysis of methane produces mainly CH_3 radicals and H atoms, which react with thermal tritium atoms to give labelled hydrogen and labelled methane, and increasing the radiation dose increases the number of these radicals and so the total yield of labelled methane and hydrogen, the radiolysis of ethane and propane produces, in addition to the radical of the parent molecule and a hydrogen atom, considerable amounts of methyl and ethyl radicals, which give final products other than labelled parent compound and hydrogen. Increase of the radiation dosage will cause thermal tritium atoms to react with these radicals also, so increasing the yield of methane in the irradiation of ethane, and of methane and ethane in the irradiation of propane. This assumption finds ready confirmation in the data of Table 10. It is interesting to note that irradiation of methane, ethane, and propane for 3 min in a flux of 2×10^{12} neutrons cm^{-2} sec^{-1} gives a higher yield of labelled hydrogen than irradiation for 1 h in the same flux; this is apparently because in the short time of 3 min the system does not have time to attain a state of equilibrium, *i.e.* the concentration of radicals has not reached a stationary value. In such a case the thermal tritium atoms will react mainly with the parent compound with the abstraction of a hydrogen atom and the formation of labelled hydrogen.

When lithium salts are used to obtain the recoil tritium atoms the dosage from the recoil atoms is considerably reduced by taking particles of the salt of a certain diameter. The free path of recoil tritium atoms of initial energy 2.7 MeV is much greater than the average size of the particles of a finely ground salt. By choosing large salt particles a large fraction of the free path of the recoil atoms will lie within the particles. The free path of α-particles is 20% less than that of the recoil tritium atoms, so that the diameter of the particles can be so chosen that all the α-particles remain in the crystal, while the tritons leave it with reduced energy. It has been shown experimentally that for a given specific activity the life of the irradiated compound is greater when using coarse particles than with the salt as a fine powder. For example, the irradiation of cholesterol mixed with 60 μ particles of lithium oxalate gave a good yield of a substance having a specific activity of 200 μc g^{-1}; the same amount of irradiation using 30 μ particles gave greater decomposition, and the use of a lithium myristate gel caused the formation of an insoluble product from which no cholesterol could be isolated[39].

The stability of various compounds to irradiation is given in Table 11; it decreases with increasing molecular weight of the irradiated compound.

TABLE 11. Stability of some organic compounds towards radiation.

Substance irradiated	Mol. wt.	Li salt in irradiated mixture, %	Flux, 10^{12} neutrons per cm^2 per sec	Period of irradiation	Introduction of tritium into irradiated compound, %	Survival of irradiated compound, %	Ref.
Methane	16	90	5	30 sec	47	100	11
Ethane	30	90	5	30 sec	41	100	11
Ethanol	46	12	2	6 h	23	95	19
Benzene	78	50	4	100 h	26	60	16
Cyclohexa-1,4-diene	80	50	4	10 h	17	30	17
Cyclohexa-1,3-diene	82	50	4	10 h	11	75	17
Benzoic acid	122	17	2	40 h	—	35	7
Ditto		5	2	154 h	—	66	7
»		1	2	700 h	—	56	7
Nicotinic acid		10	2	48 h	6	$\sim$ 50	7
Phenylacetic acid	136	3	2	3 h	31	$\geqslant$ 95	7
Glucose	180	50	0.006	72 h	10	$\geqslant$ 95	21
Galactose	180	10	2	27 h	12	$\geqslant$ 32	21
Phenyltriphenoxysilane	393	1	10	12 h	24	$\geqslant$ 76	53
Tetraphenoxysilane	411	1	10	12 h	23	73	53
Reserpine	608	10	2	2 h	18	6	7

4. THE ISOTOPE EFFECT OF RECOIL TRITIUM ATOMS

When recoil tritium atoms were reacted with partially deuterated methane molecules, the activity (calculated per atom of hydrogen or deuterium) was greater for HT than for DT[36] (Table 12). For CH_2D_2 the ratio HT/DT is 1.4, which is in good agreement with the ratio of the vibrational frequencies for C–H and C–D bonds. The ratio HT/DT = = 1.27 obtained for a mixture of CH_4 and CD_4 is a combination of the relative probability of reaction of a recoil atom with each molecule and the probability of the abstraction of hydrogen from the parent molecule. The ratio HT/DT = 1.6 for a mixture of H_2 and D_2 also includes these two probabilities, and also a factor due to the large difference in the velocities of the centres of mass in the reaction of H_2 and D_2 with a tritium atom of the given velocity[33].

TABLE 12. Reactions of recoil tritium atoms with deuterated methane and deuterium; irradiation for 48 h in a flux of 3×10^9 neutrons per cm^2 per sec.

	Pressure, mm Hg			HT/DT	HT/DT $\frac{CH_4}{CD_4}$	HT+DT $\frac{CH_3DT+CHD_2T}{}$	HT/DT $\frac{H_2}{D_2}$
CH_2—D_2	CH_2D_2	^3He	NO	1.34+0.02		0.84	
	746	29	—	1.40+0.02	—	0.83	
	260	29	—			0.83	
	102	29	—	1.42+0.02	—	0.90	
	747	14	56	1.19+0.07	—	0.82	
CH_4—CD_4	CH_4 CD_4	^3He	NO			$\frac{HT+DT}{CH_3T+CD_3T}$	
	338 398	14	—	1.09	1.29	0.82	
	552 181	14	—	3.83	1.26	0.82	
	374 374	11	56	1.28	1.28	0.80	
H_2—D_2	H_2 D_2	^3He	NO				
	396 310	17	—	1.97	—	—	1.55
	612 90	17	—	9.93	—	—	1.45
	120 581	17	—	0.35	—	—	1.68
	304 321	10	4.3	2.65	—	—	2.79

In the reaction of recoil tritium atoms with isopropyl benzoate it was found[23] that the isotope effect H/D is 1.41 for aliphatic hydrogen atoms and 1.16 for aromatic. The introduction of tritium into benzene[16] gave an isotope effect of 1.14.

The difference in the isotope effects for aliphatic and aromatic hydrogen atoms may be because in the latter case the tritium is initially captured by the aromatic bonds and this is followed by elimination of a hydrogen atom, while in aliphatic hydrocarbons there is first a weakening of the C–H bond and then replacement of hydrogen by tritium.

5. THE INTRAMOLECULAR DISTRIBUTION OF RECOIL TRITIUM ATOMS IN THE LABELLED PRODUCTS

Normally a labelled compound obtained by reaction with a recoil tritium atom is active in all hydrogen positions, but the relative tritium content in different positions varies greatly in many cases; for instance, the labelled benzoic acid obtained from *o*-hydroxybenzoic acid has 87% of the total activity of the molecule in the *ortho*-position, while the activity in the *para*-position is almost zero (Table 13).

In the general case the distribution of tritium within the parent molecules tends to an equal probability distribution. The intramolecular distribution will deviate from equal probability mainly because of steric factors; for example, the different tritium distributions in *cis*- and *trans*-cinnamic acids is because the COOH group in the former effectively screens one of the *ortho*-positions, and the tritium distribution in the *cis*-acid is approximately as if one of the *ortho*-positions has no tritium at all[25].

In cyclohexene the hydrogen at the double bond is more easily replaced by a recoil tritium atom than hydrogen at a saturated carbon atom; however, no such difference was observed with cyclohexa-1,3-diene[41].

The specific activities for individual hydrogen positions differ particularly greatly in molecules obtained as the result of decomposition of the parent molecule. It has been

TABLE 13. Intramolecular tritium distribution in the reaction products of hot tritium atoms.

Substance	Activity in the given position, %	Activity per hydrogen atom, %	Ref.
Ethanol	36 26 38	12 13	17
Cyclohexanol	60 40	5.4 40	17
Isopropyl benzoate	64 6 30	13 6 5	23
Toluene	*o* 34.0 *m* 28.0 *p* 16.0 22.0	17.0 14.0 16.0 7.3	18,40
Glucose	3 (3) 6 (6) 29 (50) 14 (2) 0 (23) 48 (16)	3 6 29 14 0 24	21(22)
Galactose	8 5 22 32 11 22	8 5 22 32 11 11	22
Benzoic acid obtained from: *o*-$NH_2C_6H_4COOH$	*p* 1 *m* 7 *o* 92	1 3.5 46	26
m-$NH_2C_6H_4COOH$	*p* 7 *m* 86 *o* 7	7 43 3.5	26
p-$NH_2C_6H_4COOH$	*p* 88 *m* 12 *o* 0	88 6 0	26
o-$NO_2C_6H_4COOH$	*p* 8 *m* 10 *o* 82	8 5 41	26
m-$NO_2C_6H_4COOH$	*p* 7 *m* 80 *o* 13	7 40 6.5	26
p-$NO_2C_6H_4COOH$	*p* 78 *m* 19 *o* 3	78 9.5 3	26

TABLE 13 (contd).

Substance	Activity in the given position, %	Activity per hydrogen atom, %	Ref.
o-HOC_6H_4COOH	*p* 0 *m* 13 *o* 87	0 6.5 43.5	26
m-HOC_6H_4COOH	*p* 8 *m* 82 *o* 10	8 41 5	26
p-HOC_6H_4COOH	*p* 77 *m* 12 *o* 11	77 6 5 5	26
o-BrC_6H_4COOH	*p* 4 *m* 7 *o* 89	4 3.5 44.5	26
m-BrC_6H_4COOH	*p* 7 *m* 84 *o* 9	7 42 4.5	26
p-BrC_6H_4COOH	*p* 72 *m* 22 *o* 6	72 11 3	26
o-IC_6H_4COOH	*p* 8 *m* 9 *o* 84	7 4.5 42	26
m-IC_6H_4COOH	*p* 12 *m* 86 *o* 2	12 43 1	26
o-FC_6H_4COOH	*p* — *m* — *o* 64	— — 32	26
m-FC_6H_4COOH	*p* — *m* 82 *o* —	41 — —	26
o-ClC_6H_4COOH	*p* — *m* — *o* 86	— — 43	26
p-ClC_6H_4COOH	*p* 72 *m* — *o* —	72 — —	26
o-$C_6H_4(COOH)_2$	*p* 7 *m* 24 *o* 69	7 12 34.5	26
Aniline obtained from: *o*-$NH_2C_6H_4COOH$	*p*, *m* 4 ±4 *o* 96±4	4 —	26
m-$NH_2C_6H_4COOH$	*p*, *m* 12±1 *o* 88±1	12 —	26
p-$NH_2C_6H_4COOH$	*p*, *m* 75±1 *o* 25±1	75 —	26
Phenylacetic acid	*p* 18.3 *m* 29.0 *o* 29.0 1.6	18.3 14.5 14.5	28
Benzoic acid	*p* 21 *m* 36 *o* 43	21 18 21.5	25
Benzoic acid	2.2 94 7.2	2.2 47 3.6	43
cis-Cinnamic acid	*p* 23.5 *m* 42 *o* 22.5 β, α 12	23.5 21 11,25 —	25
trans-Cinnamic acid	*p* 16.8 *m* 30.8 *o* 33.4 β 11.5 α 7.6	16.8 15.4 16.7 11.5 7.6	25
trans-Cinnamic acid Na salt	*p* 16.8 *m* 30.8 *o* 33.4 β 11.5 α 7.6	16.8 15.4 16.7 11.5 7.6	25
L(+)-Alanine(solid)	β 80 α 20	27.0 20	20
L(+)-Alanine(aq. soln.)	β 100 α 0	33.3 0	20
D(−)-Alanine obtained from *L*(+)-alanine	β 100 α 0	33.3 0	20
D(−)-Alanine obtained from *L*(+)-alanine(aq. soln.)	β 86.5 α 14.5		20
Cyclohexene	at the C=C bond 24.4 at the C—C bonds 75.6	12.2 9.5	41
Cyclohexene obtained from cyclohexa-1,3-diene	at the C=C bond 13.6 at the C—C bonds 86.4	6.8 10.8	41
Cyclohexa-1,3-diene	at the C=C bond 28.5 at the C—C bonds 75	12.5 12.1	41

shown[26] that in labelled benzoic acid obtained from substituted benzoic acids 70–90% of the tritium occupies the position of the original substituent atom or radical, and as a rule the activity in other positions decreases as the distance from this position increases. A compound labelled in a particular position can be obtained in this way.

With *L*(+)-alanine the intramolecular tritium distribution depends on the irradiation conditions[20]. Alanine irradiated as crystals has 82 ± 2% of the tritium in the β-position and 18 ± 2% in the α-position, while when irradiated in aqueous solution it has 98 ± 2% and 2 ± 2% of the total activity in these positions respectively.

Variation of the period of irradiation and the intensity of the neutron flux by a factor of ten has no noticeable effect on the distribution of tritium in benzoic acid obtained from substituted benzoic acids.

Comparison of the intramolecular tritium distribution in toluene, benzoic acid, and *trans*-cinnamic acid demonstrates that the substituents have little influence on the distribution of tritium within the aromatic ring.

It should be noted that Okamoto[43] obtained results on the intramolecular distribution of tritium in benzoic acid which were completely different from those obtained by Milford and Rowland[25].

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The characterisitics which have been described for the reaction of recoil atoms and ions with a substance make it possible to choose the best method for the synthesis of labelled compounds. The choice of the initial mixture to be irradiated, the irradiation conditions, and the subsequent treatment to isolate the labelled products is dictated not only by the product which must be obtained, but also by the mechanism by which the product is obtained from the initial substance. Each mixture to be irradiated and each product desired requires individual choice of materials to be added, the method of irradiation, the isolation of the product, and so on. However, the following general considerations can be applied with benefit in choosing the conditions for the hot synthesis of labelled compounds.

1. The reaction products of hot atoms contain the labelled parent molecule, but the specific activity of the latter cannot be high, since because of radiolysis the optimum period of irradiation is 100–200 h for reaction with recoil carbon-14 atoms, and 10–20 h for tritium.

A considerable fraction of the labelled compounds is made up of products obtained by substitution of carbon-14 or tritium for atoms or radicals such as nitrogen, halogens, and the C_2H_5 group. These products are obtained with high specific activity.

Hydrogenation of unsaturated compounds and dehydrogenation reactions are also characteristic of reactions with tritium. The most probable reaction is the replacement of atoms of similar mass, carbon and nitrogen for carbon, and hydrogen for tritium. In many cases the substitution is accompanied by molecular rearrangement.

A considerable fraction of radioactive atoms forms high-boiling products, polymers, particularly in the case of reaction products obtained from recoil ^{14}C atoms. Products of decomposition of the molecule, *i.e.* the gaseous fraction, play a particularly large part in the case of tritium

2. If the molecule of the initial substance takes part directly in the reaction with a hot atom, the substance must be stable to radiation, and the irradiation conditions must reduce radiation effects to a minimum.

3. If the desired labelled product is the product of reaction of a hot atom with fragments of the initial molecules produced by radiolysis, the initial substance should give the maximum number of such fragments on irradiation. The irradiation conditions will also be chosen with this mechanism of product formation in mind.

4. If the product is formed by hot reactions, the phase state of the system is unimportant; however, if the product is expected to be formed by a superthermal reaction, it is best to irradiate solid samples. For maximum yield of products of thermal reactions the irradiation is best conducted in the liquid or gaseous phase.

5. In all cases the irradiation must be effected at temperatures at which the substance is thermally stable; the temperature has no influence on the yield of products from hot reactions, but does influence the yield from thermal reactions, since altering the temperature affects the lability and life-time of individual radicals. Subsequent heating of the mixture may also be useful in increasing the yield of labelled products from thermal reactions.

6. All additives dilute the irradiated substance. To decrease the dilution effect when additives are added (*e.g.* nitrogen-containing substances in the irradiation of hydrocarbons) they may be used in an insoluble form, *i.e.* heterogeneous systems may be employed.

7. The specific action of additives is dictated by the mechanism of formation of the labelled substance. Thus the dilution effect is the main influence on the yield of hot reactions, while the addition of radical acceptors considerably reduces the yield of labelled compounds obtained by superthermal reactions.

8. Addition of substances which can become excited reduces the decomposition, by the radiation, of the initial materials and the products of their reactions with hot atoms, and so increases the yield of such products.

9. Additives which undergo normal chemical reaction with the labelled products decrease the yield of the latter, because of secondary thermal reactions.

10. Substances which under the irradiation conditions produce fragments able to take part in the formation of the required labelled compounds should presumable increase their yield.

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HYDROXIDE CHLORIDES AND HYDROXIDES OF ELEMENTS OF THE SCANDIUM SUBGROUP AND OF THE LANTHANIDES

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I. INTRODUCTION

Basic salts† and hydroxides of metals play a large part in chemical technology and chemical analysis. Several industrial processes for the fractionation of the rare-earth metals have made use of differences in the basic properties of their hydroxides. Study of heterogeneous systems of the type $M^{n+}-OH^-Cl^-H_2O$, containing sparingly soluble basic salts or hydroxides in the solid phase, reveals new properties of these systems.

Investigation of the dependence of the composition and properties of the solid phases on the composition of the solution and the conditions of precipitation have shown that systems containing different metals behave differently. For example, those containing zinc [1], indium [2], and especially cadmium [3] are sharply distinguished in behaviour from those involving the rare-earth elements (r.e.e.)[4].

The dependence of the composition and properties of basic salts and hydroxides on the anion (chloride) concentration shows the possibility of employing hydroxides or basic chlorides of zinc and cadmium in the separation of the r.e.e., these hydroxides being used not only as precipitants but also as "separators" and carriers.

A chloride solution of such a metal can be applied as eluent in the separation of the r.e.e., with an indifferent electrolyte (NaCl) for the fine regulation of pH in such systems. This opens up new possibilities in the technological separation of the r.e.e. It is therefore of interest to summarise the results obtained on the basic salts and hydroxides of the r.e.e., from the point of view of their composition and properties as affected by their conditions of formation.

Previous reviews [5,6] have been concerned mainly with the basic properties of these elements, and have compared various series of relative basicity. The generalisations made by the authors of these reviews were based on theoretical considerations and experimental work only on the potentiometric titration of salt solutions with alkalis and on some preparative work.

† The Russian text refers frequently throughout to *basic chlorides*; this has been translated *hydroxide chlorides* as oxide chlorides do not appear to be covered (Ed. of Translation).

II. METHODS OF STUDYING BASIC SALTS AND HYDROXIDES

We limit our examination of methods used in the study of basic salts and hydroxides of metals to those which are employed for the investigation of compounds formed by precipitation from salt solutions. The study of basic salts and hydroxides involves determination of the composition of the solid phase as a function of the conditions of precipitation (concentrations, temperature, time of standing of the system, etc.) and of the properties of these compounds (solubility product, solubility, thermodynamic parameters, crystalline and optical properties, etc.). Methods of studying basic salts and hydroxides can be usefully divided into two groups.

The first group comprises methods which enable only the composition of the compounds to be determined.

The composition of a precipitated solid phase can be determined by the following methods: (*a*) the preparative–analytical method [7-10], consisting in isolation of the pure solid phase with subsequent chemical analysis of the preparation, or in analysis of the product after filtration, allowing for the quantity and composition of the mother-liquor which it contains; (*b*) physicochemical analysis, based on examination of the dependence of the properties of the system on its composition, the following properties being used to determine the composition of the solid phase: solubility [8,11], pH, [11] electrical conductivity [11-13], light absorption (turbidimetry) [13,14], apparent volumes of precipitates [11,15], heats of formation of these compounds [11,16-20], and also Schreinemakers' [7,21-23] and the fourth-component methods [24,25]; (*c*) electrometric methods, including conductimetric titration [26,27], electrical conductivity [28-31], polarography, and potentiometry; (*d*) among other methods must be included acidometric titration (precipitation at constant pH) [32-37], dehydration at constant pressure [38], and thermography [22,39].

The second group combines the following methods, by means of which not only the composition but also the properties of compounds can be determined, in particular solubility products: (*a*) electrometric methods (potentiometry and polarography); and (*b*) methods employed for identification, determination of crystal structure, homogeneity, and several other properties.

Often two or more methods are combined in order to obtain a fuller characterisation of the compounds investigated. Let us examine in greater detail the methods of the second group.

1. ELECTROMETRIC METHODS

A. Potentiometry

Almost all methods for determining the most important characteristic of sparingly soluble basic salts and hydroxides, the solubility product, depend on measuring the pH of the solutions, and the most reliable and exact method for the latter purpose involves potentiometric measurements.

Potentiometric titration. This enables us to determine the pH at which precipitation starts, the quantity of alkali required for complete precipitation, and also the pH at which formation of the hydroxide salt begins [40-42].

Many investigators use pH values of the start of formation of precipitates, when alkali is added to salt solutions, for calculating solubility products of metal hydroxides, although the composition of the compound which is formed is unknown[40-45].

Determination of activity solubility products (SP_a) of metal hydroxides from variation of pH with concentration of metal salt. This method, based on the relation between pH, SP_a, and the activities of the metal ions in the equilibrium heterogeneous system, was employed by Aksel'rud and Fialkov[46].

$$pH = \frac{1}{n} \log \frac{SP_a}{K_w^n [M^{n+}] \gamma_M^{n+}} . \quad (1)$$

In order to determine SP_a a series of salt solutions of different concentrations is prepared, the corresponding metal hydroxide is added, and the solutions are shaken up until equilibrium is reached, after which the pH and the metal ion concentration are measured. From these data the solubility products (SP) are measured, and graphical extrapolation of log SP to zero concentration yields $\log SP_a$.

This method was employed by Korenman[47] to determine SP_a for lead hydroxide.

A similar method was used by Feitknecht and his coworkers[48-51].

Determination of the composition and activity solubility products of basic salts and hydroxides from variation in pH with the activity of the simple salt in solution in the heterogeneous system. In the heterogeneous equilibrium formed by the solution together with the precipitated basic salt, the dissolved compound dissociates according to the equation

$$M_x(OH)_y A_z \rightleftarrows xM^{n+} + yOH^- + zA^{m-}.$$

Replacing a_{OH} by K_w/a_H in the expression for the activity solubility product, taking logarithms, and solving for pH, we obtain

$$pH = \frac{1}{y} \log SP_a - \frac{x}{y} \log a_M - \frac{z}{y} \log a_A - \log K_w. \quad (2)$$

If no other salts are present in the solution, we have for a salt M_aA_b

$$C_{M^{n+}} = aC_{salt}, \quad (3)$$

$$C_{A^{m-}} = bC_{salt}. \quad (4)$$

Substituting for ionic activities in Eqn. (2) the product of the salt concentration, from Eqns. (3) and (4), and the mean activity coefficient of the salt $\gamma_\pm$, we obtain

$$pH = \frac{1}{y} \log SP_a - \log K_w - \frac{1}{y} \log a^x b^z - \frac{x+z}{y} \log C_{salt} \gamma_\pm. \quad (5)$$

Since the first three terms on the right-hand side of Eqn. (5) are constants, x, y, and z can be determined as the smallest integral values from the equation $nx = y + mz$ (which follows from the electroneutrality condition) and the slope of the plot of pH against $\log a_{salt}$ obtained by measuring the pH of solutions at several different salt concentrations.

The composition of a hydroxide salt is often expressed by the formula $xM(OH)_n.yM_aA_b$, and Eqn. (5) then becomes

$$pH = \frac{1}{nx} \log SP_a - \log K_w - \frac{1}{nx} \log a^{(x+ay)} b^{by} - \frac{x+ay+by}{nx} C_{salt} \gamma_\pm. \quad (6)$$

Dobrokhotov[52] used this method to study systems involving sulphates of bivalent metals. In conformity with Eqn. (6) he employed for a basic salt having the composition $xM(OH)_2.yMSO_4$ the equation

$$pH = \frac{1}{2x} \log SP_a - \log K_w - \frac{x+2y}{2x} \log C_{salt} \gamma_\pm. \quad (7)$$

Rotinyan and Kheifets[53,54] studied hydroxides and basic salts by an essentially similar method. They used an equation linking the free energy of formation of a sparingly soluble compound with pH and the activity of the salt in the solutions:

$$pH = \frac{\Delta G^0_{bs}}{2.3nxRT} - \log K_w - \frac{1}{nx} \log a^{(x+ay)} b^{by} + \frac{x+ay+by}{nx} \log C_{salt} \gamma_\pm, \quad (8)$$

where ΔG^0_{bs} is the change in free energy accompanying dissociation of the basic salt.

Correspondingly, when hydroxide is present in the solid phase we have

$$pH = \frac{\Delta G^0_h}{2.3nRT} - \log K_w - \frac{1}{n} \log C_{salt} \gamma_\pm. \quad (9)$$

The described versions of the potentiometric method are subject to important restrictions on their applicability. They can be used only for an electrolyte MA. Moreover, the solutions should contain only the salt under investigation, and must not contain any other electrolytes. Furthermore, calculations can be made on the basis of Eqns. (5) and (7)–(9) only with solutions of very low concentrations, for which the ionic strength rule is valid.

Method involving determination of three variables. Aksel'rud and Spivakovskii[55] worked out a potentiometric method for studying basic salts and hydroxides of metals by determination of the activities of all three ions forming the basic salt.

In Eqn. (2) the three variables are the activities of the metal ions, hydrogen ions, and the anions. When the solid phase in equilibrium with the solution is constant in composition, this equation represents a plane having a definite slope relative to the coordinate axes $\log a_M$, $\log a_A$, and pH. A change in composition changes the slope of the plane.

The complete differential of Eqn. (2) in partial derivatives gives

$$\left(x \frac{\partial \log a_M}{\partial pH} + z \frac{\partial \log a_A}{\partial pH} + y \right) dpH + \left(x \frac{\partial \log a_M}{\partial \log a_A} + y \frac{\partial pH}{\partial \log a_A} + z \right) d \log a_A +$$

$$+ \left(x + y \frac{\partial pH}{\partial \log a_M} + z \frac{\partial \log a_A}{\partial \log a_M} \right) d \log a_M = 0. \quad (10)$$

In order to find the composition of the precipitate, it is necessary to find the slope of the plane represented by Eqn. (2), which is readily done by making one of the variables constant, *i.e.* by finding the slope of the line of intersection of this plane with the plane perpendicular to one of the coordinate axes.

If $\log a_A$ is taken to be constant, Eqn. (10) becomes

$$\left(x \frac{\partial \log a_M}{\partial pH} + y \right) dpH + \left(x + y \frac{\partial pH}{\partial \log a_M} \right) d \log a_M = 0, \quad (11)$$

whence

$$\left[\frac{\partial \log a_M}{\partial pH} \right]_{a_A} = -\frac{y}{x}. \quad (12)$$

Similarly, by taking $\log a_M$ or pH constant, we can show that

$$\left[\frac{\partial \log a_A}{\partial \mathrm{pH}}\right]_{a_M} = -\frac{y}{z}, \quad (13)$$

or

$$\left[\frac{\partial \log a_A}{\partial \log a_M}\right]_{\mathrm{pH}} = -\frac{x}{z}. \quad (14)$$

Any of the Eqns. (12)–(14) can be used to find x, y, and z, since these quantities are linked by the equation $nx = y + mz$.

The method described is applicable to the study of systems over a wide range of salt concentrations, in the presence of high concentrations of some other salts having a common anion. By measuring the activity of the ions after definite intervals of time and determining from these data the composition and the activity solubility products, it is possible to study the aging of precipitates with time. Quintin[56–59] used this method, of determining the activities of the three ions constituting the basic salt, in studying heterogeneous systems.

B. Polarography

Kovalenko[45,60,61] employed the polarographic method to establish the start of precipitation of a hydroxide or a basic salt during potentiometric titration. The solubility products were calculated from the pH of precipitation and the composition of the solution.

2. METHODS USED FOR IDENTIFICATION, DETERMINATION OF CRYSTAL STRUCTURE AND HOMOGENEITY, AND SOME OTHER PROPERTIES

Often basic salts and hydroxides are studied by more than one method. It is not our task to make any detailed examination of these methods, and we shall therefore confine ourselves to listing those which are most frequently met: X-ray diffraction[36,39,62–81], crystal optics[13,80,82,83], electron-microscopy[83–85], absorption spectroscopy[29] (including infrared spectroscopy[86], fluorescence analysis[67], and magnetic analysis[72,83]), measurement of specific surface[79], and study of catalytic properties[87].

III. TITRATION CURVES OF RARE-EARTH SALT SOLUTIONS

Many investigators have studied the potentiometric titration of rare-earth salt solutions with alkalis.

Hildebrand[88] found that precipitation begins at pH ≃ 7 from solutions of praseodymium and neodymium chlorides, and at pH ≃ 4 from the corresponding nitrate solutions. Later Britton[40] showed that this difference is due to catalytic reduction of the NO_3^- ion at the hydrogen electrode.

Britton[40] titrated (with the hydrogen electrode) 0.01 M solutions of cerium, praseodymium, neodymium, samarium, and yttrium chlorides and lanthanum and neodymium nitrates. He showed that, whereas lanthanum begins to be precipitated at pH 8.35, the remaining r.e.e. give precipitates over a comparatively narrow pH range between 7.41 and 6.78. In spite of the small difference in pH of the start of precipitation, a diminution in basicity was established in the sequence La, Ce, Pr, Nd, Sm, and Y. Britton placed the rare-earth metals between magnesium, bivalent manganese, and bivalent nickel on his relative basicity scale of metals[89].

Sadolin[90] made a series of potentiometric titrations of lanthanum salt solutions with sodium hydroxide. Precipitation began at pH 8.4.

Šterba-Böhm and Melichar[91] found that a deposit starts to come down at pH 6.1 when a 0.1 M solution of scandium acetate is titrated with potassium hydroxide.

Bowles and Partridge[92] used a glass electrode in the titration of ~0.1 M solutions of lanthanum, cerium, praseodymium, neodymium, ytterbium, and thorium sulphates and lanthanum and neodymium chlorides with sodium hydroxide at 25°, and showed that precipitation occurs at rather lower pH values from sulphate solutions than from chloride solutions.

Oka[93] carried out a similar titration on 0.05 M solutions of lanthanum, cerium, and yttrium nitrates, and found the same sequence of precipitation as did other workers.

Moeller and Kremers[43] carried out the potentiometric titration of ~0.1 M solutions of the nitrates, sulphates, and acetates of La, Ce, Pr, Nd, Sm, Eu, Gd, Er, Tm, Yb, Lu, and Y. Their results show that there is fundamentally a fall in the pH of precipitation in the series of rare-earth elements. The precipitation pH during titration generally increases in the sequence: sulphates, nitrates, acetates. The higher precipitation pH with acetates was explained by the tendency of the acetate ion to form complexes with the r.e.e. ions, thus diminishing the activity of the latter. The low pH of precipitation from sulphate solutions was attributed to the coagulating action of the bivalent ion on the intermediate colloidal solutions.

Ivanov-Emin and Ostroumov[94] showed that basic compounds of scandium are precipitated over the pH range 4.8–5.5, and this was confirmed by Vickery[14] by a turbidimetric titration method.

Ermolenko[95] carried out the potentiometric titration of 0.01 M solutions of La, Nd, Sm, Y, Gd, and Yb perchlorates

TABLE 1. pH of start of precipitation of rare-earth basic salts and hydroxides.

Element	pH of start of precipitation				
	SO_4^{2-}	Cl^-	NO_3^-	CH_3COO^-	ClO_4^-
La	7.61 [92] 7.41 [43]	8.03 [92]	8.35 [40] 8.71 [93] 7.82 [43]	7.93 [43]	8.76 [95] 8.10
Ce	7.07 [92] 7.35 [43]	7.41 [40]	8.1 [93] 7.6 [43]	7.77 [43]	
Pr	6.98 [92] 7.17 [43]	7.05 [40]	7.35 [43]	7.66 [43]	7.40
Nd	6.73 [92] 6.95 [43]	7.02 [40] 7.40 [92]	7.00 [43] 7.31 [43]	7.59 [43]	7.6 [95] 7.3
Sm	6.70 [43]	6.83 [40]	6.92 [43]	7.40 [40]	7.57 [95] 7.13
Eu	6.68 [43]		6.82 [43]	7.18 [43]	6.91
Gd	6.75 [43]		6.83 [43]	7.10 [43]	7.45 [95] 6.81
Y	6.83 [43]	6.78 [40]	7.39 [93] 6.95 [43]	6.83 [43]	7.57 [95] 6.81
Er	6.50 [43]		6.76 [43]	6.59 [43]	6.61
Tm	6.21 [43]		6.40 [43]	6.53 [43]	
Yb	6.16 [92] 6.18 [43]		6.30 [43]	6.50 [43]	7.30 6.45 [95]
Lu	6.18 [43]		6.30 [43]	6.46 [43]	6.45
Sc		4.8 [94]		6.1 [92]	

with 0.1 M sodium hydroxide. In this case, too, a decrease in precipitation pH was observed in the series of rare-earth elements.

Available pH values for the start of the precipitation of hydroxides or basic salts, obtained by potentiometric titration, are given in Table 1.

IV. STUDY OF HETEROGENEOUS SYSTEMS OF THE TYPE M^{n+}–OH^-–Cl^-–H_2O

A modification of the potentiometric method has been developed[55] for the study of heterogeneous systems of the type M^{n+}–OH^-–Cl^-–H_2O, and hence for the determination of the composition, conditions of formation, and activity solubility products of basic salts and hydroxides of metals. This "three-variable method" has been used to study systems of the above type involving metals of the scandium subgroup and lanthanides. A solubility method[11] has also been used to study some systems (those containing cerium[96], lanthanum, and yttrium[4]).

In the three-variable method it is necessary to determine the activities of the metal ion, the anion, and the hydroxide ion. No difficulty is entailed in determining the latter two activities in systems containing the chloride anion. The determination of metal-ion activities is a considerably more complicated matter.

The rare-earth metals do not form reversible electrodes. Even those which yield amalgams cannot be used for potentiometric measurements, since on immersion in aqueous solutions they do not form electrodes which are reversible with respect to the metal ions. Therefore a method has been found for calculating approximately activities of the metal ions in solutions containing MCl_3 and NaCl.[97]

In order to calculate the mean activity coefficients of rare-earth chlorides in solutions containing sodium chloride, it is necessary to know their values $(\gamma_\pm)_0$ in the absence of other electrolytes, and also the concentration of metal ions C_M and the concentration and activity of chloride ions in the test solution. The unknown mean activity coefficient of the chloride $(\gamma_\pm)_x$ is calculated by means of the equation

$$(\log \gamma_\pm)_x = \log (\gamma_\pm)_0 + k[\log (C_M)_0 - \log (C_M)_x], \qquad (15)$$

where for the systems studied the coefficient k has the value 0.05.

From the mean activity coefficient of the chloride $(\gamma_\pm)_x$ and the activity coefficient of the chloride ion $\gamma_- = a_{Cl^-}/C_{Cl^-}$ the activity coefficient of the metal ion is calculated

$$\gamma_+ = \frac{\gamma_\pm^{1+n}}{\gamma_-^n}. \qquad (16)$$

Below are given some results obtained in the study of actual systems.

1. COMPOSITION OF HYDROXIDE CHLORIDES

Hydroxide chlorides of the rare-earth elements correspond mainly to one of the formulae $M(OH)_2Cl$ and $M(OH)_{2.5}Cl_{0.5}$.[4,96,98-101] Other types of hydroxide chlorides have also been found. Thus, yttrium and dysprosium form the compounds $M(OH)_{1.75}Cl_{1.25}$ in freshly prepared systems[4,99], cerium forms $Ce(OH)_{2.33}Cl_{0.67}$, while praseodymium yields $Pr(OH)_{2.66}Cl_{0.34}$.

On adding NaOH to $Nd_2(SO_4)_3$ solution Tananaev and Levina[102] precipitated basic salts predominantly of the composition $Nd_2(OH)_4SO_4$.

From the results obtained by a study of heterogeneous equilibria in the systems M^{n+}–OH^-–Cl^-–H_2O it can be concluded that the composition of the precipitate depends on the activities of metal and chloride ions and the length of time during which the systems have been allowed to stand. In all cases in which two or more precipitates have been formed in the systems up to a certain time, that precipitate whose composition approximated more closely to the hydroxide was formed at lower ionic activities. A decrease in the activities of metal and chloride ions was found to result in the formation of a hydroxide salt close to the hydroxide in composition or to formation of the hydroxide itself.

These results correspond to our earlier[55] theoretical ideas concerning the sequence of precipitation of basic salts and hydroxides.

Variation in ionic concentration affects the composition of the solid phase in different ways. A change in concentration of one type of ion has a considerable effect not only on its own activity but also on that of the other types of ions, and this in turn influences the composition of the basic salt which is precipitated and hence the pH at which precipitation takes place.

The composition of the precipitate depends also on its age, *i.e.* on the time which has elapsed since it was formed. During the aging of precipitates two processes can occur, change in composition and recrystallisation. Both processes yield more stable precipitates with greater changes in free energy.

The general tendency during the aging of precipitated r.e.e. hydroxide chlorides is for the relative content of hydroxide ions to increase right until the precipitates are converted into hydroxides.

The only exception which we have discovered is the conversion of freshly precipitated yttrium hydroxide into $Y(OH)_{2.5}Cl_{0.5}$ after 125 days. This can be explained by the greater stability of this hydroxide salt compared with the freshly precipitated hydroxide.

2. PRECIPITATION pH OF HYDROXIDE CHLORIDES AND HYDROXIDES

One of the most important parameters of these heterogeneous equilibria is the solution pH. The equilibrium values are determined by the nature of the ions, their activities, and the composition and state of the solutions and precipitates.

The dependence of solution pH in heterogeneous systems on these factors is represented by Eqn. (2)

$$pH = \frac{1}{y} \log \frac{SP_a}{K_w^y a_M^x a_A^z}.$$

It is evident from this equation that, when a basic salt is present in a precipitate, an increase in the activities of the metal ion and the anion should result in a decrease in pH, and this is confirmed by all the experimental results which we have obtained[4,96,98-101].

If, however, we consider the dependence of pH not on the activities but on the concentrations of the ions, we obtain a

different picture. This relation can be represented by an equation which can be derived from that given above

$$pH = \frac{1}{y}\left(\log\frac{SP_a}{K_w^y C_M^x C_A^z} - \log\gamma_M^x\gamma_A^z\right).$$

It is seen from this equation that an increase in concentration of metal ions and of the anion should result in a fall in pH. However, the change in composition of the solution is accompanied by a change in the activity coefficients of the ions. Therefore it is impossible to predict the sign or magnitude of the change in pH with change in composition of the solution in equilibrium with the precipitate, unless the variation of the ionic activity coefficients with solution composition is known.

The effect of the nature of the anion on the precipitation pH of metal hydroxides has been investigated by us previously [103]. It was shown that the chloride, sulphate, and nitrate ions influence the pH of precipitation of zinc hydroxide (from dilute solutions) to the extent that they affect the activity of zinc ions. If, however, basic salts are precipitated, the pH is influenced by the anion concentration as a result not only of the effect of the latter on the metal ion activity but also of the fact that the anion forms part of the precipitate.

Since a relation was discovered which enabled an estimate to be made of the mean activity coefficient of the chloride when mixed with sodium chloride, the possible variation in pH with change in solution composition in rare-earth systems can be traced back. As an example, Fig. 1 shows the variation of the mean activity coefficient of yttrium chloride with the logarithm of the chlorine concentration (curve *1*). It can be seen that, up to a chloride ion concentration close to 1 g-ion litre^{-1}, there is some decrease in $\gamma_\pm$, but further increase in the YCl_3 concentration is accompanied by a rapid increase in $\gamma_\pm$. In conformity with the above-mentioned rule [97], increase in the sodium chloride concentration at a constant YCl_3 concentration in the mixture should also result in the activity coefficient of the YCl_3 beginning to increase when the concentration of chloride ions in the solution exceeds 1 g-ion × × litre^{-1}.

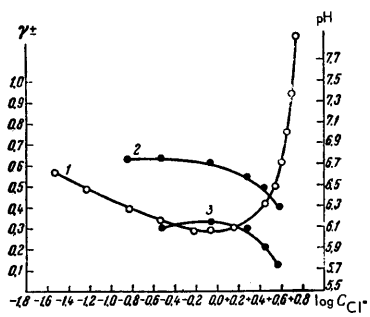


Fig. 1. Dependence, on log C_{Cl^-} of equilibrium heterogeneous system, of: 1) $(\gamma_\pm)_{YCl_3}$; 2) pH of freshly prepared system; 3) pH after standing for 30 days.

Increasing the NaCl concentration at a constant YCl_3 concentration should result in an increase in the chloride-ion activity in the solution, in conformity with curve *2* in Fig. 1, *i.e.* to a decrease in the pH of the equilibrium solution. However, at chloride-ion concentrations below 1 g-ion litre^{-1} an increase in the chloride concentration is accompanied by a decrease in activity of the yttrium ions. But this latter decrease should result in some increase in pH. Thus raising the chloride-ion concentration to 1 g-ion litre^{-1} influences the pH in opposite directions at the same time, the increased activity of chloride ions lowering the pH, while the simultaneous fall in activity of the yttrium ions raises the pH. Both effects depend on the composition of the precipitate. The closer it is to the hydroxide, the smaller the drop in pH with increasing chloride-ion activity, and this results in the decrease in yttrium activity having a more noticeable effect on the rise in pH.

At chloride-ion concentrations exceeding 1 g-ion litre^{-1} the activities of chloride and yttrium ions are both increased. Therefore an increase in the NaCl beyond this concentration of chloride ions should produce a sharp decrease in solution pH. This is confirmed by curves *2* and *3* in Fig. 1, which show the dependence of the equilibrium solution pH on the chloride-ion concentration in the presence of 0.05 M YCl_3 in the solution. Curve *2* corresponds to the basic chloride $Y(OH)_{1.75}Cl_{1.25}$ constituting the solid phase, and curve *3* to $Y(OH)_{2.5}Cl_{0.5}$. In both cases the fall in pH occurs at $C_{Cl^-} >$ > 1 g-ion litre^{-1}. In the case of curve *2* at $C_{Cl^-} <$ 1 g-ion × × litre^{-1}, the decrease in pH with increase in chloride-ion concentration is balanced by the increase in pH due to the simultaneous decrease in the yttrium ion activity. With curve *3*, however, where the composition of the precipitate has become closer to that of the hydroxide, the compensation is no longer complete, and a maximum appears on the curve.

A similar dependence of solution pH on the chloride-ion concentration is observed with systems containing other rare-earth metals.

It is often necessary to calculate solution pH for heterogeneous systems with specified concentrations of the solution components: the above considerations lead to an equation for calculating the pH in such systems [104].

When the systems are allowed to stand (age) the composition of the precipitates changes, the basic salts passing into others closer in composition to the hydroxide, or into the hydroxide itself; moreover, in time the precipitates become consolidated, which results in a decrease in the solution pH. The magnitude of this decrease after a given period of time at constant temperature depends on the concentration of the metal chloride, becoming smaller with increase in this concentration.

An exception to this rule of the fall in solution pH in heterogeneous systems with time is provided by the behaviour of systems involving relatively concentrated solutions, in particular the zinc system which we have studied [1].

The results obtained for M^{n+}–OH^-–Cl^-–H_2O systems involving r.e.e. indicate that they have very similar properties and that they vary in a regular manner. Thus, with increase in atomic number the pH of the heterogeneous systems rises in the scandium subgroup, but falls somewhat in the lanthanide group. It is interesting to trace the variation in pH of the solutions in equilibrium with the precipitates as the nuclear charge increases in systems having the same metal- and chloride-ion activities. Table 2 gives

TABLE 2. Mean difference in pH between neighbouring rare-earth elements for solutions of identical activities in heterogeneous systems (ΔpH).

Element	ΔpH	Element	ΔpH
Sc—Y	—2.23	Eu—Gd	0.13
Y—La	—1.35	Gd—Tb	0.07
La—Ce	0.42	Tb—Dy	0.04
Ce—Pr	0.25	Dy—Ho	0.05
Pr—Nd	0.17	Ho—Er	0.01
Sm—Eu	0.13		

the mean differences in solution pH in the freshly prepared heterogeneous systems (ΔpH) for adjacent elements in the rare-earth series.

The solution pH for the heterogeneous systems rises in the scandium subgroup, but falls in the lanthanide group. The value of ΔpH decreases in the scandium subgroup, being considerably greater for Sc–Y than for Y–La. This indicates that, with regard to the precipitation pH of basic salts and hydroxides, yttrium is more similar to lanthanum than to scandium.

On passing from light to heavy lanthanides the value of ΔpH between neighbouring metals becomes smaller. Hence it follows that, with increasing atomic number in this series, not only do the basic properties of the hydroxides become weaker, but the differences in these properties also diminish.

3. ACTIVITY SOLUBILITY PRODUCTS AND FREE ENERGIES OF FORMATION OF HYDROXIDE CHLORIDES AND OF HYDROXIDES OF THE RARE-EARTH ELEMENTS

The rare-earth hydroxide chlorides and hydroxides, precipitated from aqueous solutions of the salts, are sparingly soluble. Therefore the activity solubility products constitute one of the main characteristics of these compounds.

Table 3 gives the activity solubility products of the r.e.e. hydroxides and hydroxide chlorides. The free energies of formation of these compounds from the elements, also included in this table, have been calculated from the activity products and from standard values for the free energies of formation of the r.e.e. ions, hydroxide ions, and chloride ions.

For comparison, Table 4 gives values of the activity solubility products for the r.e.e. hydroxides and published values of the solubility products.

Table 4 includes also the solubility products of lanthanum, yttrium, lutetium, and scandium hydroxides estimated by Latimer [105] from available electrochemical data.

Dependence of activity solubility product on concentrations and activities of ions in solution. The activity solubility products of metal hydroxide chlorides and hydroxides often depend on the chloride-ion activity. This variation occurs mainly with the freshly prepared precipitates. Thus SP_a for almost all basic chlorides of rare-earth metals, formed in freshly prepared systems and having the composition $M(OH)_2Cl$, and compounds having a higher chlorine content depends on the chloride-ion activity, the relation $\log SP_a = f(\log a_{Cl^-})$ usually being linear (Table 4).

In some cases the SP_a of compounds $M(OH)_{2.5}Cl_{0.5}$ close to the hydroxide in composition and even of the hydroxide itself also depends on the chloride-ion activity. Although these compounds are found in aged systems, the precipitates themselves of this composition probably exist for a short time, and this applies especially to scandium and holmium hydroxides, which were formed 33 and 50 days after preparation. Values of SP_a for aged precipitates do not depend on the chloride-ion activity. The concentration of ions in the solution probably influences the structure and the rate of change of the precipitate. After the precipitates have become stabilised with time, this effect diminishes, and finally SP_a ceases to depend on the chloride-ion activity. For example, $SP_{a,Ho(OH)_3}$ depends on the chloride-ion activity according to the equation $\log SP_a = -26.18 - 0.66 \log a_{Cl^-}$ after one day's aging, but after 150 days it no longer depends on the chloride-ion activity.

Variation of SP_a during aging of hydroxide salts and of hydroxides. The changes in composition undergone by hydroxide chlorides during aging (allowing the systems to stand for a time) involve an increase in the negative free energy of the compounds, *i.e.* the activity solubility products become smaller. These changes occur in jumps associated with changes in composition of the compounds (Table 3).

The dependence of the activity products of r.e.e. hydroxides and basic salts on the age of these precipitates indicates that, when the composition of the precipitate remained constant with time, its activity product underwent a steady decrease. For example, the activity solubility product of $La(OH)_2Cl$ varied from 2.6×10^{-15} for the fresh precipitate to 4.4×10^{-16} after 65 days. With lutetium the hydroxide having $SP_a = 2.23 \times 10^{-27}$ was formed after 100 days, but after 150 days the same compound showed $SP_a = 1.02 \times 10^{-27}$. It follows from these examples that, in contrast to the stepwise change in SP_a with systems in which aging involves a change in composition of the precipitates, the change in SP_a of precipitates which age without change in composition is monotonic.

Dependence of SP_a and ΔG^0 of rare-earth hydroxides and hydroxide chlorides on atomic number. The activity solubility products of the basic salts and the hydroxides show the great similarity of rare-earth compounds of the same type and also their regular variation.

Fig. 2 shows the variation with atomic number of $\log SP_a$ for the hydroxide chlorides and the hydroxides of the scandium subgroup of elements and of the lanthanides. It shows also the dependence of the ionic radii [111] of these elements on their atomic numbers.

A similar relation is observed for the free energies of formation of the r.e.e. ions, hydroxide chlorides, and hydroxides (Fig. 3).

Values of $\log SP_a$ and of ΔG^0 of the compounds $M(OH)_2Cl$ are given for the freshly prepared precipitates, and analogous values of the compounds $M(OH)_{2.5}Cl_{0.5}$ and $M(OH)_3$ for precipitates which have been kept for 50 and 150 days respectively.

It is seen from the diagrams that, whereas the scandium subgroup shows an almost linear rise in SP_a and ΔG^0 of the

TABLE 3. Activity solubility products and standard free energies of formation of rare-earth hydroxide chlorides and hydroxides.

Compound	Age of precipitate	SP_a	$-\Delta G^0 = 2.3RT \log SP_a$, kcal mole^{-1}	$-\Delta G^0_{298}$, kcal mole^{-1}
1	2	3	4	5
$Sc(OH)_2Cl$	5 min	$10^{(-22.09+0.7\log a_{Cl^-})}$	$30.05 - 0.95\log a_{Cl^-}$	$280.25 - 0.95\log a_{Cl^-}$
$Sc(OH)_2Cl$	200 days	2.19×10^{-22}	29.55	279.75
$Sc(OH)_{2.5}Cl_{0.5}$	200 days	6.76×10^{-27}	35.70	289.02
$Sc(OH)_3$	200 days	2.00×10^{-30}	40.52	296.98
$Y(OH)_{1.75}Cl_{1.25}$	5 min	$10^{(-15.11+1.29\log a_{Cl^-})}$	$20.61 - 1.76\log a_{Cl^-}$	$289.64 - 1.76\log a_{Cl^-}$
$Y(OH)_2Cl$	30 days	$10^{(-16.44+\log a_{Cl^-})}$	$22.43 - 1.36\log a_{Cl^-}$	$293.03 - 1.36\log a_{Cl^-}$
$Y(OH)_{2.5}Cl_{0.5}$	100 days	$10^{(-22.02+0.57\log a_{Cl^-})}$	$30.04 - 0.78\log a_{Cl^-}$	$303.76 - 0.78\log a_{Cl^-}$
$Y(OH)_{2.5}Cl_{0.5}$	125 days	4.0×10^{-22}	29.20	303.92
$Y(OH)_3$	5 min	6.8×10^{-24}	31.61	308.47
$Y(OH)_3$	125 days	3.2×10^{-25}	33.42	310.28
$La(OH)_2Cl$	5 min	2.57×10^{-15}	19.90	299.30
$La(OH)_2Cl$	40 days	2.0×10^{-15}	20.05	299.45
$La(OH)_2Cl$	65 days	4.4×10^{-16}	20.96	300.36
$La(OH)_{2.5}Cl_{0.5}$	65 days	4.3×10^{-19}	25.06	308.65
$La(OH)_3$	166 days	2.0×10^{-22}	29.60	15.25
$Ce(OH)_{2.33}Cl_{0.67}$	5 min	2.0×10^{-18}	24.15	83
$Ce(OH)_3$	5 min	6.3×10^{-22}	28.92	313.18
$Pr(OH)_2Cl$	5 min	1.02×10^{-16}	21.81	298.01
$Pr(OH)_{2.5}Cl_{0.5}$	100 days	5.49×10^{-20}	26.28	306.20
$Pr(OH)_{2.66}Cl_{0.34}$	5 min	2.51×10^{-21}	28.10	308.63
$Pr(OH)_3$	100 days	8.32×10^{-23}	30.12	313.17
$Nd(OH)_{1.5}Cl_{1.5}$	5 min	$10^{(-12.92+1.4\log a_{Cl^-})}$	$17.63 - 1.91\log a_{Cl^-}$	$284.49 - 1.91\log a_{Cl^-}$
$Nd(OH)_2Cl$	5 min	2.0×10^{-17}	22.78	296.78
$Nd(OH)_3$	30 days	$10^{(-23.32-0.88\log a_{Cl^-})}$	$31.82 + 1.20\log a_{Cl^-}$	$312.77 + 1.20\log a_{Cl^-}$
$Nd(OH)_3$	110 days	1.3×10^{-24}	32.61	313.56
$Nd(OH)_3$	120 days	1.3×10^{-24}	32.61	313.56
$Sm(OH)_2Cl$	5 min	$10^{(-17.12+0.84\log a_{Cl^-})}$	$23.36 - 1.14\log a_{Cl^-}$	$296.86 - 1.14\log a_{Cl^-}$
$Sm(OH)_3$	33 days	$10^{(-25.64-0.97\log a_{Cl^-})}$	$34.98 + 1.32\log a_{Cl^-}$	$314.73 + 1.32\log a_{Cl^-}$
$Eu(OH)_2Cl$	5 min	$10^{(-17.48+1.02\log a_{Cl^-})}$	$23.85 - 1.39\log a_{Cl^-}$	$296.85 - 1.39\log a_{Cl^-}$
$Eu(OH)_{2.5}Cl_{0.5}$	50 days	$10^{(-21.63+0.52\log a_{Cl^-})}$	$29.51 - 0.71\log a_{Cl^-}$	$305.63 - 0.71\log a_{Cl^-}$
$Eu(OH)_3$	150 days	2.88×10^{-27}	36.21	315.48
$Gd(OH)_2Cl$	5 min	$10^{(-17.32+0.56\log a_{Cl^-})}$	$23.63 - 0.76\log a_{Cl^-}$	$295.93 - 0.97\log a_{Cl^-}$
$Gd(OH)_{2.5}Cl_{0.5}$	200 days	7.6×10^{-24}	31.54	305.77
$Gd(OH)_3$	200 days	1.3×10^{-27}	36.67	314.03
$Tb(OH)_2Cl$	5 min	$10^{(-17.17+0.94\log a_{Cl^-})}$	$23.42 - 1.28\log a_{Cl^-}$	$295.32 - 1.28\log a_{Cl^-}$
$Tb(OH)_{2.5}Cl_{0.5}$	5 min	5.25×10^{-22}	29.03	304.05
$Tb(OH)_{2.5}Cl_{0.5}$	50 days	5.75×10^{-23}	30.34	305.36
$Tb(OH)_3$	50 days	1.62×10^{-26}	35.18	313.34
$Tb(OH)_3$	150 days	4.90×10^{-27}	35.89	314.04
$Dy(OH)_{1.75}Cl_{1.25}$	5 min	1.0×10^{-15}	20.46	286.59
$Dy(OH)_2Cl$	5 min	$10^{(-17.54+0.71\log a_{Cl^-})}$	$23.93 - 0.97\log a_{Cl^-}$	$292.23 - 0.97\log a_{Cl^-}$
$Dy(OH)_{2.5}Cl_{0.5}$	5 min	5.0×10^{-22}	29.3	300.10
$Dy(OH)_3$	50 days	1.3×10^{-26}	35.33	309.28
$Ho(OH)_2Cl$	5 min	$10^{(-17.43-1.05\log a_{Cl^-})}$	$23.78 - 1.43\log a_{Cl^-}$	$290.68 - 1.43\log a_{Cl^-}$
$Ho(OH)_{2.5}Cl_{0.5}$	50 days	6.92×10^{-23}	30.23	300.25
$Ho(OH)_3$	50 days	$10^{(-26.18-0.66\log a_{Cl^-})}$	$35.72 + 0.90\log a_{Cl^-}$	$308.87 + 0.90\log a_{Cl^-}$
$Ho(OH)_3$	150 days	2.82×10^{-27}	36.25	309.40
$Er(OH)_2Cl$	5 min	$10^{(-17.60+0.70\log a_{Cl^-})}$	$24.01 - 0.95\log a_{Cl^-}$	$289.37 - 0.95\log a_{Cl^-}$
$Er(OH)_{2.5}Cl_{0.5}$	50 days	1.3×10^{-22}	29.86	298.34
$Er(OH)_{2.5}Cl_{0.5}$	290 days	7.62×10^{-23}	30.17	298.64
$Er(OH)_3$	290 days	2.69×10^{-27}	36.14	307.86
$Yb(OH)_2Cl$	5 min	$10^{(-17.74+1.01\log a_{Cl^-})}$	$24.20 - 1.38\log a_{Cl^-}$	$281.04 - 1.38\log a_{Cl^-}$
$Yb(OH)_{2.5}Cl_{0.5}$	50 days	7.9×10^{-23}	30.15	296.63
$Yb(OH)_3$	275 days	2.29×10^{-27}	36.34	305.89
$Lu(OH)_2Cl$	5 min	$10^{(-17.99+1.16\log a_{Cl^-})}$	$24.54 - 1.58\log a_{Cl^-}$	$280.49 - 1.58\log a_{Cl^-}$
$Lu(OH)_{2.5}Cl_{0.5}$	50 days	$10^{(-22.89+0.34\log a_{Cl^-})}$	$31.23 - 0.46\log a_{Cl^-}$	$288.51 - 0.46\log a_{Cl^-}$
$Lu(OH)_3$	100 days	2.23×10^{-27}	36.36	305.11
$Lu(OH)_3$	150 days	1.02×10^{-27}	36.82	306.57

TABLE 4. Solubility products of rare-earth hydroxides.

Hydroxide	t, °C	Solubility product	Ref.	Hydroxide	t, °C	Solubility product	Ref.
$La(OH)_3$	18	$1.2\cdot10^{-19}$	90	$Eu(OH)_3$	25	$3.4\cdot10^{-22}$	43
	18	$1.1\cdot10^{-21}$	90		25	$0.9\cdot10^{-23}$	110
	25	$0.9\cdot10^{-21}$	106		25	$2.9\cdot10^{-27}$	172
	25	$4.3\cdot10^{-19}$	93, 107	$Gd(OH)_3$	25	$2.1\cdot10^{-22}$ *	43
	25	$1.0\cdot10^{-19}$	43		25	$1.8\cdot10^{-23}$	110
	25	$1.0\cdot10^{-20}$	105		25	$1.3\cdot10^{-27}$ *	**
	18	$6.0\cdot10^{-20}$	44	$Tb(OH)_3$	25	$4.9\cdot10^{-27}$ *	172
	18	$5.0\cdot10^{-21}$	44	$Y(OH)_3$*	25	$5.2\cdot10^{-22}$	93, 107
	18	$5.5\cdot10^{-22}$	44		25	$8.1\cdot10^{-23}$	43
	25	$1.7\cdot10^{-19}$	110		25	$1.0\cdot10^{-24}$	105
	18	$9.1\cdot10^{-23}$	44		25	$1.2\cdot10^{-24}$	44
		$2.5\cdot10^{-23}$	109		25	$1.6\cdot10^{-23}$	110
	25	$3.0\cdot10^{-22}$	108		25	$3.0\cdot10^{-25}$	108
	25	$2.0\cdot10^{-23}$ *	4		25	$3.2\cdot10^{-25}$ *	4
$Ce(OH)_3$	25	$0.8\cdot10^{-20}$	93, 107	$Dy(OH)_3$	25	$1.3\cdot10^{-26}$ *	99
	25	$1.5\cdot10^{-20}$	43	$Ho(OH)_3$	25	$2.8\cdot10^{-27}$ *	172
	18	$1.3\cdot10^{-23}$	44	$Er(OH)_3$	25	$1.3\cdot10^{-23}$	43
		$3.98\cdot10^{-25}$	109		25	$4.1\cdot10^{-24}$	110
	25	$6.3\cdot10^{-22}$	96		25	$2.7\cdot10^{-27}$ *	101
$Pr(OH)_3$	25	$2.7\cdot10^{-20}$	43	$Tm(OH)_3$	25	$3.3\cdot10^{-24}$	43
	18	$6.4\cdot10^{-24}$	44	$Yb(OH)_3$	25	$2.9\cdot10^{-24}$	43
	18	$7.1\cdot10^{-24}$	44		25	$2.5\cdot10^{-24}$	110
	25	$6.7\cdot10^{-22}$	110		25	$2.29\cdot10^{-27}$*	101
	25	$8.32\cdot10^{-23}$	**	$Lu(OH)_3$	25	$2.5\cdot10^{-24}$	43
$Nd(OH)_3$	25	$1.9\cdot10^{-21}$	43		25	$1.0\cdot10^{-25}$	105
	18	$5.3\cdot10^{-24}$	44		25	$1.9\cdot10^{-24}$	110
	18	$1.2\cdot10^{-24}$	44		25	$1.0\cdot10^{-27}$ *	**
	25	$3.2\cdot10^{-22}$	110	$Sc(OH)_3$	25	$1.0\cdot10^{-28}$	105
	25	$5.5\cdot10^{-24}$	108		25	$2.0\cdot10^{-30}$ *	**
	25	$1.3\cdot10^{-24}$ *	**	$Ce(OH)_4$	18	$1.9\cdot10^{-48}$	44
$Sm(OH)_3$	25	$6.8\cdot10^{-23}$	43				
	18	$2.1\cdot10^{-24}$	44				
	25	$8.4\cdot10^{-23}$	110				
	25	$1.3\cdot10^{-24}$	108				
	25	$1.3\cdot10^{-26}$ *	98				

* Hydroxide kept for 100–150 days.

** SP_a according to our results.

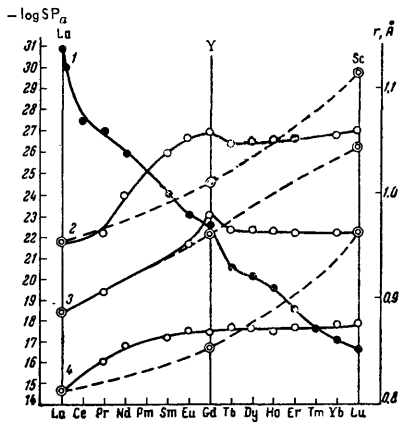


Fig. 2. Dependence of $\log SP_a$ of hydroxides and basic salts of elements of the scandium subgroup (broken lines) and of lanthanides (full curves) on the atomic number of the element: 1) variation of ionic radii with atomic number; $\log SP_a$ for the compounds: 2) $M(OH)_3$; 3) $M(OH)_{2.5}Cl_{0.5}$; 4) $M(OH)_2Cl$.

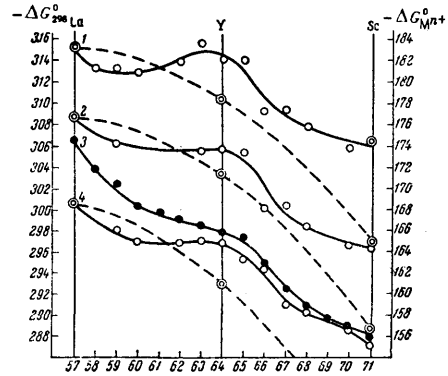


Fig. 3. Dependence of ΔG^0_{298}, on atomic number of elements of the scandium subgroup (broken curves) and the lanthanides (full curves), for the compounds: 1) $M(OH)_3$; 2) $M(OH)_{2.5}Cl_{0.5}$; 3) M^{3+}; 4) $M(OH)_2Cl$.

corresponding hydroxide chlorides and hydroxides from scandium to lanthanum, the lanthanides show the opposite dependence, a fall in SP_a and ΔG^0 with increasing atomic number. The curves exhibit a characteristic inflection [or maximum (Ed. of Translation)] at gadolinium, which becomes more marked on passing from hydroxide chlorides of the type $M(OH)_2Cl$ to the hydroxides.

The non-monotonic character of the variation in several properties of lanthanide compounds is well known. Wheelwright *et al.*[112] discovered a similar characteristic inflection on the instability constant/atomic number curve of the complexes formed by the lanthanides with ethylenediaminetetraacetic acid. This inflection, too, occurs at gadolinium. It was interpreted as due to a decrease in the coordination number starting from gadolinium, resulting from the decrease in ionic radii (steric factor). This could serve as an explanation in connection with compounds in which the ligands were large and complicated, occupying more than one coordination position. But it is difficult to explain such a variation in the properties of basic salts and hydroxides in this way.

The above phenomenon can be explained in a similar manner to secondary periodicity. The non-monotonic variation in the properties of chemical compounds of elements in groups of the Periodic System depends on the intensifying influence of the accumulating *d* and *f* electrons on bonds formed by *p* and especially *s* electrons[113]. The accumulation of 4*f* electrons and the appearance of 5*d* electrons in gadolinium affects the bonds formed by the $6s^2$ electrons.

V. BASIC PROPERTIES OF HYDROXIDES OF THE RARE-EARTH ELEMENTS

The rare-earth elements form the most basic oxides (hydroxides) of all tervalent elements[114–116]. They can form more basic oxides only when in the bivalent state[116], and less basic oxides when quadrivalent.

Evidence of the comparatively high basic strength of oxides of these metals is provided by the ease with which the oxides (even after being strongly heated, apart from scandium) dissolve in acids[116,117] and in ammonium salt solutions with the liberation of ammonia[117-121] and by the absorption of atmospheric carbon dioxide[117,122]. To these may be added the relatively high pH values at which the hydroxides are precipitated[4,96,98,99,101]. The hydroxides are such strong bases that the rare-earth metals cannot be determined by electrometric titration with caustic soda[123], this applying especially to elements of the cerium subgroup.

The high electrode potentials of the rare-earth metals[124], the tendency of the free elements to liberate hydrogen from water[105], the high heats of dissolution of the oxides in acids[125-129], and the comparatively high temperatures required for the thermal breakdown of the oxygen-containing salts[130-132] confirm the highly basic properties of these elements.

The fact that such compounds as the r.e.e. sulphides[133], cyanides[133], azides[134-136], carbides[137-139], and nitrides[137] undergo rapid hydrolysis indicates that these elements are less basic than the alkaline earth metals.

Although the r.e.e. hydroxides are such strong bases, they also possess some acidic properties, which develop especially in those hydroxides which are less basic in the series. This applies mainly to scandium. Thus, hydrated scandium hydroxide dissolves in concentrated potassium hydroxide, and from the solutions have been isolated crystals of $K_2HScO_5.6H_2O$ or $K_2[Sc(OH)_5.H_2O].3H_2O$.[14,91]

Although yttrium hydroxide does dissolve in potassium hydroxide, such solutions rapidly break down with the separation of crystalline yttrium hydroxide[91].

Fusion of lanthanum hydroxide with sodium or lithium carbonate yielded the readily hydrolysed $Na_2La_4O_7$.[140] Although Zambonini and Carobbi[141] were doubtful of the possibility of obtaining such compounds, Wunder and Schapiro[142] cited several facts in support of the amphoteric properties of neodymium and praseodymium.

Fusion of other rare-earth hydroxides with alkalis yields various compounds. Beck[143] obtained the compounds $KNdO_2$ and $KPr(OH)_4$ on fusing didymium oxide with potassium hydroxide. Zintl and Morawietz[144] prepared $NaLaO_2$ by fusing the oxides together at 500°. Products formed by reaction of oxides and carbonates of magnesium, calcium, strontium, and barium with the rare-earth elements at ~1500° have also been reported[145].

In spite of the presence of some acidic properties, it must be concluded that the rare-earth hydroxides have typical highly basic properties. These are indicated by the strength of the bond by means of which the metal ions retain the hydroxyls, and this bond strength can be measured by the free energy of dissociation of the hydroxide ($\Delta G^0 = -RT \ln SP_a$).

The work done in separating a hydroxide ion from the hydroxide can be calculated from data on the coulombic and polarisation interactions, allowance being made for the lattice energy of the hydroxide and the energy of hydration of the ions.

The basic properties of the hydroxides to some extent determine the ability of the elements to be more or less readily ionised, and of the salts to be hydrolysed in aqueous solution and to decompose on being heated.

Since the solubility of oxides and hydroxides of the metals in water and their degree of dissociation with elimination of hydroxide ions result in a change in the pH of the solution, this latter quantity, the pH of solutions saturated with the given hydroxide, can also serve as a measure of the basic strength.

The following properties and characteristics of the elements and their compounds have been used to establish relative basicities:

1. Molecular volumes of like compounds and cationic radii[146]. In the subgroups the basic strength increases in parallel with increase in these parameters.

2. Principal quantum numbers of valency electrons[116,147,148]. The principal quantum number of the valency electrons increases with increase in atomic number, resulting in a diminution in the bonding energy of the valency electrons as a Periodic Group is descended, so that the basic strength should increase. For example, in the series Sc–Y–La the valency electrons are in ns^2 and $(n-1)d'$ levels; the value of n increases in this series (4, 5, 6), so of course the basic strength also should increase. In the lanthanides subsequent electrons complete the fourth quantum level ($4f$), and with gadolinium and lutetium the $5d$ level as well, instead of filling the higher levels. As a result there is insufficient compensation of the growing forces of attraction between the nucleus and the outer electrons. These forces increase with atomic number, while the basic properties become weaker.

Hevesy's ideas[116,147,148] have found further development in the work of Stakelberg[149].

3. Ionisation potentials. An increase in ionisation potential indicates a weakening of the basic properties.

Owing to the absence of data for all metals in the lanthanide group, Klemm[150] postulated that the ionisation potentials increase in this group, and concluded that the basic properties diminish with increasing atomic number.

4. Ionic potentials‡.[153] The lower the ionic potential, the greater the basic strength of the hydroxide.

According to Cartledge[151,152] a hydroxide should be basic, amphoteric, or acidic according as the square root of the ionic potential $\sqrt{\varphi}$ is respectively < 2.2, between 2.2 and 3.2, or > 3.2.

According to Sun[154] the ionic potential is below 6 with basic hydroxides, and above 6 with hydroxides. This conclusion applies to ions having an electron octet. With 18 electron ions the limit of amphoteric properties is shifted to lower ionic potentials[115].

5. Values of AV/n^3 (A = atomic number, V = valency, and n = principal quantum number of highest quantum level in neutral atom)[155]. The basic strength increases as this quantity decreases. A hydroxide should be basic, amphoteric, or acidic according as this expression is < 1.44, ~ 1.44, or > 1.44.

6. Electrode potentials[156]. Abegg and Bodländer[156] assumed in their "theory of electroaffinity" that

‡ Z/r, where Z is the valency of the ion and r is its radius (Ed. of Translation)].

the electrode potential of a metal is an approximate measure of the strength of the corresponding base. The sequence of metals which they set up[156] does not always coincide with the relative position of the corresponding hydroxides as bases.

Heyrovský[157] attempted to rectify Abegg and Bodländer's classification by introducing the mass of the cation as a factor. However, this correction did not yield any considerable improvement.

7. Solubility. It was assumed that the basic properties of the hydroxides become stronger with increase in solubility[158].

8. Solubility products. In connection with the series rule, Tananaev[159] set up a sequence of hydroxides according to diminishing solubility product.

9. pH at start of precipitation. Britton[89] suggested a sequence of the metals according to the pH at which their hydroxides began to be precipitated from dilute solutions of the salts. An increase in pH at the start of precipitation indicates a strengthening of the basic properties of the hydroxides. Since the precipitation pH depends not only on the solubility product but also on the concentration of ions in the solution and on the nature of the anion, it is possible by varying the concentration of the salts and the nature of the anion to change both the pH of incipient precipitation and hence also the order of precipitation.

10. Heats of formation of oxides and salts, dissociation pressures of the salts, and their degree of hydrolysis. At the best these classifications can give only an approximate, qualitative, and relative characterisation of the metal hydroxides.

11. Normal pH values (pH_0)[160]. The equilibrium pH in the presence of a compound $M(OH)_yA_z$ as the solid phase in a heterogeneous system is governed by the equation

$$pH = \frac{1}{y}\log SP_a - \log K_w - \frac{1}{y}\log a_M - \frac{z}{y}\log a_A.$$

A change in the activity of the metal ions from $(a_M)_1$ to $(a_M)_2$ entails changes also in the hydrogen-ion concentration (from pH_1 to pH_2) and in the anion activity from $(a_A)_1$ to $(a_A)_2$, so that

$$pH_2 - pH_1 = \frac{1}{y}[\log(a_M)_1 - \log(a_M)_2] + \frac{z}{y}[\log(a_A)_1 - \log(a_A)_2. \quad (17)$$

This expression is valid provided that no change in the composition of the precipitate occurs during precipitation (y and z constant).

If $(a_M)_2$ is made equal to unity (*i.e.* with the metal ion at unit activity in the solution), pH_2 will represent the equilibrium value denoted by pH_0, and then

$$pH_1 = pH_0 - \frac{1}{y}\log(a_M)_1 - \frac{z}{y}[\log(a_A)_1 - \log(a_A)_2]. \quad (18)$$

The activity of the anions changes insignificantly during precipitation: *i.e.* $(a_A)_1 \simeq (a_A)_2$, and the equation becomes

$$pH_1 = pH_0 - \frac{1}{y}\log a_M, \quad (19)$$

with $(a_M)_1 = 1$ and $pH_1 = pH_0$. From the above it follows that

$$pH_0 = \frac{1}{y}\log SP_a - \log K_w - \frac{z}{y}\log a_A. \quad (20)$$

Hence it is evident that pH_0 is constant for a given anion activity and composition of the basic salt, as all the quantities in the expression for pH_0 are constants.

If, however, the hydroxide is precipitated ($z = 0$),

$$pH_0 = \frac{1}{n}\log SP_a - \log K_w,$$

i.e. for a hydroxide pH_0 is constant independently of the anion activity. Therefore pH_0 can form the basis of a quantitative classification of metal hydroxides or basic salts provided that the anion activity is constant.

Using values of SP_a which we have determined for a series of metal hydroxides, we have calculated the pH_0 values and compiled the series in Table 5.

12. Free energy of dissociation of hydroxides. In setting up the basicity series of the hydroxides it is necessary to compare ΔG^0 for metals of equal valency or else to take only that portion of ΔG^0 which corresponds to removal of the first hydroxide ion. The sequences of rare-earth metals according to basic strength obtained from the above properties of the elements are listed in Table 6.

Sequence 1 is based on theoretical considerations[116,146-155]. There were several deviations from this sequence. The atomic volumes of europium and ytterbium are extremely large. This is possibly because these elements crystallise in the cubic system, whereas all the remaining rare-earth metals belong to the hexagonal system.

TABLE 5. Sequence of hydroxides based on pH_0.

$Ba(OH)_2$	12.85	$Dy(OH)_3$	5.37	$Al(OH)_3$	3.43
$Sr(OH)_2$	12.24	$Zn(OH)_2$	5.3	$U(OH)_4$	2.75
$Ca(OH)_2$	11.38	$Tb(OH)_3$	5.23	$Pd(OH)_2$	2.5
$Mg(OH)_2$	8.80	$Eu(OH)_3$	5.15	$Tl(OH)_3$	2.19
$La(OH)_3$	6.77	$Ho(OH)_3$	5.15	$In(OH)_3$	1.84
$Pr(OH)_3$	6.64	$Er(OH)_3$	5.14	$Ga(OH)_3$	1.75
$Cd(OH)_2$	6.71	$Yb(OH)_3$	5.12	$Pt(OH)_2$	1.50
$Co(OH)_2$	6.56	$Gd(OH)_3$	5.04	$HgO(OH)_2$	1.50
$Ni(OH)_2$	6.56	$Lu(OH)_3$	5.00	$Fe(OH)_3$	1.50
$Fe(OH)_2$	6.49	$Be_2O(OH)_2$	4.73	$Sn(OH)_2$	1.34
AgOH	6.27	$Sc(OH)_3$	4.10	$Be(OH)_2$	1.10
$Pb(OH)_2$	6.05	$Cu(OH)_2$	4.06	$Zr(OH)_4$	0.99
$Nd(OH)_3$	6.03	$Bi(OH)_3$	3.88	$Ti(OH)_4$	0.46
$Y(OH)_3$	5.84	$Th(OH)_4$	3.67	$Sb(OH)_3$	0.20
$Sm(OH)_3$	5.37	$Cr(OH)_3$	3.54		

TABLE 6. Basicity sequences of the rare-earth metals.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
La	La	La	La	La		La	La	La	La	La	Dy	La	La	La	La
Ce	Ce	Pr	Pr	Ce		Ce		Pr	Pr	Ce	La	Ce			
Pr	Pr	Pr	Ce		Pr	Gd	Pr	Nd	Nd	Pr	Pr	Pr	Pr	Pr	Pr
Nd	Nd	Nd	Nd	Nd	Nd	Pr	Nd	Ce	Ce	Nd	Nd	Nd	Nd	Nd	Nd
	Y					Nd	Y	Y	Gd		Ce				Y
Sm	Sm	Sm	Sm	Sm	Sm	Y	Sm	Sm	Sm		Sm	Sm	Sm	Gd	Sm
Eu	Eu	Eu	Eu	Eu	Eu	Sm	Eu	Eu	Y		Tu	Eu		Sm	Dy
Gd	Gd	Gd	Gd	Gd	Gd		Gd	Tb	Tb			Gd		Y	Tb
Tb	Tb				Tb	Tb	Tb	Gd				Tb		Tb	Eu
Dy	Dy				Dy		Dy	Dy	Dy			Dy			
Y		Y	Y		Y						Y	Ho		Ho	Ho
Ho	Ho						Ho	Ho			Ho	Y			
Er	Er	Er	Er	Er		Er	Er	Er	Er			Er		Er	Er
Tm	Tm	Tm	Tm		Tm		Tm	Tm				Tm		Tm	
Yb	Yb	Yb	Yb	Yb	Yb		Yb	Yb				Yb		Yb	Yb
Lu	Lu	Lu	Lu				Lu								Lu
Sc	Sc	Sc	Sc					Sc	Sc	Sc		Sc		Sc	Sc
Th		Th								Th				Ce^{IV}	
Ce^{IV}	Ce^{IV}	Ce^{IV}						Ce^{IV}						Th	

The remaining sequences have been drawn up on the basis of experimental data:

Sequence 2 is based on precipitation with ammonia [161-163].

Sequence 3 on the pH at which precipitation begins during titration [6,40,90-94].

Sequence 4 on solubility and solubility products [90,93,105,158,159].

Sequences 5–9 on hydrolysis of the sulphates [164-166], nitrates [5,167], and azides [134].

Sequences 10–12 on the pH of solutions of the chlorides [168] and the nitrates [169].

Sequence 13 on the reduction potentials [170].

Sequence 14 on heats of dissolution [125-129].

Sequence 15 on thermal decomposition of the nitrates [171].

Sequence 16 on the pH_0 values [160].

For the origin of the discrepancies between the practical and the theoretical basicity series let us examine Fig. 4, in which pH_0 for the hydroxide chlorides and hydroxides of the scandium subgroup and the lanthanides is plotted against the atomic number of the element. These curves show that with the scandium subgroup there is an almost linear increase in pH_0 from scandium to lanthanum both for the hydroxides and for the hydroxide chlorides. The lanthanide group is characterised on the whole by a fall in pH_0 from lanthanum to lutetium. However, the curves show an inflection between samarium and dysprosium. This inflection is more pronounced with the hydroxides, and becomes less marked on passing from them to the hydroxide salts $M(OH)_{2.5}Cl_{0.5}$ and $M(OH)_2Cl$.

This may explain the difference in behaviour of elements located between samarium and dysprosium, on which so much has been written in review papers [5,6]. Fig. 4 enables us to show why different authors have placed yttrium in various positions in the basic strength sequences. Whereas in the hydroxide series it is located between neodymium and samarium, and between europium and terbium in the series of hydroxide salts $M(OH)_2Cl$, in the series of hydroxide salts $M(OH)_{2.5}Cl_{0.5}$ it is now located between europium and holmium.

Since the composition of the hydroxide salts depends on the conditions of precipitation, it naturally follows that the position in the basicity series of yttrium and other elements from the middle of the group will depend on these conditions. Hence if a series is compiled according to the experimental data, different types of basic salt or the hydroxides may be precipitated depending on the method adopted, and hence different positions will be obtained for these elements in the sequences. Even if a single method is used for this purpose, for example, potentiometric titration, yttrium and several elements of its group will occupy different positions in the sequence of basic strengths according to the compounds formed under different conditions of concentration of the initial salt and alkali solutions, rate of titration, temperature, etc.

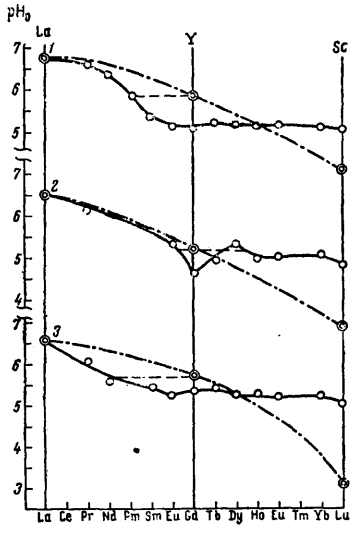


Fig. 4. Dependence of pH_0 of hydroxides and hydroxide salts on the atomic number of elements of the scandium subgroup (broken lines) and the lanthanides, for the compounds: 1) $M(OH)_3$; 2) $M(OH)_{2.5}Cl_{0.5}$; 3) $M(OH)_2Cl$.

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THIN-LAYER CHROMATOGRAPHY

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I. INTRODUCTION

The progress made in the chemistry of natural compounds in the last 10–15 years is to a considerable extent due to the extensive application of effective methods of separating mixtures of substances, particularly the method of adsorption chromatography discovered by Tsvet[1]. After the development of the method of partition chromatography, the new technique of paper chromatography was extensively applied. This makes it possible to solve a number of complex and difficult problems in the chemistry of natural compounds.

A new effective method of chromatography on plates in a thin layer of adsorbent has recently been developed and has been called thin-layer chromatography. This method originated in work by Izmailov and Shraiber[2], who first separated alkaloids present in extracts from medicinal herbs on an unfixed layer of aluminium oxide on glass. Later, Meinhard and Hall[3] used radial surface chromatography on a layer of aluminium oxide fixed with starch for the separation of a mixture of certain inorganic ions. On the basis of this work, Kirchner *et al.*[4] proposed a new method for the separation and identification of terpenes in the determination of the composition of essential oils. This method, developed by these and other workers, particularly Stahl[5-16], on layers of adsorbent fixed to a glass plate, was then used extensively for the separation of both weakly polar and strongly polar ("hydrophobic" ["hydrophilic"? (Ed. of Translation)]) substances.

In 1955, Mottier[17,18] separated various dyes on an unfixed layer of aluminium oxide. The rapid development of this procedure began only recently, and a number of papers[19-22] have appeared, describing the use of thin-layer chromatography on unfixed layers of aluminium oxide and silica gel. The simplicity and rapidity of the method using an unfixed layer of adsorbent is attracting the attention of many research workers and the number of works in which it is used is increasing continuously.

Recent experimental data[13,16,23-25] show that thin-layer chromatography is a very convenient method for separating small quantities of multicomponent mixtures of substances. The advantages of this method over paper chromatography are its rapidity, the stability of the layer to heat and to active developers, and the high sensitivity: by using several developing reagents, it is possible to detect extremely small quantities of substances (0.1–0.005 μg).

II. GENERAL SECTION

1. Methods of Separating Mixtures of Substances on a Thin Layer of Adsorbent

The essential features of the method of thin-layer chromatography are as follows. A thin layer of adsorbent is deposited on one side of a small glass plate (20 × 5 cm). The substances and their mixtures are applied to this layer on a starting line, as on the paper in paper chromatography, and the plate is placed in a vessel containing solvent. The separation of the mixtures of substances takes 30–90 min. The plate is removed from the vessel, dried, and sprayed, as in paper chromatography. The position of the test substances, which are found in the form of spots between the starting line and the liquid front (limit of ascent) is noted (Fig. 1), the distance from the centre of the spot to the starting line (length *OS*) and the distance from the liquid front to the starting line (length *OF*) are measured. The position of the spot is denoted by a constant characterising the position of the substance on the given chromatogram as the ratio of the distance between the starting line and the centre of the spot *OS* to the distance between the starting line and the liquid front *OF*, *i.e.* $Rf = OS/OF$. The Rf value is characteristic of the compound on a given adsorbent in a given system and depends on a number of conditions: the procedure, the purity of the adsorbent, the activity of the layer, the thickness of the layer, the purity of the solvent, the quantity of substances deposited, the distance moved by the solvent, and the position of the starting line, but is almost independent of temperature.

The separation of substances on a thin layer of adsorbent is carried out on layers of adsorbent fixed to the glass plate or on unfixed layers. The substance is applied to the side of the plate from which the solvent is supplied.

There are several methods of moving the solvents over the plate and adsorbent. Usually, the solvent moves only once over the plate and adsorbent to separate the substances, but a number of methods of repeated chromatography also exist. If a mixture of substances, of which some are separated better by one system of solvents and others by another system, is being separated, use is made of a stepwise chromatographic method[8]; the separation is first carried out with a system which separates the less polar

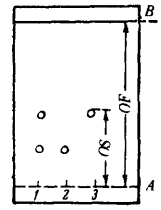


Fig. 1. Separation of a mixture of substances on a plate with a thin layer of adsorbent: *A*) starting line; *B*) liquid front. 1) Mixture of two substances 2 and 3; 2) and 3) individual substances.

substances. The solvent moves almost to the end of the plate. The chromatogram is then dried to remove the solvent and the chromatographic process is repeated with another system which moves over a shorter distance than the first system of solvents. This method often gives good results. Stepwise separation of mixtures using a third stage is also possible. In this case the third stage of the separation is carried out in a new solvent with the plate rotated through 180°. In this case the system moves in a direction opposite to that for the first two systems[26,27].

Two-dimensional chromatography is carried out on square plates (usually 20 × 20 cm) carrying adsorbent[10,28,29]. The mixture of substances to be analysed is applied at one corner of the plate and the separating liquids move first in one direction and then, after the chromatograms have been dried, in another system in a direction at right angles to the first. Two-dimensional chromatography is often used and gives particularly good results in the separation of multicomponent mixtures of substances. The two-dimensional method of separation using the same system of solvents in both directions, the so-called "separation, reaction, separation" method, is used to determine the homogeneity of a substance[10]. In some cases, two spots appear on the chromatogram and it is not clear whether the second spot is another form of the same substance or a product of a change which this substance undergoes during separation on the plate (for example, oxidation, isomerisation, etc.). If no such change takes place during the chromatographic process, the spots should lie on the plate diagonal. If, however, reaction products are formed, the spots of the new substance lie above or below the diagonal.

Sometimes, to improve the separation of substances, it is desirable to increase the length of the path of solvent flow. Use is then made of a second chromatographic process in the same system, or of a flow method of chromatography[30], based on the continuous supply of fresh solvent to the plate and adsorbent. A sheet of glass is placed above the plate, out of contact with the layer, to prevent volatilisation of solvent. The solvent reaching the end of the plate drains away or simply evaporates.

In work with an unfixed layer of adsorbent, the plate is placed at an angle of 15°–20°. In work with a fixed layer, however, any plate position is possible, and the vertical position is usually employed. The process is known as ascending chromatography when the solvent moves from below upwards under the influence of capillary forces. The height to which the liquid rises in this case has a definite limit. The process is known as descending chromatography when the solvent moves from above downwards, mainly under the influence of gravity[31–33].

A method involving horizontal movement of solvent is used in radial (circular) chromatography on plates. In this case the plate with a fixed layer of adsorbent is placed on a Petri dish with the layer facing downwards. The solvent is supplied from the dish by means of a wick in the centre of the plate. The substance to be separated is applied in a circle around the centre of the plate.

2. Chromatography on a Fixed Layer of Adsorbent

The chief adsorbent used for thin-layer chromatography on a fixed layer is silica gel, whose chromatographic properties enable it to be used for both adsorption and partition chromatography. Other adsorbents used include aluminium oxide, kieselguhr (for strongly polar compounds), magnesium silicate[34], calcium hydroxide, cellulose powder, polyamide resins, etc.

The silica gel should have a macroporous structure and suitable particle size (150–180 mesh). Its capacity with respect to water should be 80–100%. Good results are obtained with Soviet KSK grade silica gel[35–37], ground and passed through a 150 mesh sieve (hole size 0.1 mm). The silica gel should first be washed free from iron impurities, if these are present, by boiling with concentrated hydrochloric acid and washing free from chloride ions with distilled water. Fine suspension should then be removed by shaking and decantation and the product dried at 120° for 48 h.

The layer of adsorbent is usually fixed to the glass by means of a suitable fixing agent. Plaster[4], gypsum (medical)[35], and rice or maize starch† are used for this purpose.

As a result of the development of thin-layer chromatography with a layer fixed to glass, it has been found necessary to standardise the conditions of working in order to obtain reproducible results. For this purpose Stahl proposed the following conditions for standardising the layers[6]:

1. The layer should be even, smooth, 0.25–0.30 mm thick, and without cracks or bubbles. Such a layer is best obtained with a special apparatus. After deposition of the layer, the plate should be activated in a drying oven at 105° for 30 min and kept in a desiccator over blue gel (calcined silica gel impregnated with cobalt salts) or calcium chloride. This layer has an activity corresponding approximately to an aluminium oxide activity of II/III on the Brockmann scale. To obtain a less active layer, the plates are sometimes dried in air.

2. The layer should be sufficiently strong and resistant to active developing agents. These conditions are completely satisfied by KSK silica gel containing 5% medical gypsum or by silica gel G (Merck).

3. The capillary properties of the layer should be such that when a mixture of the three dyes Indophenol Blue, Sudan Red-IV, and *p*-dimethylazobenzene is deposited on the plate, it remains at the starting line when hexane is used as solvent (plate immersed in the liquid to a depth of 0.5 cm) and gives three spots with benzene. The rate of movement of the solvent depends on the quality of the layer, the solvent, and the degree of saturation in the vessel, and in the separation of the above dyes in benzene, the time taken for the liquid to rise to a height of 10 cm should be not more than 30–45 min. Under these conditions the variation in the Rf values is ±0.05. It is fairly difficult to obtain an even layer of this type without special apparatus, but results obtained on a layer prepared without this apparatus are quite suitable for characterising the compounds being studied if the Rf value obtained is related to the Rf value of a known compound subjected to the chromatographic process on the same plate.

Several pieces of apparatus have now been described for applying a thin fixed layer of substance. The best of these, which is used everywhere and is manufactured industrially, is Stahl's apparatus[9], designed to produce five 20 × 20 cm plates with a layer thickness of 0.27 mm (Fig. 2*a*). There are also several simpler models made of plastic, giving a layer of about 0.30 mm[38] or 0.25 mm[39], etc. (Fig. 2*b* and 2*c*).

† Some foreign firms prepare special silica gel G, kieselguhr G, and aluminium oxide G containing 5% gypsum for thin-layer chromatography by Stahl's method (Desaga of Heidelberg, or Merck of Darmstadt).

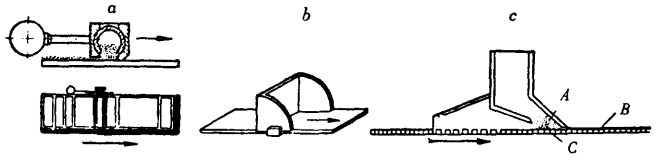


Fig. 2. Apparatus for obtaining a thin layer of sorbent. *a*) Stahl's apparatus, *b*) and *c*) plastic apparatus. The arrows indicate the direction of movement of the apparatus; *A*) adsorbent; *B*) thin layer of adsorbent; *C*) glass plate.

Glass of any quality can be used as a base in the preparation of the thin layers (window glass, photographic plates with the emulsion removed, mirror glass, and Pyrex). The dimensions usually employed are 20 × 20 cm and 5 × 20 cm.

To obtain a 0.27 mm thick layer on five 20 × 20 cm plates, 25 g of silica gel containing 5% gypsum are mixed thoroughly with 24 ml of water and the resulting mass is spread on the surface of the glass by means of Stahl's apparatus. The plates are then dried in air, activated, and stored as described above. An 11 × 17 cm plate with an approximately 0.3 mm thick layer is prepared, without apparatus, as follows: 6.9 g of silica gel and 0.35 g of gypsum are shaken thoroughly with 18 ml of distilled water in a 100–150 ml flask with ground stopper. The resulting thick uniform mass is poured on to the glass and spread evenly over its surface by means of a spatula with shaking. The plate is left for 20 min on a horizontal surface and then activated and stored in the usual way. The layer can also be fixed on the plate by means of starch[40], but this method is almost never used at the present time.

To obtain a cellulose layer, cellulose powder is shaken with water or acetone and applied to the plate using Stahl's apparatus.

Sometimes it is necessary to prepare so-called modified layers[8,13], for which solutions of acids, alkalis, buffers, etc. are used instead of water in the preparation of the layer. Acidic layers are obtained by adding 0.5 *N* oxalic acid[41] or 0.1 *N* boric acid[42]. Alkaline layers are prepared with 0.1–0.5 *N* potassium hydroxide[43] or sodium hydroxide[44]. Layers with Sörensen's phosphate buffer are prepared by adding equal volumes of 0.2 M potassium dihydrogen phosphate solution and 0.2 M disodium hydrogen phosphate solution[11]. A layer with acetate buffer is prepared with 0.02 M sodium acetate[11,13]. A cellulose layer can be impregnated with a 20% solution of formamide in acetone[45].

Use is also made of layers impregnated with hydrocarbons[46,47], liquid paraffin, tetradecane or the petroleum fraction with boiling point 240°, kerosene with boiling range 240°–250°, and silicone oils of low molecular weight (viscosity 50 cS) or high molecular weight (viscosity 1000 cS). The impregnation is usually carried out by carefully lowering the plate into a 5% solution of these substances in ether or petroleum ether, after which the plate is dried to remove the solvent.

In some cases, if the substance itself does not fluoresce in ultraviolet light, fluorescent layers are used, particularly for preparative separations. These are prepared by adding aqueous solutions of fluorescent substances which are firmly held by the adsorbent and are not wetted by the usual solvents. For a silica gel layer, Rhodamine G-6 is normally used for this purpose (0.0011 g in 54 ml water)[40].

In work with a fixed layer of silica gel, the ascending method is usually employed. The chromatographic separation is carried out in a flat-bottomed vessel, of any shape, with a size appropriate to the dimensions of the plate. The height of the vessel should be about 25 cm for work with 20 × 20 cm plates.

The quantity of solvent poured into the vessel is such that a plate with applied substance, placed almost vertically in the vessel, is immersed in the solvent to a depth of 5 mm. A sheet of filter paper moistened with solvent and reaching to the foot of the vessel is placed against one wall of the vessel to ensure supersaturation of the atmosphere inside the vessel. A ground lid is used to close the vessel. In a supersaturated atmosphere the spots are deeper and the duration of flow of liquid is reduced by one-third. The height to which the liquid rises should be not more than 10–11 cm, since when the distance moved by the solvent is high, diffusion of the spots and therefore greater variation in the *Rf* values are observed. With this method of working[48], the variations in the *Rf* values are of the same order of magnitude as those observed in paper chromatography.

3. Chromatography on an Unfixed Layer of Adsorbent

The chief adsorbents used for thin-layer chromatography on an unfixed layer are aluminium oxide and silica gel. The unfixed layer can be prepared using commercial "chromatographic" grade aluminium oxide with the required activity on the Brockmann scale[49].

The choice of an adsorbent with suitable quality and activity is of very great importance for an effective separation of mixtures, and it is necessary to remember that certain adsorbents, for example, aluminium oxide, may induce side reactions during the chromatographic process.

If the substance is not stable to alkalis, the aluminium oxide is washed until neutral, dried at 350° for 6–8 h, and deactivated by adding distilled water until the necessary activity on the Brockmann scale is reached[49].

The activity of aluminium oxide can be conveniently determined by thin-layer chromatography[50]. For this purpose, a standard mixture of azo-dyes (azobenzene, *p*-methoxyazobenzene, Sudan Yellow, Sudan Red, and *p*-aminoazobenzene) is separated by means of carbon tetrachloride on a plate with a thin layer of the test specimen of aluminium oxide and the activity is determined from the published Table[50].

An unfixed thin layer is prepared using KSK silica gel treated as described in Section II. 2. The silica gel prepared in this way is deactivated by adding 3–25% distilled water to give an adsorbent with the required activity.

The method of preparing an unfixed layer of adsorbent is very simple. The adsorbent is sprinkled on the glass (preferably matt) and spread evenly over the surface by means of a stainless steel roller thickened by 0.5 mm or 1 mm (±0.01–0.02 mm) at the ends, or by means of a glass tube with pieces of rubber tubing placed over the ends. The distance between the thickened ends of the roller or tube should be 10–12 mm less than the width of the plate used. The roller or tube is moved slowly by means of the thickened ends along the edges of the plate to give even layers

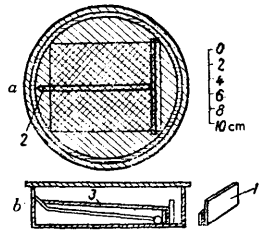


Fig. 3. Apparatus for the separation of a mixture of substances on an unfixed layer: 1) device for producing slit; 2) T-shaped glass rod; 3) glass plate with thin layer; *a*) view from above; *b*) side view.

of adsorbent. When the substance has been applied, the plate is placed in a glass crystallisation dish containing solvent, at an angle of 15°–20°, and one edge is lowered into the solvent[17,19,22]. Alternatively, the solvent may be supplied to the plate by means of a capillary slit[21], in which case a total of 25–30 ml of solvent is required for the separation. The top of the crystallisation vessel is covered with ground glass. Fig. 3 illustrates a vessel for work with an unfixed layer of adsorbent. The plate is placed in the vessel on the step of the device that forms the slit and on a bent glass rod with cross-piece. The device that forms the slit consists of two strips of glass 2 cm wide and 1 cm high. Pieces of Teflon [PTFE (Ed. of Translation)] or cover glass are placed between these strips along the edges. The strips are fastened to one another with Nichrome wire. The device is held in a vertical position by means of the cross-piece of the glass rod. With this method of working the distance travelled by the liquid has no influence on the R_f value. The variations in the R_f value from the mean value amount to not more than 2% of the distance between the starting line and the liquid front.

4. Application of Substance

Between 0.1 and 50 μg of the test substance is applied in a 0.1–0.5% solution, usually in a volatile solvent such as ether or chloroform. Drops of this solution are applied through a 0.1 ml pipette or a specially prepared capillary to a starting line at a distance of up to 1.5 cm from the edge of the plate. The distance between the points at which the specimens of substance are placed should be not less than 1 cm. The substances are applied carefully to avoid damage to the adsorbent layer. The quantity of compound or mixture applied plays a significant part in the separation of substances by thin-layer chromatography. The sensitivity of the detecting reagent is equally important. Very large quantities of compound may be difficult or impossible to detect if a reagent with low sensitivity is used. The R_f value depends on the quantity of substance applied to the plate. Very large quantities of substance often give spots which are far too large and of poor shape, and which merge with the spots given by compounds with similar R_f values.

Fig. 4 shows that in the identification of glycine, the best results are obtained with a quantity of substance equal to about 0.5–1.0 μg[51].

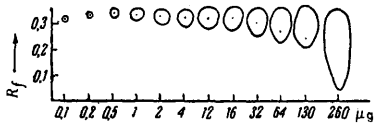


Fig. 4. Dependence of the R_f value on the quantity of substance (μg) taken for the separation, for the case of glycine[51].

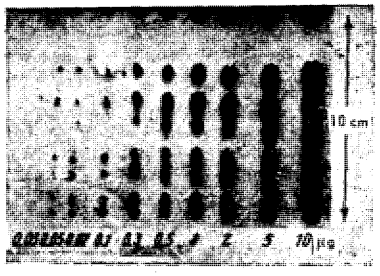


Fig. 5. Chromatogram for a mixture of sugars. The quantities of mixture applied increase from left (0.03 μg) to right (10 μg)[12].

Considerable attention is now being paid to the question of the sensitivity of the reagents used in thin-layer chromatography. Reagents are available for the detection of down to 0.005 μg of substance[15]. To obtain accurate results, therefore, it is necessary to know the sensitivity of the detecting reagent and to choose the correct quantity of compound or mixture of substances to be tested. In order to choose the necessary quantity of a mixture of substances, specimens of different quantities of the mixture, for example, from 1 to 10 μg[8] or from 0.03 to 10 μg[11], are applied to the plate, the mixture is separated in a suitable system, and detected with an appropriate reagent. The sensitivity of a reagent is verified in the same way, usually with the individual compounds. Fig. 5 illustrates the separation of a mixture of eight sugars[12]. The best separation is achieved with 0.5 μg of mixture, although separation is still observed with smaller quantities of substance.

5. Choice of Adsorbent and Solvent

The solvents used in thin-layer chromatography should be pure and thoroughly dry. The purification and drying of the solvents is carried out by the methods usually employed for other forms of chromatography.

The separation of mixtures of substances can be carried out with a single solvent, but systems consisting of two, three, and even four solvents are usually employed. A given portion of solvent or system cannot be used again for a second chromatographic separation.

In the choice of adsorbent, allowance must be made for the polarity and chemical stability of the substances to be

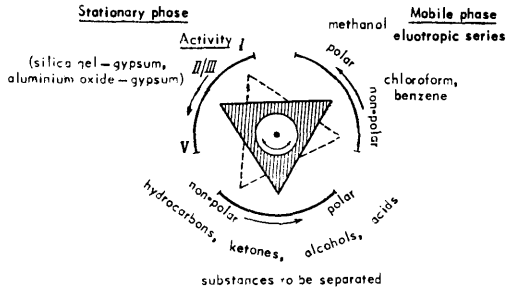


Fig. 6. Selection of conditions for chromatography on a thin layer of adsorbent. The Roman numerals indicate the activity on the Brockmann scale. The shaded triangle rotates around its centre. One angle of the triangle indicates the compounds to be separated, another indicates the necessary activity of the adsorbent, and the third indicates the solvent.

separated. Hydrophilic (polar) adsorbents (aluminium oxide, silica gel, kieselguhr) adsorb a substance more strongly, the greater the number of polar groups it contains and the greater its degree of unsaturation. Weakly polar compounds are usually chromatographed on strongly active adsorbents, and strongly polar compounds on weakly active adsorbents.

The adsorptive activity of compounds containing functional groups increases in order:

$$CH{=}CH < OCH_3 < COOR < C{=}O < CHO < SH < NH_2 < OH < COOH.$$

In the choice of solvent for adsorption thin-layer chromatography, use is made of the eluotropic series[16], starting from a non-polar solvent and finishing with a strongly polar solvent. For this purpose a microcirculation method is used, with the following essential features. Several specimens of substance are applied to a strip of glass with a layer of adsorbent in the usual way at a distance of 2 cm from one another. After a few minutes, the solvent or system being studied is applied by means of a thin capillary to the centre of each point where the substance or mixtures have been applied. The chromatogram is dried and developed to reveal the substances, separated more or less successfully, in the form of circular rings. A suitable solvent or system can then be selected.

On the basis of the above experiment, Stahl has proposed a simple graphical method of selecting conditions for chromatography on a thin layer of adsorbent[16]. This is illustrated in Fig. 6.

Recently, thin-layer chromatography has been used not only for adsorption chromatography, but also for partition chromatography. A recent paper[52] deals with the theoretical basis of the method. The use of Hecker's mixotropic series[53] for selecting a solvent for thin-layer partition chromatography is recommended. Initially, the mobile phase is always saturated with the stationary phase.

6. Detection of the Spots

In work with coloured substances, coloured spots of the separated components are observed. To detect colourless substances, it is first necessary to determine whether the substance fluoresces in ultraviolet light.

For substances which do not fluoresce, the chromatograms are sprayed from an atomiser with solutions of reagents which give colour reactions with the compounds being studied. The spraying is carried out with the smallest possible quantity of detecting agent to avoid damage to the layer and change in the shape of the spot. In some cases plates containing a fluorescent substance are used, or the plate may be sprayed with a solution of a fluorescent substance.

Most of the reagents used in paper chromatography can be used to detect the spots obtained in a thin layer of adsorbent. An advantage of thin-layer chromatography is the possibility of working with purely inorganic layers on which almost all substances can be detected by spraying with reactive detecting agents such as concentrated sulphuric acid, with or without aldehydes (vanillin, anisaldehyde, etc.), or a mixture of concentrated sulphuric and nitric acids. After spraying with these reagents, it is sometimes necessary to heat the plate at 80°–100°, or even to 400°. Good results are often obtained by spraying with $SbCl_3$ and $SbCl_5$ solutions and then heating to 80°–100°.

Compounds containing a double bond or capable of adding on iodine are detected with iodine vapour. When the plate is heated to 100°–150° after saturation with iodine vapour, compounds which undergo dehydration readily are revealed.

The carbonyl group is detected by spraying with 2,4-dinitrophenylhydrazine solution. Aldehydes are detected with a solution of *o*-dianisidine in acetic acid. Acids are detected with a weakly alkaline solution of Bromocresol Green, etc.

In the detection of the spots obtained on an unfixed layer, the spraying is carried out carefully with the atomiser at a distance of 1 m from the moist or dry plate. Under these conditions the compounds are detected without disturbing the layer. In an alternative method proposed for detecting the substances on an unfixed layer of aluminium oxide, the plate is dried in air after the substances have been separated, and the layer of aluminium oxide is impregnated with concentrated acids in a direction at right angles to that of the separation. In this case the colouring takes place immediately[54].

In the classified section of this review, reagents used for detection purposes are described in each subsection.

7. Preparative Separation of Mixtures of Substances

Thin-layer chromatography can be used for the preparative simultaneous separation of mixtures of substances in quantities of 0.4–0.5 g or more. The yields are almost quantitative.

Preparative separation on a fixed layer is usually carried out on a fluorescent silica gel–gypsum layer. The spots of substance are detected with ultraviolet light, marked, scraped from the plate, and the substance is extracted from the adsorbent with a suitable solvent. The chromatographic process is carried out several times and the solutions obtained by extracting identical spots are combined. The individual compounds are isolated after removal of the solvent.

On an ordinary 20 × 20 cm plate with a fluorescent silica gel–gypsum layer, the mixture of substances can be applied in the form of a continuous line, in quantities of up to 1 mg.

In this case the individual compounds are detected with ultraviolet light in the form of bands which are marked and treated as described above.

The method of preparative separation on an unfixed layer of aluminium oxide and silica gel is particularly convenient[19]. The separation is carried out on plates up to 40 cm broad and up to 80 cm long with an adsorbent-layer thickness of 1.5–3 mm. For a layer thickness of 1.5 mm, the quantity of substance applied can amount to about 20–25 mg per 1 cm length of starting line.

The mixture of substances is dissolved in a suitable volatile solvent and applied to the plate in the form of a continuous line, after which the plate is impregnated with pure solvent to ensure deeper penetration of the substance into the layer. The solvent is evaporated and the mixture of substances is separated in a suitable system. If a substance does not fluoresce in ultraviolet light, the plate is sometimes sprayed with morin and the bands of separated substances are detected in ultraviolet light and their positions are marked. Alternatively, the chromatographic process can be carried out on a layer of aluminium oxide impregnated with morin[55]. The substance and adsorbent are removed from the plate by means of a simple apparatus (see Fig. 7). A stopper with bent tube is placed in a funnel with porous filter (No. 3 and No. 4). The lower end of the funnel is connected to a water pump. The adsorbent and substance are removed by suction from the plate through the tube by means of the water pump. The substance is extracted from the adsorbent by a suitable solvent in the same funnel.

The detection of a substance may be carried out with iodine vapour. For this purpose crystals of iodine are placed in the funnel and a current of air is blown carefully through the tube placed in the stopper. At the same time the end of the funnel is moved slowly over the layer of adsorbent along the two edges of the plate. The sections coloured by the iodine on both edges of the plate are marked and joined up to one another. The zones containing the substances, marked out on the plate, are collected in the funnel and extracted as described above.

Several examples of the quantitative separation of mixtures of substances on a thin layer of adsorbent have been described. These include a visual method, based on measurement of the size and intensity of the spot[32,41,56,57], and a photometric method[58–60].

Various techniques have been recommended for the documentation of chromatograms: drawing on oil-paper, black-and-white photocopying[6], storage on coloured film, fixation of the results with paraffin wax[17,18], and photocopying in ultraviolet light[30].

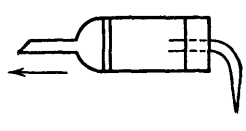


Fig. 7. Apparatus for removing substance and adsorbent from the plate.

III. CLASSIFIED SECTION

1. Mono-, Sesqui-, Di-, and Tri-terpenes

The development of thin-layer chromatography began with the study of the composition of essential oils[4]. It was found that on a thin layer of silica gel–starch in a hexane–ethyl acetate (85 : 15) system it is possible to separate terpene hydrocarbons, alcohols, esters, cinnamaldehyde, and normal caprylic acid. The common reagent used to detect the terpenes was concentrated sulphuric acid and its mixture with nitric acid (95 : 5), with subsequent heating to 500° and detection in ultraviolet light. Compounds capable of adding on bromine were detected by the fluorescein–bromine test, aldehydes were detected by spraying with a 1% solution of dianisidine in acetic acid, and acids were detected with Bromocresol Green. Use was also made of chromatography on a silica gel–gypsum layer with added fluorescent substances (zinc cadmium sulphate or zinc silicate) and irradiation with short-wave ultraviolet light.

The method of thin-layer chromatography on a layer of silica gel[61] has been used for the control of the fractions obtained in the separation of essential oils by column adsorption chromatography, and has been used successfully for the separation of many essential oils[62–64].

Various saturated and unsaturated aliphatic, aromatic, and terpene hydrocarbons have been examined systematically on a silica gel layer in hexane[65].

Detailed studies have also been made[66] of 32 examples of the separation of different terpene alcohols, aldehydes, ketones, ethers, and epoxides on a silica gel–gypsum layer, but for these compounds a number of other systems were used: (I) hexane–ethyl acetate (85 : 15); (II) chloroform–ethyl acetate (9 : 1); (III) benzene–ethyl acetate (85 : 15); (IV) chloroform–ethyl acetate (95 : 5); (V) hexane–nitropropane (1 : 1); (VI) hexane–ethyl acetate (70 : 30); (VII) chloroform–ethyl carbonate (85 : 15); (VIII) hexane–isopropyl formate (70 : 30); (IX) hexane–isopropyl ether (1 : 1); (X) hexane; (XI) chloroform.

Good results were obtained by spraying the chromatograms with concentrated sulphuric acid containing 1% vanillin[67–68]. This method has been used to determine *L*-menthol, *L*-menthene, *L*-menthyl acetate, and *L*-limonene in Japanese mint, on an SiO_2 layer in the hexane–ethyl acetate (85 : 15) system.

The preparation of a fluorescent layer by the addition of Rhodamine G-6, which does not give addition products with the substances being tested and is firmly held by silica gel, has also been suggested[40,69]. Good results were obtained with detection by ultraviolet light. Thus ketones were detected by spraying the plate with a solution of 2,4-dinitrophenylhydrazine (0.4 g DNPH in 100 ml 2 *N* HCl). The spots were marked in daylight and in ultraviolet light. The chromatogram was then heated at 105° for 10 min and re-examined in daylight and in ultraviolet light. This repeated examination made it possible to detect several substances which were previously not observed.

A layer of silica gel–starch in the hexane–ethyl acetate (85 : 15) system has been used to separate 12 aliphatic and terpene aldehydes and ketones[40,64], and, in the same system, diterpenes of the phytol class[55,70,71]. In the latter case, in addition to the usual methods, the ethers were detected by spraying with 0.25% aqueous potassium permanganate solution.

A number of essential oils have also been studied on a silica gel–gypsum layer in benzene. Borneol, cineol, bornyl acetate, thujone, linolyl acetate, and pinene were detected[72]. Menthol, cineol, menthone, menthyl acetate, menthofuran, pinene, and phellandrene were detected in the benzene–ethyl acetate (95 : 5) system[73].

A particularly interesting example is the separation of epimeric compounds, namely the isomeric γ-menthols, on a layer of silica gel–gypsum in the n-hexane–ethyl acetate (85 : 15) system[74] and later in the benzene–methanol (95 : 5) system[75].

The sesquiterpenes and their alcohols[76]: patchoulene, patchoulyl alcohol, and eugenol have been separated on a silica gel–starch layer in a n-hexane–ethyl acetate (85 : 5) system containing 5% chloroform, and detected with sulphuric acid.

Multicomponent mixtures of triterpenes have also been separated successfully on a silica gel–gypsum layer[77]. This method has been used for the separation of a number of triterpenic acids and also for neutral triterpenes (ethers, alcohols, and hydrocarbons). The compounds were detected by spraying with chlorosulphonic and acetic acids (1 : 2) and then drying at 130° for 5 min, and also by using ultraviolet light. The lower limit of detection with the above reagent is 0.02 μg in the case of oleanolic acid.

The following systems have been used for the separation of acids: (I) diisopropyl ether–acetone (5 : 2); (II) diisopropyl ether–acetone (5 : 2) containing 5% pyridine; (III) ethyl acetate–methanol–diethylamine (14 : 4 : 3); (IV) chlorobenzene–acetic acid (9 : 1); and (V) methylene chloride–pyridine (7 : 2).

Hydrocarbons and esters have been effectively separated in the following systems: diisopropyl ether–acetone (5 : 2); diisopropyl ether–cyclohexane; and benzene–methylene chloride.

The same layer has also been used to separate methyl bredemolate and the acetonide of methyl bredemolate in the diisopropyl ether–acetone (10 : 19) system[78] and to separate five new triterpenic acids, isolated from the resin of *Commiphora gladulosa*, in the chloroform–ethyl acetate (4 : 1) system[79].

The quantity of squalene and other terpenes and sesquiterpenes in essential oils has been determined on a silica gel–gypsum layer in benzene[6,7]. This method has also been used[80] for the semi-quantitative estimation of geranyl acetate, asarone, and isoeugenol methyl ether in certain essential oils.

2. 2,4-Dinitrophenylhydrazones

Aliphatic aldehydes and ketones are conveniently separated as their 2,4-dinitrophenylhydrazones. The best system for the separation of aliphatic aldehydes[81] in the form of these derivatives on a thin layer of silica gel–starch was found to be a saturated benzene–water solution (98:8.2).

A number of aldehydes and ketones present in essential oils: carvone, citral, menthone, cinnamaldehyde, benzaldehyde, fenchone, vanillin, salicylaldehyde, lauric aldehyde, furfural, and piperonal, have been identified as the 2,4-dinitrophenylhydrazones on a silica gel–starch layer in the ligroin–ether (2 : 8) system[82] and on a silica gel–gypsum layer in the hexane–ethyl acetate (17 : 3) system[83].

The 2,4-dinitrophenylhydrazones of a number of aromatic aldehydes and ketones have been identified with good reproducibility on a silica gel–gypsum layer in the benzene–petroleum ether (b. p. 60°–80°) (3 : 1) and benzene–ethyl acetate (95 : 5) systems[84].

3. Steroids and Cholesterol Esters

The first steroids to be separated on a thin layer of silica gel–gypsum were the lactones of Δ^5-3β, 20-dihydroxycholic acid and Δ^5-3β-acetoxy-20-hydroxycholic acid, cholesterol, its acetate, and the lipids from blood extract[9]. The separation was carried out in chloroform in a supersaturated vessel and the spots were detected by spraying with a saturated solution of antimony trichloride in chloroform, with heating at 110°.

The separation of cholesterol esters is very important in biological and medical chemistry and has recently aroused considerable attention. Work on the separation of the lipid extracts of blood on a silica gel–gypsum layer have been continued[26,27]. Good results have been obtained using a three-stage method of separation. The separation was first carried out in a propanol–ammonia (2 : 1) system. When the liquid front had moved a distance of 30 mm, the plate was removed, the solvent was evaporated, and the chromatographic process was repeated in a chloroform–benzene (3 : 2) system until the liquid had risen to a height of 100 mm. The plate was then removed, turned through 180°, and the chromatographic process was repeated by the ascending method in carbon tetrachloride (height of liquid ascent 40 mm). The chromatogram was sprayed with a solution of $SbCl_3$ in chloroform and examined in ultraviolet light. This method separated cholesterol and its esters, leucine, cephalin, and oleic, butyric, palmitic, and stearic acids.

The separation of cholesterol esters[85] and certain other weakly polar steroids was examined in detail on a thin layer of silica gel–gypsum in 13 different solvents and systems. It was found possible to separate, in 90 min, the neutral fraction of the products of the oxidation of the side chain of cholesterol, consisting of more than 20 compounds, and even, by a semi-quantitative method, to estimate the concentration of some of these in the total mixture.

Fig. 8 illustrates the semi-quantitative separation of the neutral fraction of the products of the side chain oxidation of cholesterol, on a silica gel–gypsum layer, by visual comparison of the spots with spots containing known quantities of these compounds.

In addition to the above systems, tetrachloromethane has been used to separate the cholesterol esters present in blood serum[86].

In a more detailed study of this problem[87], the following esters of cholesterol with saturated and unsaturated acids were specially synthesised and prepared in pure form: cholesterol formate, acetate, propionate, palmitate, stearate, oleate, linoleate, linolenate, and erucate. In the above systems, many of the cholesterol esters have the same Rf values. Best results in the separation of the esters were obtained in the tetralin–hexane (1 : 1) system[87]. The author was unable, however, to find a system which would give a sharp separation of the esters of the higher aliphatic saturated acids. For this purpose the separation was carried out on a silica gel–gypsum layer impregnated with liquid paraffin, in the ethyl methyl ketone–acetonitrile

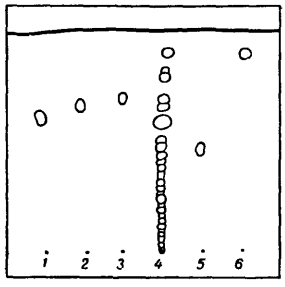


Fig. 8. Chromatogram of the neutral products of the side chain oxidation of cholesterol, obtained on a silica gel–gypsum layer:
1) 3β-acetoxyandrost-5-en-17-one;
2) 3β-acetoxypregn-5-en-20-one;
3) 3β-acetoxy-26-norcholest-5-en-25-one;
4) neutral fraction of the oxidation of cholesterol acetate dibromide;
5) 3β-acetoxy-chol-5-en-(24,20)-olide;
6) cholesteryl acetate.
The neutral fraction contains: 1) 4 ± 1%; 2) 3 ± 1%; 3) 3 ± 1%; 4) 22 ± 2%; 5) 12 ± ± 2%.

(7:3) system. This gave good separation of the cholesterol esters of unbranched higher aliphatic acids with short and long chains. Mixtures of saturated and unsaturated cholesterol esters were separated by a two-dimensional method in the tetralin–hexane (25:75) and ethyl methyl ketone–acetonitrile (7:3) systems using partial hydrophobisation of the layer with paraffin wax. The compounds were detected with molybdophosphoric acid.

Very good separations were obtained[38] on a silica gel–gypsum layer in ethyl acetate–cyclohexane (15:85 and 30:7) systems, for weakly polar steroids, chiefly esters of etianic acid, whose separation by paper chromatography was unsuccessful.

The more polar steroids cholic and deoxycholic acid have been separated in ethyl acetate on a plate with a silica gel–starch layer deactivated in air. The *Rf* values of the following compounds have been found for the systems indicated: 5β-cholestan-3-one 0.71, 5α-cholestan-3-one 0.86, and cholest-4-en-3-one 0.63 in the ethyl acetate–cyclohexane (15:85) system and 5β-cholestan-3β-ol 0.15 and 3α,4α-epoxycholestane 0.85 in the ethyl acetate–cyclohexane (30:70) system. The spots were detected by spraying the chromatograms with antimony trichloride solution. The carbonyl compounds were detected by spraying with 2,4-dinitrophenylhydrazine.

A number of steroids[35] were recently separated on a layer of KSK silica gel and medical gypsum using mixtures of cyclohexane and ethyl acetate in different proportions. The spots were detected with the above reagents and also with concentrated sulphuric acid and with ultraviolet light.

Mixtures of the epimeric 5,6-α- and 5,6-β-epoxides of epiandrosterone 3β-acetate and the 5,6-α- and 5,6-β-epoxides of ethynylandrostenediol 3β-acetate have been separated in the cyclohexane–ethyl acetate system[35]. Later, the epimeric cholest-4-en-7α- and -7β-ol-3-ones were separated in the benzene–ethyl acetate (2:1) system[88].

Recently, steroids have been separated on silica gel–gypsum and aluminium oxide–gypsum layers in the more polar systems: benzene–chloroform, benzene–acetone, chloroform–acetone, chloroform–ether, and butyl acetate–methanol in different proportions[89].

In the study of the Uzara root, 3β-hydroxypregn-5-en--20-one and 3β-hydroxy-5α-pregnan-20-one, present as the glycosides, and also β-sitosterol, were detected[90]. The products obtained were identified by oxidising with chromium trioxide and separating the oxidation products on silica gel–gypsum plates in diisopropyl ether or the diisopropyl ether–ethyl acetate (5:2) system.

Thin-layer chromatography has also been used to follow the course of the reactions of steroids involving microbiological methods (the introduction of hydroxyl groups, double bonds, etc.)[91].

A number of oestrogen hormones have been separated on silica gel–gypsum or silica gel–starch layers in pentane–ethyl acetate (9:1 and 3:2) systems[92] and in the benzene–ethanol (9:1) system[93]. The spots were detected with a solution of antimony trichloride in chloroform with heating at 200°–250°, and in ultraviolet light. In the case of the plates prepared with starch, the compounds were detected with iodine vapour or with 0.5% potassium permanganate solution followed by water. A method for the spectrophotometric determination of the composition of a mixture of these substances has also been described[93].

A new effective method for separating steroids[19] involves chromatography on a thin unfixed layer of aluminium oxide or silica gel. This method makes it possible to use adsorbents of any activity. The separation was carried out on a layer of aluminium oxide (activity V) in different simple systems and solvents (benzene, ether, and mixtures of hexane and benzene, benzene and ether, and ether and ethanol). A study was made of the dependence of the adsorptive properties[19] of different steroids, chiefly of the androstane and cholestane series, on their polarity and the position and configuration of the functional groups in the steriod skeleton. The compounds were detected with H_2SO_4.

Bases were detected with Dragendorf's reagent. The lower limit of detection with sulphuric acid varied from 5 to 100 μg for six compounds.

Detection has also been carried out by spraying with morin solution or by carrying out the chromatographic process on a layer of aluminium oxide impregnated with morin[55].

The preparative separation of the epimers 5α-cholestan-3α-ol and 5α-cholestan-3β-ol in the benzene–ether (7:3) system on a layer of neutral aluminium oxide impregnated with morin has been described[19]. The separation is quantitative. Good results have been obtained in the analysis of a number of epimeric 3α- and 3β-steroids. The isomers with a polar substituent in the equitorial position are generally more firmly held on aluminium oxide. The only exceptions are androst-5-en-3β-, 17α-en--3β-, 17β- doils.

Good results have also been obtained in the separation of steroids of the pregnane series on an unfixed silica gel layer in the benzene–ethyl acetate (1:1) system[19].

Steroids have also been separated on an unfixed layer of aluminium oxide with activity III, in mixtures of benzene and ethanol in different proportions[20]. 50 steroids containing from one to five functional groups have been separated. The influence of various substituents on the overall adsorptive properties of steroids has been discussed[20]. It has been shown that separations on commercial (alkaline) and specially purified (neutral) specimens of aluminium oxide give identical results. In the case of alkaline aluminium oxide, however, partial hydrolysis is observed in the case of very unstable compounds, and compounds such as steroid trichloro- and trifluoro-acetates are decomposed completely.

4. Glycosides

Thin-layer chromatography on a silica gel–gypsum layer has been used to confirm the structure of certain cardiac glycosides extracted from the Uzara root[94]. This method is particularly effective for the separation of allo-uzari-genins and other uzarigenins. The *Rf* values of a number of cardenolides have been determined in the diisopropyl ether–acetone (3 : 1) system and in ethyl acetate. The spots were detected by drying the plate, heating at 130° for 5–10 min, spraying with a solution of chlorosulphonic acid in acetic acid (1 : 2), heating for 5 min at 130°, and examining in ultraviolet light.

Separation on a thin layer of silica gel–gypsum has also been used for the rapid analysis of mixtures of glycosides from Digitalis and Podophyllum[12]. The Digitalis cardiac glycosides were separated in a methylene chloride–methanol–formamide (80 : 19 : 1) system. The compounds were detected with trichloroacetic acid and chloramine (16 : 1) with subsequent heating at 110° for 10 min and examination in ultraviolet light. This detected down to 0.1 μg of cardiac glycoside in daylight and down to 0.01 μg in ultraviolet light. Existing methods of paper chromatography can detect not less than 3–5 μg. This method has been used to separate secondary-glucosides, digilanides A, B, and C, desacetyl-digilanides A, B, and C, and digitaloids.

The separation of the lignanglycosides and aglycones present in both forms of Podophyllum has been carried out by a two-stage process. The separation was first carried out in a chloroform–methanol (90 : 10) system, in which the glycosides were separated, and then in a chloroform–acetone (65 : 35) system, in which the aglycones were separated. The solvent was removed between the two stages with cold air for 5 min. The products were detected by spraying with a 1 : 1 mixture of sulphuric and acetic acids with subsequent heating at 100° for 10 min. The lower limit of detection was 0.3 μg. This method has been used to separate glucosides (α-peltatin-β-glycoside, podophyllotoxinglycoside, and β-peltatin-β-*D*-glycoside) and aglycones (4,4′-dimethylpodophyllotoxin, α-peltatin, podophyllotoxin, β-peltatin, and 1-desoxypodophyllotoxin).

A recent paper[95] described the separation, on a layer of polyamide powder, of 14 glycosides, whose aglycones were kaempferol, quercitin, and myricetin, and whose carbohydrate fraction included rhamnose, arabinose, glucose, and galactose. A sharp separation of 3-monosides, 3-biosides, and 3,7-glycosides was also achieved. The separation was carried out in the ethanol–water (3 : 2), water–ethanol–acetylacetone (4 : 2 : 1), and water–ethanol–ethyl methyl ketone–acetylacetone (13 : 3 : 3 : 1) systems. The spots were detected in ultraviolet light.

5. Lipids

In recent years, considerable attention has been paid in biochemical studies to the determination of the composition of natural lipids. Usually, the hydrolysis products are studied, and the latter are separated and identified by chromatographic methods.

In the first paper devoted to the separation of lipids by thin-layer chromatography[96] it was shown possible to separate various classes of compound present in lipids. A silica gel–gypsum layer in the petroleum ether (b.p. 60°–70°)–ether (92 : 8) system was used to separate lipid hydrolysis products consisting of higher aliphatic alcohols, esters, acetylglycerides, diacetylmonoglycerides, and diacetylglyceryl ethers. The compounds were detected by the action of iodine vapour on a plate sprayed with a 0.2% alcoholic solution of α-cyclodextrin, by Rhodamine B, or by spraying with concentrated sulphuric acid.

The separation and identification of the products of the hydrolysis of natural fats, oils, and waxes on a silica gel–gypsum layer in the hexane–ether (95 : 5) and petroleum ether–ether–acetic acid (70 : 30 : 1 and 70 : 30 : 2) systems has also been described[97]. The chromatogram was sprayed with a 0.2% alcoholic solution of 2′,7′-dichlorofluorescein.

In addition to the adsorption method, a partition method has also been used for the analysis of lipids by thin-layer chromatography[98].

An impregnated layer[98] in ether gives good separation of various classes of compound obtained in the hydrolysis of lipids, from hydrocarbons to phosphatides. The petroleum ether (60°–70°)–ether–acetic acid (90 : 10 : 1) system has been used to separate higher aliphatic hydrocarbons, alcohols, aldehydes, acids, and esters. The more polar compounds, the monoglycerides, glyceryl ethers, and phosphatides were separated in the petroleum ether–ether–acetic acid (70 : 30 : 1) system. The chromatogram was sprayed with a 0.2% alcoholic solution of 2′,7′-dichlorofluorescein. Unfortunately, the *Rf* values for homologous series of compounds with long hydrocarbon chains are the same. By analogy with the separation of homologous series on impregnated paper, a silica gel–gypsum layer impregnated with a 5% solution of silicone oil in ether was used. In the acetonitrile–acetic acid–water (70 : 10 : 25) system this method separated mixtures of the methyl esters of higher aliphatic acids.

The unsaturated compounds were detected with an α-cyclodextrin–iodate solution. Unsaturated compounds were detected with iodine vapour.

A number of recent papers[46,47,99,100] have been devoted to a detailed study of the separation of lipids by thin-layer chromatography. Model systems of lipid hydrolysis products and mixtures obtained from natural lipids have been studied.

Paper I[99] describes the separation of the following classes of compound: higher aliphatic aldehydes, acids, keto-acids (C_{14}, C_{16}, C_{18}, C_{20}), and monoglycerides, on a silica gel–gypsum layer in ether. The mono- di-, and tri-glycerides of the higher aliphatic acids were separated in isopropyl ether. The triglycerides of aliphatic acids, hydroxy-, dihydroxy-, epoxy-, and diepoxy-aliphatic acids were also separated in isopropyl ether +1.5% acetic acid.

Alcoholic molybdophosphoric acid solution and Rhodamine B solution were used for detection. 11 compounds

of various classes were separated by a two-dimensional method on the same layer (Fig. 9).

The same paper[99] describes the separation of homologous series of higher aliphatic alcohols and saturated and unsaturated acids in the acetonitrile–acetic acid (1 : 1) system on a silica gel–gypsum layer impregnated with undecane. Epoxy- and epithio-aliphatic acids were separated on the same layer in 80% acetic acid. The plates were then sprayed with molybdophosphoric acid. Diglycerides were separated with the chloroform–methanol–water (5 : 15 : 1) three-component system. The use of water is necessary to decrease the solubility of undecane in chloroform. Rhodamine B was used for detection. Other systems have been used, for example, the acetone–acetonitrile (7 : 3) system, in which both saturated and unsaturated triglycerides were separated. The use of a two-dimensional method with a layer impregnated with undecane gives better separation than that with a non-impregnated layer. A chromatogram illustrating the separation of di- and triglycerides and aliphatic acids is shown in Fig. 10.

Paper III‡ describes a new method for colouring thin-layer chromatograms[100], based on fixation of the layer with dichloromethylsilane. This makes it possible to immerse the plate in aqueous solutions and thus to use the specific methods of detection used in paper chromatography. Examples are given of the separation of higher aliphatic acids on a kieselguhr–gypsum layer in the acetic acid–acetonitrile (1 : 1) system, of phosphatides in the chloroform–methanol–water (11 : 5 : 11) system, and of triglycerides in the acetone–acetonitrile (8 : 2) system. The acids were detected with copper acetate and rubeanic acid. Phosphatides were detected with a 1% solution of molybdophosphoric acid in a 1 : 1 chloroform–ethanol mixture; after removal of the solvents the plates were washed in running water and immersed in a 1% solution of stannic chloride in 2 *N* hydrochloric acid. The triglycerides were detected after immersing the plate in 20% aqueous ethanol, by the transparency method[101].

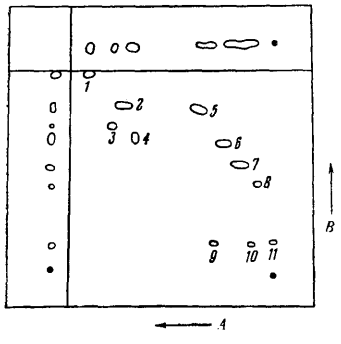


Fig. 9. Chromatogram for the separation of compounds of different classes by a two-dimensional method on a silica gel–gypsum layer. Systems: *A*) ether (30 min); *B*) isopropyl ether + 1.5% acetic acid (45 min). 1) Tristearin; 2) myristyl aldehyde; 3) distearin; 4) stearyl alcohol; 5) stearic acid; 6) stearic acid 9,10-epoxide; 7) 12-hydroxystearic acid; 8) stearic acid 9,10-12,13-diepoxide; 9) monostearin; 10) stearamide; 11) 9,10-dihydroxystearic acid. Compounds detected with molybdophosphoric acid.

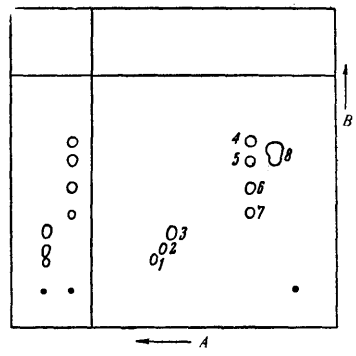


Fig. 10. Chromatogram for the separation of a mixture of di- and tri-glycerides and acids by a two-dimensional method on a silica gel–gypsum layer impregnated with undecane before separation in the *B* direction. Systems: *A*) dichloroethane; *B*) acetone–acetonitrile (7 : 3). 1) Triolein; 2) trimyristin; 3) trilaurin; 4) dilaurin; 5) dimyristin; 6) dipalmitin; 7) distearin; 8) aliphatic acids. Compounds detected with molybdophosphoric acid.

Paper IV by the same author and coworkers describes a more detailed study of the separation of triglycerides[46], including 20 synthetic and many natural triglyceride compounds, on a kieselguhr–gypsum layer impregnated with hydrocarbons or silicone oils. Several hydrocarbons were rested: undecane, liquid paraffin, dodecane, and tetradecane, or the petroleum fraction with b.p. 240° (the so-called Tetradecane Stand.). The last of these was found to be most convenient and was used for impregnating the layer. The same paper[46] describes the separation of saturated and unsaturated triglycerides and their mixtures on a kieselguhr–gypsum layer impregnated with tetradecane, in an acetone–acetonitrile (8 : 2) system 80% saturated with tetradecane. The compounds were detected with iodine vapour and by spraying with Rhodamine B solution.

The same paper gives examples of the separation of saturated synthetic triglycerides in the methanol–acetonitrile (5 : 4) system on a kieselguhr–gypsum layer impregnated with low-molecular-weight silicone oil with a viscosity of 50 cS. Unsaturated triglycerides were separated in the methanol–acetonitrile–propionitrile (5 : 4 : 1.5) system. Natural triglycerides were also separated on the same layer in a methanol–acetonitrile–propionitrile (5 : 4 : 1.5) system 95% saturated with high-molecular-weight silicone oil (1000 cS). The spots were detected with iodine vapour and molybdophosphoric acid.

Paper V[47] by the same author describes the separation of various synthetic keto-acids, 2-hydroxy-acids and lactones with long chains on an impregnated kieselguhr–gypsum layer. 14 synthetic aliphatic keto-acids and lactones were separated on a kieselguhr–gypsum layer impregnated with tetradecane in an acetic acid–water (80 : 20) system 80% saturated with tetradecane. The same acids and lactones in a mixture with aliphatic acids were separated on a layer impregnated with undecane, in an acetic acid–water (80 : 20) system 75% saturated with undecane.

The same paper gives an example of the separation of 2-hydroxy-acids and aliphatic acids and their mixtures on a layer impregnated with tetradecane, in acetic acid–water (75 : 25 and 90 : 70) systems 75% saturated with tetradecane. The compounds were detected with Rhodamine B solution.

‡ Paper II[87] describes the separation of cholesterol esters of aliphatic acids and is dealt with in the section "Steroids and Cholesterol Esters" (p. 373).

Thin-layer chromatography has been used[102,103] to separate various structural isomers of higher aliphatic acids and esters containing hydroxy- and chloro-groups. 9-Hydroxy--*trans*-10-*cis*-12-octadecadienoic and 13-hydroxy-*cis*-9--*trans*-11-octadecadienoic acids have been separated on a silica gel–gypsum layer in the petroleum ether–ether (8 : 2) system[102]. The same layer was used[103] to separate *threo*--12-chloro-13-hydroxyoleic and *threo*-13-chloro-12--hydroxyoleic acids and their esters, in the petroleum ether (b.p. 30°–45°)–ether system (9 : 1) in the case of the esters and in the same system with 1% acetic acid added in the case of the acids. The compounds were detected with sulphuric acid, 2′,7′-dichlorofluorescein, and ultraviolet light. The result indicates that in many cases thin-layer chromatography is more effective than paper chromatography, which has not yet given a separation of these compounds.

Even gas–liquid chromatography, which provides the most effective method of separating the aliphatic acids as their methyl esters, cannot give complete separation of very complex mixtures. For example, the esters of saturated normal and branched acids overlap the esters of highly unsaturated acids with shorter chains, and this makes the quantitative analysis of lipids by this method difficult or impossible. A combination of the methods of gas–liquid and thin-layer chromatography makes this task easier. For this purpose[104], the esters of the unsaturated acids were converted into the acetoxymercury derivatives and the latter were separated from the esters of the saturated acids on a silica gel–gypsum layer by a two-stage process. The saturated esters (Rf 0.9) were separated from the mercury derivatives of the unsaturated esters (Rf 0.1) in the petroleum ether (b.p. 60°–70°)–ether (4 : 1) system (distance travelled 15–18 cm). The mercury derivatives were then separated in the same direction in the propanol–acetic acid (100 : 1) system (distance moved 12–14 cm; time 3–4 h). The mercury derivatives of acids containing one double bond (Rf 0.85), two double bonds (two spots with Rf 0.55 and 0.45), three double bonds (Rf 0.15), and more highly unsaturated acids (Rf 0.0) were then separated. The plate was dried and sprayed with a 1% alcoholic solution of diphenylthiocarbazone. The spots corresponding to the saturated esters (Rf 0.9) were then removed from the plate, the substance was extracted, and the saturated acids isolated were analysed by gas–liquid chromatography.

Thin-layer chromatography on a silica gel–gypsum layer in the ether–petroleum ether (b.p. 66°–67°) (8 : 92) has been used to follow the course of the acetylation of monoglycerides isolated from various fats[105], and the same layer in the petroleum ether (b.p. 30°–60°)–ether (95 : 5) system has been used to control the synthesis of linolenic aldehyde[106].

The separation of aliphatic acids and α-glyceryl ethers present in the alkoxyglycerides isolated from fish liver oil[107] and the use of thin-layer chromatography to determine the composition of extracts from faeces and faecaliths[108] have also been described.

In the study of lipids obtained by decomposing human brain, rapid identification of the main fractions obtained by column chromatography is necessary. Thin-layer chromatography on a silica gel–gypsum layer has been used for this purpose[109]. The method gives better separation than paper chromatography, thanks to the sharper separation of the zones. The time required for the separation is only 60–90 min, the distance moved being 10–15 cm. The universal reagent proposed[109] for the detection makes it possible to detect certain lipid components present to the extent of only 0.2% in the mixtures. The lower limit of detection varies from 0.1 to 1 μg. 30 specimens of lipids and their derivatives, some of which were specially synthesised, were examined in 12 different systems and solvents and a method for their separation was described.

The following two solutions were proposed as a universal reagent for lipids: (1) 50 g Bromothymol Blue, 1.25 g boric acid, 8 ml 1.0 *N* NaOH, and 112 ml water, and (2) 40 g Bromothymol Blue and 100 ml 0.01 *N* NaOH. The lower limits of detection lie between 0.1 μg (for example, sphingomyelin) and 1 μg (for example, cerebron sulphate).

A number of special reagents have been given for determining cholesterol and its esters (lower limit 2–4 μg), saturated and unsaturated α-monoglycerides (lower limit 1–3 μg), and phospho- and glyco-lipids (lower limit for cerebon 4 μg and for cerebron sulphate 10 μg). The same author[110] used this method to study the composition of the sphingo-lipid fraction of normal and pathologically altered human brain on the same layer in the n-propanol–12% ammonia (8 : 2) system.

The separation of the cerebroside fraction of the sphingo--lipids of cattle brain on a thin layer of KSK silica gel–gypsum was recently studied[36]. Four individual cerebrosides: cerebron, kerasin, nervon, and hydroxynervon, were detected in the chloroform–methanol (8 : 2) system. Concentrated sulphuric acid was used for detection. The results obtained on the plate were used for the separation of these compounds on a silica gel column.

Thin-layer chromatography has also been used to separate glyco-lipids and phosphatides[111] on a silica gel–gypsum layer in the chloroform–methanol–water (60 : 35 : 8) system. This method detected cerebroside and cerebroside sulphate. Lysolecithin, sphingomyelin, lecithin, colaminecephalin, cerebroside, and cardiolipin were separated in the same system with the ration 65 : 25 : 4. The compounds were detected with Rhodamine B and Dragendorf's reagent.

The same layer was used to separate some products of the ganglioside fraction of human brain in the n-butanol-pyridine–water (3 : 2 : 1) system[112]. The quantitative determination of colaminecephalin and lecithin in medicinal plants by thin-layer chromatography has also been described[60].

6. Carbohydrates and Polyhydroxy-Compounds

The separation of hydrophilic compounds such as the carbohydrates by thin-layer chromatography has been possible only by using modified layers of adsorbent. A number of sugars have been separated on a kieselguhr–gypsum layer[11,13] impregnated with 0.02 M sodium acetate solution, using the ethyl acetate–65% isopropanol (65 : 35) system in a supersaturated vessel. The sugars were applied to the plate in pyridine solution and were detected by spraying with a freshly prepared solution of concentrated sulphuric acid and anisaldehyde in ethanol§. This method was found to be 20 times more sensitive than previously-known methods of analysis on paper. The optimum quantity of a mixture of sugars for separation on paper is 100–500 μg and the lower limit of detection is not less than 5 μg. For analysis on a kieselguhr–gypsum layer using anisaldehyde–sulphuric acid to detect the compounds, the

§ 0.5 ml concentrated sulphuric acid and 0.5 ml anisaldehyde in 9 ml 95% ethanol.



Fig. 11. Chromatogram for a mixture of sugars on a buffered kieselguhr–gypsum layer. The figure shows the sugars: 1) lactose; 2) saccharose; 3) glucose; 4) fructose; 5) *D*(+)-xylose; 6) *D*(−)-ribose; 7) *L*(+)-rhamnose; 8) *D*(+)-digitose; 9) *L*(+)-arabinose; 10) *D*(+)-mannose; 11) *D*(+)-galactose; 12) maltose; 13) *L*(−)-sorbose; CI) Mixture containing 1–8; CII) mixture containing 9–12; CIII) mixture containing 5–9.

lower limit of detection for the sugars is 0.05 μg. The best separation is achieved with 0.5 μg of substance and the maximum quantity of sugar which can be applied is 5 μg. A chromatogram for a mixture of sugars on a buffer kieselguhr–gypsum layer[11,13] is shown in Fig. 11.

The qualitative and quantitative separation of sugars has also been carried out on a silica gel–gypsum layer impregnated with boric acid (6 ml 0.1 *N* boric acid to 4 g silica gel)[42]. In this case the separation was carried out in the acidic benzene–methanol–acetic acid (1 : 3 : 1) and ethyl methyl ketone–methanol–acetic acid (3 : 1 : 1) systems and the compounds were detected by spraying with a mixture of 20% sulphuric acid and a 0.2% solution of naphthoresorcinol (1,3-dihydroxynaphthalene) in ethanol (1 : 1) with drying at 105°. Mono- and di-saccharides and uronic acids were detected by this method. The method for the quantitative separation of sugars, described in the same paper, is based on the elution of the sugars from the spots after removal of the latter from the plate, and transformation of the compounds isolated.

In connection with the study of the chemistry of macrolide antibiotics[37], the possibility of detecting polyhydroxy-compounds on a thin layer of silica gel–gypsum has been examined. Studies have been made of carbohydrates and related substances (glucose, lactose, glucosaccharin), polyhydric alcohols (ethylene and propylene glycols, glycerol, 3-methylhex-1-yn-3,4-diol), and polyhydroxy-acids (tartaric and 2,3-dihydroxy-2-methylpentanoic acids). The compounds were detected with the reagents for the α-glycol group usually employed in paper chromatography: a mixture of 5% aqueous silver nitrate solution and ammonia, an alkaline solution of sodium periodate and potassium permanganate, lead tetraacetate with subsequent spraying with rosaniline, and potassium periodate with benzidine. Most of the substances studied were detected only in quantities of 20–50 μg. The sensitivity of all the reagents in this case was found to be less than that on paper by a factor of 2–5.

7. Phenols, Phenolcarboxylic Acids, and Quinones

There have been several examples of the separation of volatile phenols in different systems on a thin layer of silica gel fixed to the plate with starch[4] or gypsum[7,8]. A detailed description has been given[113] of the analysis of phenol, *o*-, *m*-, and *p*-cresols, guaiacol, eugenol, and thymol in chloroform, xylene, and their mixtures (75 : 25, 50 : 50, and 25 : 75) on a thin layer of silica gel–kieselguhr–starch (1 : 1 : 1). In all cases the compounds were detected by spraying with diazotised sulphanilic acid, and also with an alcoholic $FeCl_3$ solution and with concentrated sulphuric acid.

This method has also been used[114] to follow the stepwise methylation of β-resorcylic acid. Study of the methylation products during the reaction, by thin-layer chromatography on a fluorescent silica gel layer, made it possible to direct the reaction as required. The petroleum ether (b.p. 66°–67°)–ether (3 : 7) system was used. This method was also used to study a number of aromatic polyhydroxy-compounds.

The separation of a number of phenols and phenolcarboxylic acids on a silica gel–gypsum layer in the acidic benzene–dioxan–acetic acid (90 : 25 : 4) and benzene–methanol–acetic acid (45 : 9 : 4) systems has recently been described[115]. The compounds were detected by means of the following reagents, which were first diazotised: benzidine, sulphanilic acid, 5-nitro-2-aminoanisole, and 1-amino-4-benzoylamino-2,5-diethoxybenzene, and also with tetrazotised di-*o*-anisidine.

Some aromatic hydroxy-acids[13] and polyphenols have also been separated in the benzene–methyl acetate–80% formic acid (4 : 4 : 2) system. Natural benzoquinones have been successfully separated in the hexane–ethyl acetate (85 : 15) system on silica gel–starch plates deactivated in air.

The separation of a mixture of 2,2′-methylene-bis-(4-chlorophenol) and 2,2′-methylene-bis-(3,4,6-trichlorophenol) on a silica gel–starch layer in hexane saturated with acetic acid has also been described[117]. The compounds were detected with solutions of ferric chloride and potassium cyanoferrate(III).

8. Coumarins and Flavones

Several substituted coumarins have been isolated and characterised in a study of lemon extract by adsorption column chromatography and chromatography on thin fluorescent silica gel–gypsum[118] or on starch[119] layers in the hexane–ethyl acetate (75 : 25) system. This method was later used[57] for the quantitative photometric determination of some of the above coumarins and also for their determination in certain foodstuffs[120] and medicinal products[121].

Acidic systems of the toluene–ethyl formate–formic acid (5 : 4 : 1) type[13,14] have recently been used to separate multicomponent mixtures of α- and β-pyrones, coumarins, flavones, and hydroquinones by thin-layer chromatography. The method was found to be much more sensitive than paper chromatography. With detection by long-wave ultraviolet light the sensitivity for coumarins was 0.1 μg. Thin-layer chromatography has been used to separate the following coumarins: esculin, esculetin, scopoletin, 4-methylumbelliferone, xanthotoxin, bergenin, imperatorin, and atamanine.

The flavones robinetin, morin, toxipholin, quercetin, kaempferol, naringenin, and chrysin, separated by this method, were detected with a 1% solution of β-aminoethyl

diphenylborate in methanol and examination in ultraviolet light. The sensitivity of the method is 0.1 μg. Hydroquinone and its esters and glycosides were detected with Millon's reagent, prepared by dissolving 5 g mercury in 10 g fuming sulphuric acid and adding 10 ml water. The lower limit of detection for arbutin and methylarbutin is 5 μg, that for hydroquinone and its methyl ether 1 μg, and that for its diethyl ether 10 μg.

Flavone glycosides have been separated using the ethyl acetate–ethyl methyl ketone–formic acid–water (5 : 3 : 1 : 1) system. This paper also described the separation of aromatic hydroxy-acids, certain tannins, and phenolglucosides in the toluene–ethyl formate–formic acid (5 : 4 : 1) system and also the separation of substances present in lichens.

Flavones have also been separated on a thin layer (0.1–0.2 mm) of Silon (Kapron) [a type of Nylon (Ed. of Translation)] polyamide powder[122].

9. Carotenoids and Vitamins

Certain carotenoids were separated on a silica gel–starch plate in the hexane–ether (3 : 7) system as early as 1958.[23] Pigments of the tetrahydropyrrole series were separated on the same layer in the benzene–ethyl acetate–ethanol (90 : 20 : 7.5) system[23].

In the last two years thin-layer chromatography has been used extensively[123] to study different classes of carotenoids, particularly carotenoid aldehydes, which occur in very small quantities in natural products. A new sensitive reagent has been proposed for detecting these compounds[124,125]. The plate is sprayed with an alcoholic solution of Rhodanine and then with a concentrated aqueous solution of ammonia or sodium hydroxide. This reagent makes it possible to detect down to 0.03 μg of a polyene aldehyde. Retinene (vitamin A) and β-apo-8-carotenal were recently separated on a silica gel–gypsum layer impregnated with liquid paraffin, in methanol saturated with liquid paraffin[125].

Carotenoid aldehydes have been separated with both impregnated and non-impregnated layers[126]. A silica gel–gypsum–$Ca(OH)_2$ (5 : 20) layer impregnated with liquid paraffin in the petroleum ether–benzene (1 : 1) system or, in some cases, the same system with 1% methanol added, has been used to separate carotenoid aldehydes with the following Rf values:

C_{40}	C_{37}	C_{35}	C_{32}	C_{30}	C_{27}	C_{25}	C_{20}
0.28	0.34	0.377	0.473	0.488	0.633	0.588	0.855

A non-impregnated layer shows clearly two series with Rf values corresponding to C_{40}, C_{35}, C_{30}, and C_{25} aldehydes on the one hand and to C_{37}, C_{32}, and C_{27} aldehydes on the other.

Seven synthetic β-apocarotenals of the C_{25}–C_{40} series have also been separated on a calcium hydroxide–silica gel–gypsum (6 : 1) layer in the petroleum ether–benzene (2 : 3) system, and six methyl esters of β-apocarotenoic acids (C_{27}–C_{30}) have been separated in the same system[127].

This method was used to detect fat-soluble vitamins of α-tocopherol and vitamin A in the separation of lipids on a silica gel–gypsum layer in the ethyl acetate–petroleum ether (2 : 8) system[128]. The compounds were detected with sulphuric acid.

Thin-layer chromatography has also been used to separate vitamins of the B group (B_1, B_2, B_6, nicotinamide, biotin, and calcium pantothenate) and vitamin C.[129] The separation was carried out on a silica gel–gypsum layer containing 2% of a fluorescent substance (ZS-Super), in the acetic acid–acetone–methanol–benzene (5 : 5 : 20 : 70) system. In this system vitamin B_1 remains at the starting line. In the detection of the spots, the plate was first examined in ultraviolet light with a wavelength of 366 mμ, in which the fluorescent layer remains dark and the vitamin B_2 (Rf 0.35) shines brightly on a dark background. The plate was then illuminated with ultraviolet light with a wavelength of 254 mμ, in which dark spots of vitamin B_1 (Rf 0.0), vitamin C (Rf 0.30), and nicotinamide (Rf 0.65) are observed against a light background. Biotin was detected by spraying another plate with potassium iodoplatinate, which revealed biotin (Rf 0.80), vitamin B_1, nicotinamide, and vitamin C in the form of spots of different colours. To detect vitamin B_6 and calcium pantothenate, the lower part of another plate was sprayed with a 0.1% solution of dichlorobenzoquinone chlorimide in ethanol saturated with ammonia vapour. This revealed vitamin B_6 (Rf 0.15). The plate was then heated to 160° and the upper part of the plate was sprayed with a 0.5% solution of ninhydrin in ethanol. The plate was then reheated to 160° to reveal the calcium pantothenate. The sensitivity of the method is 1–10 μg for vitamins of the B group and 5–30 μg for vitamin C.

In the separation of A vitamins and provitamins and vitamins K_1, K_2, and K_3 [54] on an unfixed layer of aluminium oxide, the use of 70% perchloric acid and 98% sulphuric acid to detect these compounds is recommended. After the separation, the plate is dried in air and the aluminium oxide layer is impregnated with the above acids in a direction at right angles to the direction of separation.

10. Antioxidants and Plasticisers

Thin-layer chromatography on a silica gel–gypsum layer has also been used to separate and identify antioxidants in the food industry[130], and has made their study much easier. The best system was found to be a chloroform–methyl cellosolve (80 : 20) mixture. This method was used successfully to separate 24 different antioxidants. The compounds were detected by spraying the plate with a 2% solution of molybdophosphoric acid in methanol and treating with ammonia vapour after 1–2 min. The plate was then heated for 10 min at 120° to reveal some additional spots. It is also possible to spray with a 1% solution of 2,6-dichlorobenzoquinone chlorimide in ethanol and then with a 2% solution of borax in 40% ethanol. Antioxidants have also been separated by two-dimensional chromatography. The separation was carried out in one direction in benzene and in the other direction in chloroform.

Good results in the analysis of α-, β-, γ-, and δ-tocopherols and their mixtures have been obtained[58] by separation on a silica gel–gypsum layer in chloroform and on an aluminium oxide–gypsum layer in benzene. In both cases, the β- and γ-tocopherols, differing in the position of the hydroxyl groups, were found to have identical Rf values when molybdophosphoric acid solution was used for detection. Spraying with cerium(IV) sulphate reagent[131], however, gives spots of different colours, making identification easy. The quantitative separation of tocopherols has also been described.

The use of a modified silica gel–kieselguhr layer containing added oxalic acid[41], in the benzene–ethyl acetate (6 : 4) system, makes possible the qualitative and quantitative (with an accuracy of ±5%) determination of norhydroguaiaretic and ascorbic acids in a mixture of gallates. 2,6-Dichlorobenzoquinone chlorimide can be used instead of the cerium(IV) sulphate reagent for detection, in which gase the silica gel–kieselguhr layer should be impregnated with borax in the ratio 25 : 4.5. The quantitative separation of antioxidants is based on measurement of the size of the spots and by graphical interpolation.

Mixtures of plasticisers[132] have been separated on a silica gel–gypsum layer containing 0.05% Ultraphor, in the following systems: isooctane–ethyl acetate (9 : 1); benzene–ethyl acetate (95 : 5), and dibutyl ether–hexane (9 : 1). The compounds were detected in ultraviolet light with a wavelength of 365 mμ. This method achieved separation of the following compounds: glyceryl triacetate, ethyl *o*-ethoxycarbonylbenzoylglycolate, triethyl acetylcitrate, triethyl phosphate, diethyl phthalate, butyl *o*-butoxycarbonylbenzoylglycolate, 2-ethylhexyl diphenyl phosphate, tributylacetylcitrate, di-n-butyl phthalate, diisobutyl adipate, dibutyl sebacate, dinonyl phthalate, di-2-ethylhexyl phthalate, and butyl stearate. A number of specific colour reactions for detecting plasticisers have been given.

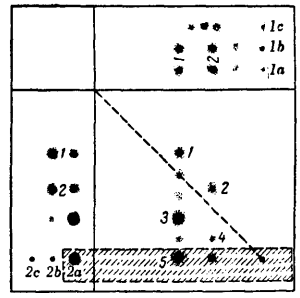


Fig. 12. Chromatogram for a pyrethrum concentrate on a silica gel–gypsum layer. 1*a*, 1*b*, 2*a*, 2*b*) Pyrethrum concentrate; 1c, 2c) mixture of dyes; 1) pyrethrin I; 2) pyrethrin II; 3) pyrethrin I peroxide; 4) pyrethrin II peroxide; 5) lumipyrethrin. After separation in the first direction the hatched part of the plate was exposed to ultraviolet light.

11. Insecticides

It has been reported[133] that a mixture of pyrethrin I (R_f 0.42) and pyrethrin II (R_f 0.21) can be separated on a silica gel–gypsum layer in the hexane–ethyl acetate (80 : 20) system. This system was then used to analyse pyrethrum extract on a silica gel column.

Under the influence of light and air, pyrethrins are rapidly converted into lumipyrethrins *via* their peroxides. Thin-layer chromatography has been used in the study of this process[10]. A particularly interesting feature of this work is the successful use of the "separation–reaction–separation" technique. By this method, changes in the polarity of the individual components of a mixture of organic compounds as a result of the action of, for example, γ-rays, X-rays, ultraviolet light, increased temperature, and various gases, on the mixture are readily detected. In the study of the oxidation of pyrethrins in this work, a two-dimensional method of separation was employed, using the hexane–ethyl acetate (75 : 25) system in both directions. The compounds applied to the plate were exposed to sunlight or ultraviolet light and heated. If no oxidation had taken place, the spots would have lain almost on the diagonal of the chromatogram, but since oxidation takes place, substances with different R_f values are produced (see chromatogram in Fig. 12), so that the spots for the reaction products (pyrethrin I and II peroxides and lumipyrethrins) lie below the diagonal.

Thin-layer chromatography has recently been used[134] to separate various synthetic insecticides. Thus a silica gel–gypsum layer in the hexane–acetone (4 : 1) system has been used to separate thiophosphates with the following R_f values: Diazinon 0.76–0.82, parathion 0.65–0.68, Meta-Systox 0.62–0.64, malathion 0.52–0.54, chlorthion 0.43–0.45, Fac 0.20–0.26, and Rogor 0.04–0.07. The compounds were detected by means of readily-oxidised 0.5% palladium(II) chloride solution.

The following chlorine-containing insecticides were separated on an aluminium oxide–gypsum layer with activity II on the Brockmann scale, in hexane in a supersaturated vessel: aldrin 0.78–0.82, DDT 0.59–0.62, Perthane 0.48–0.50, hexachlorocyclohexane 0.39–0.41, dieldrin 0.17–0.19, and methoxychlor 0.10–0.12. The compounds were detected by spraying with a solution of 0.5 g *NN*-dimethyl-*p*-phenylenediammonium in sodium ethoxide solution (1 g Na in 100 ml ethanol). The plate was then sprayed with water and heated by means of a quartz lamp for 1 min. The sensitivity of the method is < 5 μg.

Thin-layer chromatography has also been used to separate certain thiophosphate esters[16] on a silica gel–gypsum layer in the methylene chloride–methanol–10% ammonia (8 : 2 : 3) system. When iodine–azide reagent is used for detection, the lower limit is 1–5 μg.

12. Amino-Acids, Amines, Peptides, and Nucleotides

The first separation of amino-acids[135] in the form of their sodium salts was carried out in 1958 on a thin unfixed layer of aluminium oxide on glass. Four systems were used, the best being the n-butanol–ethanol–water (60 : 40 : : 40) system.

One year later, good results were obtained in the separation of the sodium salts of a number of amino-acids on a silica gel–gypsum layer by a two-dimensional method using the propanol–water (1 : 1) system in one direction and the phenol–water (10 : 4) system in the other[29]. The amino-acids were detected with ninhydrin solution.

Almost simultaneously, amino-acids were separated on a silica gel–gypsum layer with phosphate buffer[28]. In the preparation of the layer, a solution of 0.2 M KH_2PO_4 and 0.2 M Na_2HPO_4 (1 : 1) was used instead of water. The separation was carried out in 96% ethanol and in the 96% ethanol–25% ammonia (4 : 1) and 96% ethanol–25% ammonia–water (7 : 1 : 2) systems. In the two-dimensional separation, the first two systems were used. The compounds were detected with the reagents usually employed for this purpose in paper chromatography.

Finally, a silica gel–gypsum layer has recently given excellent results[136], thanks to a careful and thorough study of the technique of separating amino-acids by thin-layer chromatography. It was found that on a silica gel–gypsum layer, the spots obtained are smaller and of better shape, as a result of the less marked diffusion, than those obtained on paper, and that to obtain good results in the preparation of the layer, the plate should not be activated by heating, but simply by drying in air. The height to which the liquid rises should not be more than 10 cm from the starting line. The quantities of acids applied to the plate should be not more than 1–5 μg, since the size of the spot depends on the quantity of substance taken. When these conditions are observed, reproducible results are obtained and the variation in the R_f values is ±0.05. Five systems were examined. The best results were obtained by separation in the n-butanol–acetic acid–water (60 : 20 : 20) and phenol–water (75 : 25) systems, the results being particularly good when two-dimensional separation in these systems was used. The time required for the separation is 1.5–2 h.

In the detection of the compounds, the plate is dried for 10 min at 100° and sprayed with a freshly prepared 50 : 3 mixture of two solutions: (1) a solution of 0.2% ninhydrin in 50 ml absolute alcohol, 10 ml acetic acid, and 2 ml 2,4,6-collidine; and (2) a 1% solution of $Cu(NO_3)_2.3H_2O$ in absolute alcohol. The sensitivity of the method is 10 times greater than that of paper chromatography.

The results of the two-dimensional separation of amino-acids by paper chromatography and by thin-layer chromatography on a silica gel–gypsum layer in the same systems are compared in Fig. 13. Ten amino-acids on paper are shown on the left, and fourteen amino-acids on a silica gel–gypsum layer are shown on the right.

The separation of the same amino-acids, with even better results, on a silica gel–gypsum layer by a two-dimensional method using the chloroform–methanol–17% ammonia (2 : 2 : 2) system in the first direction and the previously used phenol–water (75 : 25) system in the other, has recently been described[137].

In the separation and identification of amino-acids, *N*-(2,4-dinitrophenyl)amino-acids, and their 3-phenyl-2-thiohydantoins[51,30], thin-layer chromatography has shown its advantages over paper chromatography. There is a saving in time, the time required for the determination being 1–3 h, and an increase in sensitivity by a factor of at least 10.

A silica gel–gypsum layer can be used to separate the dinitrophenyl (DNP) derivatives of almost all the protein amino-acids, soluble or insoluble in water and acids.

Dinitrophenylamino-acids soluble in water and acids have been identified in the n-propanol–34% ammonia (7 : 3) system[51]. Five systems have been used to separate the water-insoluble derivatives: (I) toluene–pyridine–ethylene chlorohydrin–0.8 *N* ammonia (100 : 30 : 60 : 60); (II) chloroform–benzyl alcohol–acetic acid (70 : 30 : 3); (III) chloroform–t-pentyl alcohol–acetic acid (70 : 30 : 3); (IV) benzene–pyridine–acetic acid (80 : 20 : 2); and (V) chloroform–methanol–acetic acid (95 : 5 : 1).

The best results were obtained by two-dimensional separation in these systems. The same paper also describes the results of a flow method of separation[30], which was used for the complete separation of various pairs of compounds, requiring an increase in the distance moved by the separating system. In this case good results were obtained in the separation of: (1) leucine and isoleucine; (2) *N*-(2,4-dinitrophenyl)leucine, *N*-(2,4-dinitrophenyl)isoleucine, and *N*-(2,4-dinitrophenyl)norleucine; (3) *N*-(2,4-dinitrophenyl)valine and *N*-(2,4-dinitrophenyl)-norvaline; and (4) *NN*-di-(2,4-dinitrophenyl)tyrosine and *NN*-di-(2,4-dinitrophenyl)lysine.

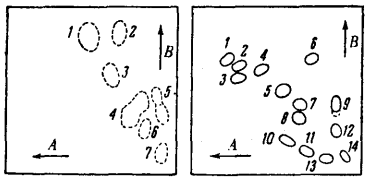


Fig. 13. Comparison of chromatograms for amino-acids on paper and on a silica gel–gypsum layer, obtained under identical conditions. Systems: *A*) n-butanol–acetic acid–water (6 : 2 : 2); *B*) phenol–water (75 : 25).
Paper chromatogram (*left*): 1) phenylalanine + isoleucine; 2) proline; 3) tyrosine; 4) glycine + glutamic acid; 5) arginine + lysine; 6) aspartic acid; 7) cysteine.
Thin-layer chromatogram (*right*): 1) phenylalanine; 2) isoleucine; 3) tyrosine; 4) valine; 5) alanine; 6) proline; 7) glycine; 8) serine; 9) histidine; 10) glutamic acid; 11) asparagine; 12) arginine; 13) cysteine; 14) cystine.

One-dimensional chromatography[51] makes it possible to detect down to 0.1 μg, and two-dimensional chromatography down to 0.5 μg of substance in daylight. Detection by photocopying in ultraviolet light is particularly sensitive. In this case 0.1–0.2 μg of amino-acid in a mixture of amino-acids is sufficient. The sensitivity for a single acid is 2×10^{-3} or 10^{-4} μmole (for example 0.02 μg for DNP-serine). With the application of ~100 μg of one DNP-amino-acid, it has been possible to detect the presence of ~0.05% of another DNP-amino-acid.

Mixtures of 3-phenyl-2-thiohydantoins (PTH) of amino-acids can readily be separated[51] on a silica gel–gypsum layer by one- or two-dimensional chromatography. 14 of the 19 amino-acid PTH studied were separated. The remainder are readily separated by a simple oxidation with hydrogen peroxide or by acid hydrolysis followed by separation of the free amino-acids on a thin layer of silica gel.

The amino-acid PTH were detected using a modified chlorotoluidine test[133]. The sensitivity of detection is 3×10^{-4} μmole, which corresponds, for example, to 0.05 μg for proline PTH.

The separation of amines, amino-acids, and adrenaline–noradrenalines on neutral and buffer silica gel–gypsum layers and on cellulose powder in the n-pentyl alcohol–acetic acid–water (4 : 1 : 5) system has been studied in detail[45]. The same paper also describes the separation, on neutral, phosphate-buffer, or acetate-buffer silica gel–gypsum layers, of the following amines: methylamine, ethylamine, n-propylamine, isopentylamine, cadaverine, putrescine, ethanolamine, histamine, tyrosine, phenylethylamine, benzylamine, and tryptamine. For the neutral layers, the

96% ethanol–25% ammonia (4 : 1), phenol–water (8 : 3), or butanol–acetic acid–water (4 : 1 : 5) systems were used. On the plates with Sörensen's phosphate buffer (pH 6.8), the separation was carried out in 10% aqueous ethanol, and on the plates with acetate buffer the separation was carried out in the butanol–acetic acid–water (4 : 1 : 5) system. On the neutral plates, the primary and secondary amines were best identified as the 3,5-dinitrobenzamides in the chloroform–ethanol (99 : 1) system.

The compounds were detected with a solution of iodine in chloroform, with α-naphthylamine solution, or with light from a quartz lamp.

An interesting example of the application of this method is provided by the separation of adrenaline and noradrenaline. Decomposition of these amines by oxidation during the chromatographic process is possible, but is prevented by the addition of a small quantity of sodium hydrogen sulphite as an antioxidant during the preparation of the phosphate-buffer layer. The separation was carried out in 70% ethanol. The spots were detected by spraying with a solution of iodine in chloroform and a solution of potassium cyanoferrate(III) in phosphate buffer and examining in ultraviolet light. The same amines were separated on a plate with a thin layer of cellulose powder in the n-pentyl alcohol–acetic acid–water (4 : 1 : 5) system.

A method for thin-layer ionophoresis and two-dimensional combined thin-layer ionophoresis and chromatography on a glass plate has recently been described[139]. Silica gel–gypsum, kieselguhr–gypsum, and aluminium oxide–gypsum layers were used for the ionophoretic separation of the amino-acids and a silica gel–gypsum layer was used for the combined ionophoretic and chromatographic separation.

In the determination of amino-acids and polypeptides by paper chromatography[140], quantities of substance of about 1 μmole (sometimes 0.1–0.2 mole) are required. The use of thin-layer chromatography on a thin layer of silica gel–gypsum for this purpose makes it possible to work with quantities of ~ 0.01 μmole. Glycyl-*L*-proline dipeptide thiohydantoin (R_f 0.36) and *L*-prolyl-*L*-leucylglycine tripeptide thiohydantoin (R_f 0.42) were identified in the heptane–pyridine–ethyl acetate (5 : 3 : 2) system[140]. To obtain good results, it was necessary to ensure that the layer was not saturated with atmospheric moisture, which has a marked effect on the R_f values. The compounds were detected with a starch–iodine–azide reagent: the plate was sprayed first with a 0.5% aqueous starch solution, then with iodine solution, and finally with sodium azide solution. The lower limit of detection is 0.01 μg of the peptide thiohydantoin.

A silica gel–gypsum layer has been used for the qualitative and quantitative separation of the natural bile acids: lithocholic, cholic, desoxycholic, and chenodesoxycholic acids, and the synthesised peptide derivatives formed with glycine (glyco-conjugates) and taurine (tauro-conjugated)[141]. The separation was carried out in two stages. The free acids moved with the upper phase of a toluene–acetic acid–water (5 : 5 : 1) mixture, and the conjugates remained close to the starting line. The glyco- and tauro-conjugates were then separated in the butanol–acetic acid–water (10 : 1 : 1) system. In this case the free acids moved with the liquid front. The compounds were detected with molybdophosphoric acid solution and heating for 5 min at 110°. The spectrophotometric determinations were carried out using 65% sulphuric acid, which was used to elute the substances from the silica gel. The quantity of substance in the mixture was determined by comparing the extinction coefficients.

Derivatives of the nucleic acids have been separated on a thin layer of cellulose[142]. Nucleic bases and nucleotides were separated with distilled water. The nucleotides were separated in the n-butanol–acetone–acetic acid–5% ammonia–water (4.5 : 1.5 : 1 : 1 : 2) system. The compounds were detected in ultraviolet light. The sensitivity of the method is $\sim 10^{-3}$ μmole for the adenine compounds and slightly more for the cytosine compounds.

Chromatography on a silica gel–gypsum layer has also been used to characterise certain intermediate products in the synthesis of (N-methyltyrosine)$_2$-oxytocin[143]. The same layer has been used to follow the synthesis of models of aminoacylribonucleic acids[144].

13. Alkaloids

The use of thin-layer chromatography for the rapid analysis of small quantities of alkaloids is particularly important in the study of medicinal products and in toxicology.

In 1960, a silica gel–gypsum layer with Sörensen's phosphate buffer[45] in the chloroform–ethanol (8 : 1) system was used to separate alkaloids containing different purine groups: caffeine, theobromine, and theophylline. The chromatogram was sprayed with an alcoholic solution of iodine and potassium iodide (1 g I and 1 g KI in 100 ml ethanol) and then with a solution of 25% HCl in 96% ethanol (1 : 1). The same paper describes the separation of ergoalkaloids on cellulose powder impregnated with a 20% solution of formamide in acetone. The results were better than those obtained by paper chromatography. In this case a two-stage separation was used in the benzene–heptane–chloroform (6 : 5 : 3) and benzene–heptane (6 : 5) systems.

The same authors separated several other groups of alkaloids: the Belladonna, Rauwolfia, opium, and other alkaloid groups[43]. The Belladonna alkaloids were separated on a neutral or alkaline silica gel–gypsum layer. In the case of the neutral layer, a dimethylformamide–diethylamine–ethanol–ethyl acetate (1 : 1 : 6 : 12) system was used and in the case of the alkaline layer (2 N KOH) the 70% ethanol–25% ammonia (99 : 1) system was used. The same alkaloids were also separated by a two-stage method on a cellulose layer impregnated with formamide, in the heptane–diethylamine (500 : 1) (distance moved 15 cm) and benzene–heptane–chloroform–diethylamine (6 : 5 : 1 : 0.02) (distance moved 10 cm) systems.

The Rauwolfia alkaloids were separated on a silica gel–gypsum layer in the chloroform–96% alcohol (9 : 1) or methanol–ethyl methyl ketone–heptane (8.4 : 33.6 : 58.0) systems. The same alkaloids were also separated on cellulose powder impregnated with a 20% solution of formamide in acetone, in the heptane–ethyl methyl ketone (1 : 1) system in an atmosphere of ammonia. The spots were detected in ultraviolet light or with trichloroacetic acid and ferric chloride.

The opium alkaloids were separated on neutral and alkaline silica gel–gypsum layers. The chloroform–ethanol (9 : 1) system was used in the case of the neutral layer, and the chloroform–ethanol (8 : 2) system in the case of the alkaline layer. These alkaloids were also analysed on a cellulose layer impregnated with formamide, in the benzene–heptane–

chloroform–diethylamine (6 : 5 : 1 : 0.02) system. The compounds were detected with Dragendorf's reagent.

Lobelia alkaloids were separated by chromatography on cellulose impregnated with formamide, in the benzene–heptane–diethylamine (1 : 6 : 0.02) system, and Helidonia alkaloids were separated on a silica gel–gypsum layer in the chloroform–ethanol (3 : 1) system. The alkaloids coniine, anabasine, nicotine, and arecoline were isolated by steam distillation and separated on an alkaline (2 *N* KOH) silica gel–gypsum layer in the chloroform–ethanol (8 : 2) system.

Thus thin-layer chromatography provides the most rapid method for the analysis of alkaloids and has been used successfully[44] for the systematic analysis of these compounds. As a result of the study of more than 50 alkaloids in seven different systems and solvents, it has been shown from their behaviour in these systems that the alkaloids can be separated into two groups. When the group to which the alkaloids being studied belong has been established, they are analysed in the systems cited and can be identified from a table of R_f values and colour reactions[44]. The separation was carried out on silica gel–gypsum, aluminium oxide–gypsum, and alkaline silica gel–gypsum layers in seven systems.

The alkaloids were detected by intense spraying with iodoplatinate reagent prepared from equal volumes of 0.3% aqueous chloroplatinic acid solution and 6% aqueous potassium iodide solution.

Thin-layer chromatography on a silica gel–gypsum layer in the methanol–ethyl methyl ketone–heptane (84 : 33.6 : 58) system has been used to separate the indole alkaloids reserpine and rescinnamine[145]. These alkaloids were determined quantitatively by spectrophotometry.

The separation of the opium alkaloids[146] on a thin layer of alkaline aluminium oxide (pH 5) in mixtures of ethanol, n-butanol, and water in different proportions has been described. These alkaloids have also been separated on a silica gel–gypsum layer in methanol[39]. This method has also been used to detect the alkaloids ergine and isoergine in the alkaloid fraction from *Rivea corymbosa* seeds[147].

14. Pteridines

The pteridines, representatives of the folic acid group, are of considerable physiological importance and play an important part in the exchange of substances in the organism. In papers on the synthesis of these compounds, the R_f value is often quoted as an important physical constant. Many pteridines are difficult to separate on paper. The use of thin-layer chromatography for this purpose has given good results[148] which could not previously be obtained on paper. The separation was carried out on a silica gel–gypsum or aluminium oxide–gypsum layer. A total of 24 neutral, alkaline, and acidic systems and solvents were studied. R_f values have been given for 14 pteridines[148].

The separation was carried out in the systems: dimethylformamide–water (190 : 10); 1, 5, and 10% citric acid; 5% malic acid; and 5% tartaric acid. In the case of leucopterin, 6-methylisoxanthopterin, 7-methylxanthopterin, isoxanthopterin, xanthopterincarboxylic acid, and a number of aminohydroxypteridines, the separation was carried out in ammonia solutions of different concentrations (1–25%) and certain other systems. The compounds were detected with ultraviolet light. The lower limit of sensitivity of this method is 1 μg.

15. Heterocyclic Compounds

The separation of small quantities of mixtures of indole derivatives on a silica gel–gypsum layer in a supersaturated vessel at 20° in the dark has recently been described[15]. Two reagents were used for detection: (1) Ehrlich's reagent, a solution of *p*-dimethylaminobenzaldehyde in a mixture of 50 ml 25% hydrochloric acid and 50 ml 96% ethanol, and (2) Procházka's reagent, a solution of 10 ml 35% formaldehyde, 10 ml 25% hydrochloric acid, and 20 ml 96% ethanol, with subsequent heating at 100° and examination in ultraviolet light. The latter reagent is very sensitive and in some cases can detect 0.005 μg of substance.

An unfixed layer of aluminium oxide with activity II/III, in the benzene–acetone (1 : 1) system, has been used to separate the following heterocyclic compounds[21]: the isomeric *N*-benzoyl- and *N*-acetyl-decahydroquinolinols (four isomers), the different 4-phenylpiperidin-4-ols, *NO*-diacetyldecahydroquinolin-4-ols, and cyanoethylcyclohexane-1,3-diones. The isomeric *O*-acetyldecahydroquinolin-4-ols were separated on the same layer in the acetone–methanol (3 : 1) system. The compounds were detected with iodine vapour and ultraviolet light.

16. Other Examples of the Use of Thin-Layer Chromatography

A number of other examples of the use of thin-layer chromatography to separate and identify various compounds and their mixtures have been described. The limits of applicability of this method are gradually being extended, and there are examples of the analysis of various hydrocarbons, alcohols, acids, organic peroxides, nitro-compounds, dyes, inorganic compounds, etc.

A thin layer of silica gel–gypsum in petroleum ether has been used to separate azulene and cadalene[5,7] and the same layer in the hexane–ethyl acetate (9 : 1) system has been used to separate chamazulene, chamazulenyl alcohol, and the acids of azulenic sesquiterpene and proazulene.

Anthracene derivatives[13] can be readily separated in the benzene–methyl acetate–80% formic acid (4 : 4 : 2) system or, more effectively, in the benzene–ethyl formate–formic acid (75 : 24 : 1) system[14]. The compounds are detected with a 2.5% solution of KOH in methanol and in long-wave ultraviolet light.

An unfixed aluminium oxide layer has been used to separate a number of acetylenic carbinols and the corresponding glycols in the benzene–ether (2 : 3) system. The spots were detected with iodine vapour and ultraviolet light[149].

Silica gel–gypsum layers in the benzene–methanol–acetic acid (45 : 8 : 4) and benzene–dioxan–acetic acid (90 : 25 : 4) systems[150] have been used to identify the following dibasic acids: oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids. The compounds were detected by drying the plate for 1 h at 120° and then spraying with bromophenol solution acidified with citric acid. The same layer in the first system was used to separate fumaric (Rf 0.23) and maleic (Rf 0.07) acids. The compounds were detected with permanganate solution made alkaline with sodium carbonate.

The same series of acids from oxalic to sebacic acid, were separated on a silica gel–gypsum layer in the 96% alcohol–water–25% ammonia (100 : 12 : 16) system[151]. The same paper also describes the separation of various aliphatic and aromatic acids: citric, tartaric, phthalic, terephthalic, benzoic, and *p*-toulic acids, and also phosphoric acid. The compounds were detected with Bromocresol Green.

Organic peroxides and acid peroxides have been separated[152] on silica gel–starch plates in the carbon tetrachloride–acetone (2 : 1) system. The compounds were detected with potassium iodide solution or a mixture of $Fe(NH_4)_2(SO_4)_2$ and KSCN.

A number of β-dicarbonyl compounds have been separated and identified on a silica gel–starch layer in the benzene–ethyl acetate (7 : 3) system[153]. The spots were detected with iodine vapour.

Various natural vegetable dyes[17,18] have been separated on an unfixed layer of aluminium oxide in mixtures of n-butanol, ethanol, and water in different proportions. Dyes of the Sudan Green series have been separated on a silica gel–gypsum layer[7].

A silica gel–gypsum layer in the hexane–ethyl acetate (85 : 15 and 1 : 1), benzene–ether (17 : 3), benzene–pyridine (1 : 1), and benzene systems has been used to separate various aromatic nitro-compounds and amines, azo-, azoxy- and hydrazo-compounds[154]. The spots were detected by spraying the plate with a mixture of 5% KOH solution and acetone (2 : 1) or with a 10% solution of $SnCl_2$ in concentrated hydrochloric acid. The nitro-compounds are usually detected after spraying and heating or after heating and subsequent spraying with conc. H_2SO_4 and HNO_3 (1 : 1). In the latter case, nitroamines are also detected.

Thin-layer chromatography on a silica gel–starch layer has been used[155] for the detection of blood meprobamate (2-methyl-2-n-propyl-propan-1,3-diol dicarbamate) in the absolute ethanol–cyclohexane (15 : 85) system. The compounds were detected with concentrated sulphuric acid.

Thin-layer chromatography has also been used to study medicinal products[29,156–162] and in clinical analysis[163].

The separation and identification of inorganic compounds of mercury, bismuth, cadmium, lead, copper, iron, zinc, cobalt, manganese, chromium, nickel, and aluminium on a thin layer of silica gel–gypsum has been described[164]. This method has been used for the separation and identification of U^{VI} and Ga^{III} in a mixture of cations[165]. The chromatographic separation and identification of the cations of the alkali-group Li^+, Mg^{2+}, Na^+, and K^+, [166] and of the halide anions F^-, Cl^-, Br^-, and I^- [167] has also been described. The analysis of orthophosphoric, pyrophosphoric, phosphorous, and hypophosphorous acids has been described[168].

This review has shown the development of the method of thin-layer chromatography on fixed and unfixed layers of adsorbent from 1938 to the present time. Chromatography on a thin layer of adsorbent is a simple and rapid method which rivals the method of paper chromatography and in a number of cases is more sensitive than the latter by factors of 10–20. The method is extending rapidly and is widely used in almost all fields of organic chemistry. It can be used not only for the separation of mixtures of substances and the identification of individual compounds, but also to examine their purity. The use of thin-layer chromatography is very convenient for the analysis of the fractions obtained in column chromatography and for following the course of chemical reactions in organic synthesis. Combined with gas–liquid chromatography, this method sometimes makes it possible to solve problems which cannot be solved by other methods of separation. Thin-layer chromatography on an unfixed layer of adsorbent will undoubtedly find extensive application for preparative purposes.

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INFLUENCE OF FINE GRINDING ON THE PHYSICOCHEMICAL PROPERTIES OF SOLIDS

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1. INTRODUCTION

An increase in the degree of dispersion of solids produces an increase in the rate of heterogeneous chemical processes which is proportional to the specific surface of the species involved, and it also results in activation and the more effective utilisation of many materials. Dispersion raises the activity of several catalysts, improves the covering power of pigments and the quality of fillers for rubbers and plastics, lowers the temperature for sintering articles in powder metallurgy, etc. One of the most universal and widely used methods for the dispersion of solids is their mechanical disintegration — grinding — which is applied to very many materials employed in various branches of industry. Among them are cements, ores, metals, fuels, and paints, the total annual production of which is counted in hundreds of millions of tons. The degree of dispersion of solids which have undergone grinding is continually being raised, and the corresponding range of production extended.

With the modern level of development in grinding and mixing techniques the velocity of heterogeneous processes can be increased tens of thousands of times by grinding. However, this is not the sole result of the mechanical disintegration of solids. At the present time a considerable body of experimental data has accumulated showing that fine grinding produces also a considerable increase in the specific reactivity (calculated per unit surface) of substances in the solid state. Several other of their physical and physicochemical properties are also changed, such as density, phase transformation points, and adsorption capacity.

The study of the physicochemical properties of disperse systems forms part of a new field of science, physicochemical mechanics, developed by P. A. Rebinder and his

school. The aim of this branch of science is to obtain materials having a specific structure and strength[1], and also to find a basis for optimum methods of mechanical working by the application of physicochemical factors. The active medium used has been found to exert a considerable influence on the disintegration of solids. The mechanism of this effect involves penetration of molecules from the medium into the structure of the solid, which substantially changes the character of the breakdown[2]. It is therefore not surprising that the conditions of grinding and especially the participation of the active medium in this process will appreciably influence also the accompanying changes in the physicochemical properties of the ground solids.

The causes of the increased specific reactivity and of the change in other physicochemical properties of solids resulting from mechanical dispersion can be summarised as follows:

1. Decrease in particle size, increase in curvature of the surface, and growth in the contribution of the surface layers[3-11]. This phenomenon, which is common to all disperse systems, independently of their mode of preparation, is complicated with ground materials, however, by formation of considerable numbers of flats and edges, aggregation of particles, and surface damage by "amorphisation"[12].
2. Mechanical distortion of the crystal lattice in the surface layers of solids, their transformation as a result of plastic deformation into a quasi-amorphous state, metastable at ordinary temperatures, with an increase in free energy[12-46]. Mechanical dispersion causes even substances which are amorphous in the usual sense to become considerably more active than their unground analogues[21,32].
3. Exposure of fresh surfaces, accompanied by the formation on them of unbalanced valencies, free radicals[3,37,38,47-50]. Such surfaces react vigorously with various media, and this explains, for example, the pyrophoric properties of metals, the oxidising power of quartz, and the spontaneous combustion of graphite[3,12,38]. The formation of free radicals during the mechanical working of polymers in the process of mechanochemical synthesis[50-59] is especially valuable.

In several cases grinding distorts the secondary aggregation structure of highly disperse materials: carbon blacks, sols, Tripoli earths, clays, etc. This process may not be accompanied by appreciable increase in the primary dispersion, but the redistribution or breakdown of bonds between particles and the formation of unsaturated radicals substantially change the behaviour of such substances as fillers in rubbers and plastics and in the production from them of articles which are subjected to extrusion and baking[60-62].

The widespread industrial application of fine grinding has made necessary research of direct practical value. The most complete and systematic study has been made of the effect of grinding on such physicochemical properties of solids as adsorptive power[27,33-35,63-65] and solubility[31-33,66]. These properties are quite general, and in several cases may characterise adequately the activity of the materials. A considerable number of papers are also known in which the effect of grinding has been assessed directly from technological parameters[66-97].

It is difficult to generalise the extremely varied experimental work on the effect of grinding on the physicochemical properties of solids. This is due firstly to insufficiently clear definitions for disperse systems of such basic concepts as interface, particle size, and surface energy; and secondly to the complexity of measurements in disperse systems, for example, of particle size. Methods for the quantitative assessment of change in structure and activity of the surface layers in the grinding of solids are also insufficiently developed. For these reasons careful analysis of the method of measurement and of the experimental conditions is also required in order to compare results of investigations on the same problems. However, by no means all papers give a detailed account of experimental techniques, and it is not yet possible to establish a more or less rigorous relation between degree of dispersion, structural changes, and the activity of solids.

2. DECREASE IN PARTICLE SIZE

The influence of a decrease in particle size on the activity of solids has been examined by the methods of thermodynamics[3-10]. This leads to the well-known Kelvin formula for the equilibrium saturated vapour pressure or solubility of small spherical particles or drops

$$\ln\frac{C}{C_\infty} = \ln\frac{P}{P_\infty} = \frac{2\sigma M}{RT\rho r}, \qquad (1)$$

where C and P are respectively the solubility of and the saturated vapour pressure over drops or particles of radius r, C_∞ and P_∞ are their values over a plane surface or at sufficiently large r, R is the gas constant per mole, T the absolute temperature, σ the specific interfacial energy, ρ the density of the particles, and M their molecular weight. It follows from the Kelvin formula that, as the particles become smaller, their solubility and vapour pressure rise. Phase transformation temperatures fall with decrease in particle size. For spherical particles of small dimensions the variation in phase transformation temperature at constant pressure is governed by the expression[7]:

$$\frac{T_\infty - T}{T_\infty} = \frac{2\sigma M}{rQd}, \qquad (2)$$

where T_∞ and T are the temperatures corresponding to massive systems and to small particles of radius r respectively, and Q is the molar heat of phase transformation. Formula (2) makes it possible to determine $T(r)$ at constant pressure.

The thermodynamics of disperse systems has been developed in connection with problems involved in the formation and growth of condensed phases (drops, crystals) in the works of Gibbs[4], Curie[5], Vul'f[6], Volmer[7], and other writers[8-10]. Recently Poltorak has made attempts to generalise the thermodynamics of disperse systems by taking into account the change in density of the substance in a thin layer adjacent to the surface[10]. When this factor and also the edge energy are allowed for, the expression for the excess chemical potential of one component in the small particles, relative to its value in large particles, becomes

$$\Delta\mu_j = \frac{\overline{V}_j}{v}\left\{\frac{2}{3}\sum_i S_i\sigma_i + \frac{1}{3}\sum\tau_k l_k\right\}, \qquad (3)$$

where v is the volume of the particle, $\overline{V}_j(r)$ the partial molar volume of the j-th component in the disperse phase, the mean of the internal volume and the volume of a surface layer of thickness δ, S_i the surface area of the crystal face, l_k the length of the edge, σ_i the specific surface energy corresponding to the faces, and τ_k the specific

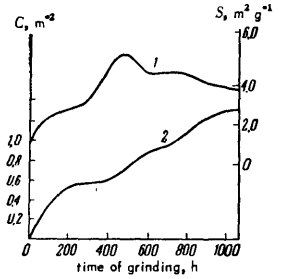


Fig. 1. Effect of grinding of kaolin on: 1) specific surface (determined from the adsorption of nitrogen at -90° K); 2) extent of dissolution (per unit surface area in wt.% of kaolin dissolved in 0.75 *N* HCl at room temperature during 48 h)[12].

linear energy corresponding to the edges. Summation is carried out over all edges and faces of the particle. If $\overline{V}_j(r)$ is expressed in terms of the thickness of the surface layer, the size of the particle, and the concentration of the j-th component, an expression is obtained for the excess chemical potential, which can be written in approximate form

$$\Delta\mu_j = \left\{\frac{2}{3}\sum_i \sigma_i S_i + \frac{1}{3}\sum_k \tau_k l_k\right\} \frac{2\overline{V}}{\overline{V}^\delta + \overline{V}}, \qquad (4)$$

where $\overline{V}^\delta$ is the mean partial molar volume in the surface layers.

If the density were greater in the surface layers, $2\overline{V}/(\overline{V}^\delta + \overline{V}) > 1$, and the total chemical potential of the substance at the given degree of dispersion would be higher than that calculated from the Gibbs equation[10].

However, the postulate of increased density in the surface layers of highly disperse phases is hardly applicable to systems obtained by mechanical grinding. A series of papers will be examined below, in which it has been shown experimentally that the density of the surface layers of pulverised solids has decreased[14,15]. Tolman and Kirkwood consider that a layer 2–5 molecular diameters thick, with a continuous decrease in density, is present at the interface between a condensed phase and a vapour or a solution. Several experimental facts can be explained on this assumption[98].

Determining the density of the surface layers is not the only difficulty in the thermodynamics of disperse systems. The problem of the change in specific surface energy has not been clarified at all. This parameter is usually regarded as independent of particle size, but there are indications that it does vary[98,99]. Another difficulty is, as has been mentioned, the uncertainty in measurements of the interfacial area and the particle dimensions.

For many solids $M = 30-80$, $\rho = 2-3$ at 300°K, and $\sigma = 100-1000$ ergs cm^{-2}. On the basis of the classical formula (1), ignoring later corrections, we have

$$\ln\frac{C}{C_\infty} = \ln\frac{P}{P_\infty} \simeq \frac{A}{r},$$

where $A = 10^{-6}-10^{-7}$ cm. Consequently an appreciable change in activity can be expected only with extremely low particle sizes, of the order of 10^{-6} cm and below. Experiment, however, shows an increase in reactivity with considerably larger particles[13,16-31].

The absence of a direct relation between degree of dispersion and reactivity in solids is shown especially clearly with very prolonged grinding. In this case, after a considerable increase in degree of dispersion, a limit to the degree of pulverisation is reached or even some decrease ensues, as a result of the very dense aggregation of highly disperse particles[12,33]. At the same time, the specific reactivity steadily grows as grinding is prolonged, as Gregg showed in the case of kaolin (Fig. 1). After 1000 h of grinding the extent of dissolution of the kaolin in 0.75 *N* hydrochloric acid had reached 58% after 48 h, whereas the dissolution of unground kaolin under the same conditions was insignificant. Similarly, the temperature at which removal of constitutional water effectively begins is lowered (from ~550° to 250° after 1000 h). The latent heat involved in the elimination of water is also diminished. All this also points to profound changes in the structure of solids occurring in the course of grinding[12].

3. CHANGE IN STRUCTURE OF SOLIDS

The mechanical processing of solids changes substantially several physicochemical properties of their surfaces[3]. Thus when metals are polished, an amorphous layer is formed on their surface which is termed the Beilby layer, and is chemically more reactive than the unpolished metal. A similar increase in activity occurs in the polishing of the surfaces of glass and other non-metallic materials. X-Ray examination of the surface layers shows that their crystal lattice has been strongly distorted, in many cases with the disappearance of any long-range order in the arrangement of the atoms. Amorphisation and other changes in crystal structure are produced also in the course of mechanical subdivision[37]. Much work has been done on the properties of the deformed surface layers of disperse solids, most of it, however, without regard to the conditions of grinding, in particular without taking account of adsorption of the medium. Yet it follows from the basic assumptions of physicochemical mechanics that these factors should have a considerable influence on the thickness and properties of the deformed surface layers[1,2].

The most extensive group of investigations on the physicochemical properties of highly disperse solids have been devoted to the silicates. In 1921 Lencher first showed that quartz is partly converted into an amorphous form by prolonged grinding[13]. Subsequent work on the physicochemical properties of silicate dusts developed in connection with the problem of silicosis[100,101]. It was then assumed that silicosis results from poisoning of the organism by products of the interaction of quartz with proteins in living tissues (pH 7.4 at 37°)[6]. An investigation was therefore made of the dissolution of powdered quartz and natural dusts in buffer solutions of various pH values, and also of the influence of both chemical and thermal treatments of the powders on the dissolution of foreign impurities. The most systematic and complete work was done by Ritchie and coworkers[20-28] during 1952–1954. Although it was subsequently discovered that silicic acid, formed in the dissolution of silicates, is very rapidly eliminated from the organism, and is consequently unable to cause silicosis[29], the above work exerted a great influence on the evolution of ideas both on the nature of silicosis and on the properties of powdered quartz.

It was shown that the high solubility of ground quartz is due to the formation, on the surface of its particles, of a thin layer analogous to the Beilby layer[21]. Removal of the surface layers by dissolution in hydrofluoric acid results in a sharp drop in solubility to the normal value typical of the corresponding crystalline and amorphous modifications (Table 1). The degree of dispersion of the specimens was the same before and after treatment with acid.

Similar results are obtained also on the dissolution of the surface layers from particles of quartz, quartz sand, and vitreous quartz in a borate buffer (pH 7.5, 37°). Mechanical treatment (polishing) of particles from which the surface layer has first been removed by dissolution restores their original high activity. X-Ray examination of powders before and after removal of the active surface layers[17-19] showed them to have an amorphous structure. However, the substantially higher activity of such layers compared with vitreous quartz suggests that the structures differ.

The density of the surface layers on the quartz particles is rather lower than that of crystalline quartz, which appreciably diminishes the mean density of the finely ground powder[14,15]. Pulverising vitreous quartz, however, results in the formation, on the surface of its particles, of a layer which has a rather higher density than has fused quartz (Table 2). No denser crystalline forms of silica were then detected in the products obtained by grinding vitreous quartz. The increase in density is probably due to the exposure of microscopic cavities on the breakdown of the particles[15].

Various methods, including differential thermal analysis[24,25], electron diffraction[25], and X-ray diffraction[18], have been used to measure the thickness of the active amorphous layers formed by grinding on the surface of crystalline particles of quartz. Data on the change in density[17] and solubility measurements[17,18] have been utilised. When it was necessary in this work to measure particle size in order to calculate the thickness of the amorphous layer, the mean values were determined from the specific surfaces measured by the air-permeability method.

The results obtained in this work (Table 3) show considerable discrepancies in the thickness of the amorphous layer. This may be explained by the quartz powder undergoing strong molecular aggregation on dry grinding[33-35]. Moreover, with very fine powders ($r < 1\ \mu$) the air-permeability method gives results which are not very reliable and which

TABLE 1. Extent of dissolution (mg per 100 ml after 40 days) of silica in borate buffer (pH 6.5, 37°).

Rock crystal*		Quartz sand		Vitreous quartz	
irreversible	reversible	irreversible	reversible	irreversible	reversible
2.30	0.15	0.99	0.44	6.70	1.14

* A form of colourless quartz (Ed. of Translation).

TABLE 2. Effect of grinding on the density of quartz and vitreous quartz, g cm^{-3}.

Test substance	Time of grinding	Mean particle size, μ	Density of powder at 18°	Density of amorphous layer
Rock crystal	initial	250	2.664	—
	5 min	70	2.647	—
	2 h	2.4	2.640	2.590
	17 h	1.3	2.606	2.551
Vitreous quartz	initial	450	2.201	—
	17 h		2.230	—

TABLE 3. Estimated thickness of amorphised surface layer quartz.

Method of determination	Thickness of layer, μ
Solubility	0.02—0.03
X-Ray diffraction	0.03
Density measurements	0.03—0.05
Electron diffraction	0.03—0.06
Chemical analysis	0.04—0.07
Differential thermal analysis	0.11—0.15

are in any case too low by factors of 2–3. Therefore the data quoted, which were obtained without regard to the specific features of the grinding, are to be considered only as comparative results.

A study has been made[33,34] of the effect on the amorphisation of quartz of the conditions of grinding, including the influence of the medium and also the relation between degree of dispersion and degree of amorphisation. The amorphised phase in pulverised quartz sand, originally containing not less than 98% of crystalline quartz in the low-temperature α-modification, was estimated quantitatively by differential thermal analysis, from the size of the temperature peak corresponding to the $\alpha \rightleftharpoons \beta$ transformation at 574°. The degree of dispersion was determined from the specific surface of the deaggregated powders measured by the B.E.T. method.

Since the surface layers of the particles become amorphous on grinding[21], a comparison of the content of amorphous phase in the powders Q with their specific surface S enables us to determine the mean thickness of the amorphous layer on the crystal nuclei, which for not too fine particles is $l = Q/\rho S$ (when $r \gg l$).

As follows from the experimental data plotted in Fig. 2, the thickness of the amorphous layer on quartz particles ground in dry air changes very sharply on sufficiently prolonged grinding, from ~20 Å when the dispersion is coarse to a few hundred ångström units. In contrast to this, on grinding in an active medium (with water) the thickness of the amorphous layer remains constant at 20 Å over a considerable range of specific surfaces, up to 50–60 m^2 g^{-1}, and increases slightly only on further rise in the degree of

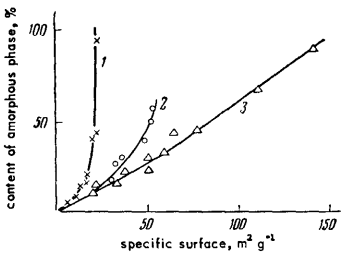


Fig. 2. Comparison of degree of dispersion and amorphisation of quartz on grinding: 1) in dry air; 2) with 1.2% of water; 3) with 80% of water.

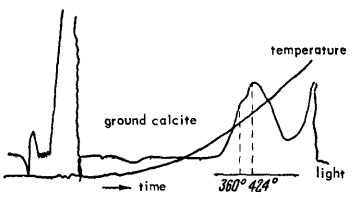


Fig. 3. Thermoluminescence of ground calcite[46].

dispersion. The depth of amorphisation of the coarse particles obtained by grinding with 1.2% of water is the same as for particles which have been ground with 80% of water, but it increases quite rapidly with growth in the specific surface to 30–50 $m^2 g^{-1}$. This sharp transition corresponds to a decrease in the surface concentration of liquid to 1–0.5 of a saturated monolayer. Thus the thickness of the amorphous layer on the crystalline grains of ground quartz does not remain constant, as had been supposed earlier, but depends both on the duration of grinding and especially on the medium in which the grinding is effected.

X-Ray examination of powders ground to different extents shows[33,37] that, with increasing duration of grinding, the background blackening of the X-ray photographs gradually becomes greater, while the diffraction maxima characteristic of the quartz lattice remain quite distinct, without appreciable broadening. Consequently the amorphisation of quartz cannot be attributed to a gradual decrease in size of the individual crystals, as can occur, for example, in the grinding of graphite[36]. In view of the fact that the high temperatures necessary for the fusion of quartz (1700°) do not arise in the mill, plastic deformation of the particles must be regarded as the most probable cause of amorphisation. Such deformation may arise in thin layers adjacent to cleavage surfaces, where the greatest shearing stresses are concentrated at the instant of rupture. Such layers are very shallow, in any case not deeper than the thickness of the amorphous layer, 20 Å for coarse grinding, as previously mentioned. In this connection, the role of plastic deformation in the breakdown of coarse particles is just as small, but it increases with fine subdivision, when the particle size becomes comparable with the depth of the amorphised layer.

Comparison of the density curves for the X-ray photographs of vitreous quartz and of quartz which has been amorphised in a vibratory mill to almost complete destruction of the crystalline phase indicates a certain similarity in their structures in the sense that there is a complete absence of long-range order in the arrangement of the atoms. On this basis it may be supposed that the energy consumed in the irreversible deformation is not less than the specific heat of amorphisation of quartz, 4.4×10^9 ergs cm^{-3}.[32] The same value for the energy of the limiting irreversible deformations can be obtained from theoretical models if the limiting shearing stress is taken to be about 0.1 E, where E is the modulus of elasticity. If appreciable scale strengthening is assumed to be absent, the limiting density of elastic energy for quartz is considerably less than $\sim 2 \times \times 10^6$ ergs cm^{-3}.

Subdivision has a substantial effect on the structure not only of quartz but also of several other solids. A change in crystalline structure has been observed on grinding graphite and metals[41]. In nickel powders unstable crystalline modifications have been found which pass spontaneously at room temperature into the normal state. Graphite is enriched with the rhombic modification, and in the absence of adsorbed layers of moisture it is actively amorphised on prolonged grinding. Its structure becomes similar to that of amorphous charcoals and carbon blacks[36]. In contrast to quartz, graphite is amorphised with an appreciable gradual decrease in size of the crystallites and with enrichment in two-dimensional networks, as is discovered on analysis of the density curves for the diffraction maxima on the X-ray photographs. As has been shown by X-ray diffraction, prolonged grinding of organic substances such as sugar and cellulose[43] also results in their amorphisation. An investigation has been made of the effect of water on the amorphisation and the degree of dispersion of particles during the grinding of mica[44]. After identical times a considerably greater change in the structure of mica is observed with dry grinding than with grinding in water. This is consistent with the above data on quartz and graphite.

Thus amorphisation or other changes in structure resulting from mechanical working occur quite generally with all solids. This conclusion is supported also by experiments done by Pucheger[45], who showed that even such a brittle and hard material as diamond is subject to plastic deformation under mechanical stress. The interesting phenomenon of the triboluminescence of calcite[46] is probably also a consequence of such plastic deformation, leading to the formation of a quasi-amorphous structure. Ground calcite shows several thermoluminescence peaks, in contrast to the unground material (Fig. 3).

4. EXPOSURE OF CLEAN SURFACES AND FORMATION OF FREE RADICALS

Apart from amorphisation, one of the main causes of the high chemical activity of pulverised solids, which is not directly due to the decrease in particle size, is the exposure of clean surfaces and the formation of free radicals. This probably explains the pyrophoric properties of the usually extremely inert graphite, observed by Veselovskii and Ormanskaya after dispersing it in liquid argon[102]. Considerable evolution of heat was noted also by Feigin[103] when finely ground graphite was brought into contact with

air. Carbon black which has been ground in a ball mill or a roller mill ignites spontaneously on contact with air. Its ignition temperature falls to 425°–538°.[60] Zarif'yants *et al.*[47] investigated the chemisorption of oxygen on graphite which had been ground in an atmosphere of argon in a vibratory mill. According to their results, the surface becomes saturated with oxygen at a pressure close to atmospheric, and 80% of the oxygen chemisorbed at saturation is already irreversibly sorbed at ~100 mm Hg. Subsequent sorption of oxygen on the oxidised specimens is negligible. The specific values of the chemisorption do not depend on the degree of dispersion. The density of the saturated layer of oxygen on the graphite surface is ~2 μmoles m^{-2}, which is close to the values of ~ 5 μmoles m^{-2} obtained for milled carbon blacks[60]. This allows the density of active centres to be estimated as 2–5 per 10 surface atoms of the graphite or carbon black.

Free radicals were detected on vibratory-milled quartz by electron paramagnetic resonance[48]. Their presence is also indicated by the electron emission found when the surface of crushed quartz is examined with Geiger counters[49]. In agreement with the views of Weyl[37], this phenomenon can probably be explained as a result of the rotation of the silica tetrahedra emerging at the surface under the influence of polarisation forces. Storage in argon for up to 30 days does not appreciably lower the chemisorbing activity of vibro-milled graphite[47]. Similar data were obtained by Bentur[38], who studied the oxidation of a graphite surface and the evolution of free oxygen by quartz and by olivine. Thus the active state of the surface of finely ground solids is well maintained at normal temperatures in an inert atmosphere. When the temperature is raised to 300° the activity of solids resulting from grinding is appreciably diminished.

Extremely interesting results have been obtained on the interaction of the highly active surfaces of finely ground solids with organic substances. Free radicals effect, for example, the mechanochemical synthesis of polymers — graft polymerisation. Thus Kargin and Plate[51,52] observed the polymerisation of styrene, methyl acrylate, and methyl methacrylate on vibro-milling them with quartz, graphite, or common salt at room temperature.

The interaction of ground metal particles with polymer layers causes several peculiarities in the semiconductor properties of such compositions[53]. Systems obtained by adding ready-made polyisoprene (natural rubber) to form films on particles of powdered iron differ from those obtained by the polymerisation of isoprene in a vibro-mill. In the first case n-type conductivity is observed, and in the second p-type. The Seebeck coefficient of 5 $\mu V\ deg^{-1}$ in the first case had increased to 12–14 $\mu V\ deg^{-1}$ in the second. The resistivity was also greater in the second than in the first case. These differences perhaps indicate that stronger bonding between metal and organic substances and a more uniform distribution of polymer result from using the vibration procedure for shearing and activating surfaces.

It has been shown comparatively recently that free macroradicals react chemically with the surface of the filler, thereby forming stable compounds[54]. Therefore the physicochemical surface properties and the structure of the filler have a considerable influence on the strength of filled high polymers. An investigation of the effect of grinding carbon blacks in a ball mill on the properties of butyl rubber[60] showed that on prolonged grinding the carbon blacks undergo considerable changes in their physical and chemical properties. The particle shape changes from spherical to irregular, with rough edges, the degree of dispersion increases, the structural factor — reticulation of the structure — diminishes, aggregations break down, the oil-absorption decreases, and the density of packing of the carbon black particles increases. Similar changes are observed also in the vibro-milling of carbon blacks[61,62]. On interaction of the ground carbon blacks with butyl rubber the amount of "combined rubber–carbon black gel" is increased 2–3 times compared with unmilled carbon blacks, which appreciably improves the strength and technological properties of the vulcanised rubbers.

Fig. 4 shows how the strength and the elongation of a vulcanised butyl rubber filled with the processed carbon black are increased compared with a vulcanised rubber filled with ordinary carbon black. Used of processed blacks produces a considerable improvement also in the dynamic properties of butyl rubber: the flexibility is increased, the energy lost as heat on periodic loading is diminished, and elastic fatigue is decreased. Since, with sufficiently prolonged milling of the carbon blacks, the strength parameters of the vulcanised rubbers cease to depend on the duration of vulcanisation (Fig. 5), the technical processing of the butyl rubber is simplified. The shortening of the minimum time of vulcanisation at 149° from 92 to 26 min allows goods with improved properties to be obtained. Thus the life of the vulcanised rubbers is increased by 25–30%, and the electrical resistivity by more than two orders of magnitude.

The dispersion of carbon blacks and other constituents has a favourable effect on graphitic carbon used in electrical engineering (brushes, electrodes). The strength is doubled, the hardness trebled, and the resistivity halved[62].

All these effects can be explained in terms of the above ideas on the change in aggregation structure accompanying mechanical dispersion and the high reactivity of freshly formed solid surfaces. The increased activity of the carbon blacks probably results from the rupture of surface bonds and the increased number of unpaired electrons produced by breakdown of the particles[54]. This view is consistent with the investigations of Weyl[37] and of Bentur[38], and is supported by measurements of the chemisorption of oxygen on finely ground graphite[47].

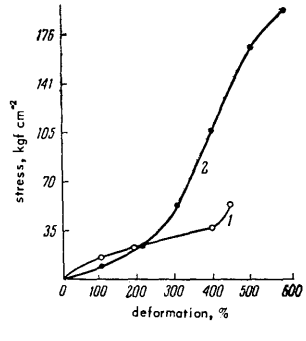


Fig. 4. Dependence of deformation on stress with vulcanised butyl rubber and: 1) ordinary carbon black; 2) carbon black processed in a ball mill[60].

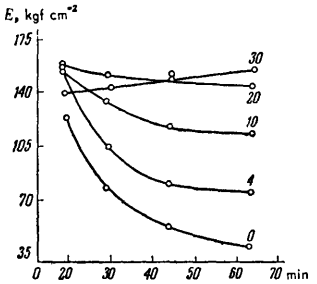


Fig. 5. Effect of time of valcanisation (min at 153°) on limiting tensile strength. (E, kgf cm^{-2}) for vulcanised butyl rubber with milled carbon black. The numbers on the curves indicate the time of grinding (in h) in a ball mill[60].

As in the case of minerals, mechanical working of the polymer results in the formation of unsaturated radicals. However, the life of such macroradicals in the free state is comparatively short at ordinary temperatures, as has been shown by electron paramagnetic resonance. At low temperatures, however, free macroradicals remain for quite a long time[48].

The breakdown of high-polymer molecules takes place also under the influence of high pressures. In this case the polymers undergo "chemical flow", the essence of which is that, at sufficiently high pressures, the polymers flow not only by displacement but also by mechanical rupture of the molecules and displacement of the fragments relative to one another. In contrast to ordinary viscous flow, chemical flow occurs also in systems having three-dimensional structures[55].

Free macroradicals are formed also by other mechanical processes, such as wear, rolling, mixing, freezing, and melting. This interesting phenomenon, which plays an important part in the chemistry of polymers, has been described in several special reviews (for example, see Refs. 56–58). However, the mechanism by which freshly formed surfaces and free radicals influence the synthesis of polymers and the formation of linear structures still remains obscure. The low density of active centres compared with the number of polymerisation acts indicates this to be a chain process, in which free radicals play the part of initiators of chain reactions[50]. The effect of different types of free radical acceptor on the mechanical degradation of polymers can be explained on this basis[59].

5. INCREASE IN ADSORPTION CAPACITY

Surface activation of finely pulverised solids on grinding is accompanied by an appreciable increase in their adsorptive power. Gibb and Ritchie[27] showed that the adsorption of dyes on pulverised quartz of particle size 125–200 μ is appreciably diminished after heat-treatment of the powder above 300°. The dimensions of the particles, and hence their specific surface, did not change in the course of such treatment. Removal of the active surface layer by washing with acid produces a similar effect. In this case, too, the decrease in particle size is negligible. In this way it was shown that adsorptive power is directly linked with the activity of the surface layers.

The adsorption of water vapour is especially sensitive to the condition of the surface. Zhdanov[63] found, by comparing the isotherms for the adsorption of water on vacuum-ground quartz, on silica gel, and on porous glass, that the first has considerably the higher specific adsorption capacity. It follows from his results that even repeat isotherms for water vapour on ground quartz with a surface of practically maximum hydration lie considerably higher than the isotherms on other forms of silica. It must be noted that the hydration of ground quartz is slow[63], probably owing to migration of water molecules from the surface layer to deeper layers and into narrow pores. In all the above cases either the surface layers of the particles were amorphous as a result of the grinding or the specimens themselves had been obtained in an amorphous form.

The difference in specific adsorptive capacity of different specimens of quartz depends on the conditions under which they have been obtained. The medium in which subdivision occurs has the greatest effect on the shape of the adsorption isotherms. Thus the specific adsorptive power is appreciably increased by grinding with small additions of water. The mode of mechanical subdivision and the size of the surface also influence adsorptive power[64].

Another factor having a considerable influence on the adsorption characteristics of finely divided solids is the molecularly compact aggregation of highly disperse particles[33]: as a result of mechanical working during grinding, the particles collect into dense aggregates, the internal surface of which is not available for the adsorption of nitrogen molecules at low temperatures. All known methods of dispersion analysis record such aggregates as single particles — diffraction methods cannot be used because of the amorphisation of the particles. However, when such aggregated powders are ground in water for such a short period that the increase in degree of dispersion resulting from breakdown of the primary particles can be neglected, their specific surface measured by the B.E.T. method is sharply increased severalfold. Such dense aggregation has been shown to occur on grinding the powder not only dry but also in benzene, acetone, and alcohol and with small additions of water and other liquids. Only large amounts of water, exceeding 40 wt.% based on the powder, possess a deaggregating power[33,34].

The effect of the molecular aggregation of highly disperse particles on adsorption characteristics can be assessed from determinations[35] of the adsorption isotherms of water and nitrogen on samples of quartz obtained by wet grinding completed by dry grinding. With such final grinding the adsorption of nitrogen vapour and the B.E.T. specific surface diminish, whereas the adsorption of water increases (Fig. 6). It can be assumed from these experiments that the ability of water molecules to penetrate into very narrow pores is greater than that of nitrogen molecules at low temperatures. Particle aggregation during grinding occurs also with corundum, calcite, etc.[33,34] The surface of quartz is equally accessible to the adsorption of water and to hydration.

Thus amorphisation of the surface layers of solids, depending on the conditions of grinding, and molecular aggregation exert a considerable effect on their specific adsorptive power. These factors, and also the differing abilities of molecules of different vapours to penetrate the

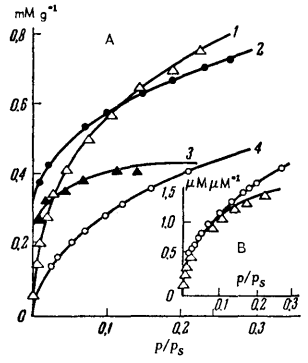


Fig. 6. A) Adsorption isotherms of water vapour (1 and 4) and nitrogen (2 and 3) on samples of quartz ground in water ($S = 53$ m^2 g^{-1}) (2 and 4) and of the same quartz but with grinding completed dry (1 and 3); B) adsorption isotherms of water vapour on the same specimens based on their content of structural water.

very narrow pores of the aggregates formed on grinding, cast doubt both on the values of the specific adsorption and hydration parameters calculated earlier from crystal-chemical considerations and on the correctness of measurements of the specific surface of ground materials. Unfortunately, these problems, which are of scientific and practical interest, have not yet been adequately studied.

6. INCREASE IN SOLUBILITY

As noted above, several investigations have established that solids acquire enhanced chemical reactivity as a result of decrease in particle size and surface degradation during grinding. This phenomenon has been studied in the greatest detail in the case of the solubility of quartz[31,33]. This substance was chosen for observation of the effects of grinding primarily because it is a typical brittle and hard crystalline material possessing great chemical stability. In this connection, the conversion of quartz into an extremely active form of silica on grinding is very significant. Furthermore, various methods of determining particle size, amorphous phase content, and degree of dissolution from the quantity of silicic acid in solution have been comparatively well developed for quartz, which facilitates experiments.

We have studied[31] the effect of grinding on the kinetics of the dissolution of quartz in water at room temperature. The concentration of silicic acid in solution was determined photocolorimetrically by the molybdate method. It can be assumed, on the basis of several investigations, that the molybdate method records only the silicic acid which is in true solution[20,21]. This is confirmed by the fact that boiling centrifuged solutions for several hours did not increase their content of "molybdate-active" silicic acid. The equilibrium solubility in water of carefully washed unground quartz sand at 20° did not exceed 1 mg litre^{-1}.

The dissolution of quartz in water is thermodynamically reversible. Raising the temperature to 100° increases the concentration of silica in solution (see Table 4), and prolonged storage of supersaturated solutions at room temperature lowers the concentration to close to the equilibrium value. Such comparatively rapid change in concentration takes place only in the presence of finely pulverised quartz. The silica content of a supersaturated solution, prepared by boiling finely divided quartz in water and then centrifuging to remove the highly disperse particles, falls considerably more slowly at 20°, even in the presence of the unground sand.

The rapid increase in solubility with rise in temperature is peculiar to amorphous silica. With crystalline quartz, however, raising the temperature even to 150° produces only an insignificant increase in its solubility[32]. The data in Table 4 indicate that the surface layer of particles of ground quartz does not consist of a conglomerate of intergrown submicroscopic crystals but, as has been shown above, represents a quasi-amorphous structure. In the case of extremely fine particles (of the order of a few intermolecular distances) these structures cannot be distinguished by either X-ray or electron diffraction.

The kinetics of the dissolution, in water at room temperature, of quartz of different degrees of subdivision is well represented by a first-order kinetic equation. The plot of $\ln[C_{eq}/(C_{eq} - C)]$ against t, the time of dissolution, where C is the quantity of silica in solution and C_{eq} the equilibrium concentration, is a straight line, the slope of which gives the rate constant k of dissolution. The value of k is independent of the duration of grinding or the specific surface of the powders, but differs with different pulverisers, depending on the intensity of their action.

Neither the equilibrium concentrations nor the rate constants for the dissolution of quartz in water are directly linked with the specific surface of the powders measured by the B.E.T. method. Experimental results show that the values of C_{eq} are higher for quartz ground dry in a vibro-mill for 8 h to a B.E.T. specific surface of 6 m^2 g^{-1} than for quartz after wet grinding for 11 h and having a B.E.T. specific surface of 74 m^2 g^{-1}.

Thus the physicochemical properties of ground quartz, which govern its dissolution in water at room temperature, are determined not by its degree of dispersion, its particle size, but by the state of the amorphised surface layers. This conclusion is also confirmed by a simple calculation of the solubility from the Kelvin formula. The equilibrium solubilities of quartz obtained by extrapolation of the kinetic curves increase with increasing duration of grinding, in several cases reaching 120–140 mg litre^{-1}. This exceeds by a factor of at least 15 the solubility of crystalline quartz with the same degree of dispersion calculated from data on the specific surface (B.E.T. method) and the normal solubility

TABLE 4. Reversibility of the dissolution of quartz in water (mg litre^{-1}).

C_{eq}	Boiling for		Storage at 20° for	
	1 h	3 h	11 days	25 days
60	82	169	—	77
73	116	222	109	87
89	160	210	125	115

of crystalline quartz[32]. In view of the absence of any recrystallisation effect, the high solubilities of ground quartz cannot be attributed to the fraction comprising the finest particles. Prolonged storage of the solutions (for more than a year) produces no appreciable decrease in the equilibrium concentration of silicic acid[31].

In experiments on the kinetics of the dissolution of quartz in water at room temperature, 0.1–0.25% of the solid passed into solution. The content of the amorphous phase was between 7–8% and 33% respectively. Consequently the values of the solubility and the rate constant for the dissolution of quartz in water represent the activity of only a very thin outer portion of the amorphised layers. In order to study the effect of grinding on the deeper-lying layers, measurements were made of the kinetics of dissolution of the powders in 20% alkali, with which silicic acid reacts in aqueous solution to form readily soluble salts. The amount of alkali taken was intentionally greater than that able to combine with all the silica passing into solution. As a result of this, the rate of dissolution of the quartz is limited mainly by the physicochemical properties of the test powder, not by saturation phenomena as in the case of dissolution in water. The absence of any appreciable decrease in the concentration of silica in the alkaline solutions when the temperature was lowered from 100° to room temperature can be regarded as supporting this assumption.

When powdered quartz is dissolved in alkaline medium at room temperature, depending on the duration of grinding, 5–15 wt.% passes into solution during a period of about two months, and this constitutes ~30% of the amorphised phase. After removal of the very thin surface layers (~2–5% of the amorphous phase) the rate of dissolution does not change further, which indicates a certain constancy of activity inside the amorphised layer. In these experiments, as in those on dissolution in water, the kinetic curves for quartz powders having the same content of amorphous phase but differing substantially in specific surface were identical.

Raising the temperature of the alkaline medium to 100° increases the rate of dissolution many times. The data illustrated in Fig. 7 show that in this case too, when almost all the amorphised phase passes into solution, the kinetics of dissolution of quartz under otherwise identical conditions depends only on the conditions (in this case the duration) of dispersion, not on the specific surface. Such a result cannot be due to an incorrect method of measuring the silicic acid concentration. That the method chosen was sufficiently sensitive to the effective surface area is confirmed by the fact that halving the weight taken in the same volume of liquid results in practically the same decrease in rate of dissolution.

Thus the chemical activity of ground quartz, which makes possible its use in several technological processes, such as the preparation of lime–sand binder, the manufacture of water-glass, etc., is due mainly, not to its disperse character, but to its degree of amorphisation, represented by the thickness and the physical state of the active layer. Nevertheless, this property is not taken into account in the majority of papers on the fine grinding of quartz and its technological application.

The solubility of the amorphised layer is diminished after heat-treatment of the powders. Raising the temperature and increasing the duration of heating result in a corresponding decrease in solubility. This and other

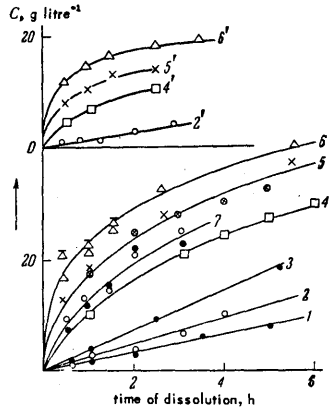


Fig. 7. Kinetic curves for the dissolution of quartz in 20% NaOH at 100° (5 g powder per 250 cm³ solution). Particle fractions: 1) 60–88 μ; 2) 25–30 μ; 3) 10–15 μ; 4) ground dry for 2 min (S = 11 m² g⁻¹); 5) 8 min dry (17 m² g⁻¹) and with 80% of water (50 m² g⁻¹); 6) 16 min dry (20 m² g⁻¹) and 32 min dry (22 m² g⁻¹); 7) 4 min grinding dry (14 m² g⁻¹) and with 80% of water (20 m² g⁻¹); 2′), 4′), 5′), and 6′) kinetic curves for the dissolution of 2.5 g powder in 250 cm³ solution, corresponding to curves 2, 4, 5, and 6.

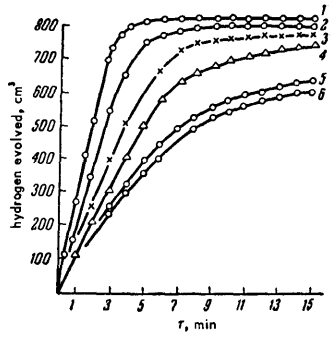


Fig. 8. Effect, on rate of dissolution of ground iron powders in 1 *N* HCl (τ = time of dissolution), of heating at 950° for different periods: 1) 0 (not heated); 2) 2 min; 3) 15 h; 4) 30 h; 5) 50 h; 6) 100 h.[66]

effects associated with the increased activity accompanying mechanical disintegration of solids are explained by the peculiar quasi-amorphous state of their surface layers, the molecules of which can, on heating, occupy sites of lower free energy[26]. However, insufficient work has yet been done on many physicochemical properties of the amorphised layers resulting from mechanical degradation, and especially their molecular structure. Experiments on the alkaline

etching[39] of pulverised quartz powders show merely the considerable non-uniformity of their structure. Such etching increases the specific surface from ~6 to ~200 $m^2 g^{-1}$. In this case, in contrast to silica gels of equally high dispersion, the cores of the nuclei remain crystalline, while the amorphised sheath is to a considerable extent removed. This may be of interest in several cases of adsorption and catalysis, for example, for the separation of optically active substances by successive adsorption on dextrorotatory and laevorotatory quartz[40].

Mechanical working considerably increases also the chemical activity of powdered iron, which is of great value in its use as a reducing agent[66]. The activity was determined by dissolving the powders in 1 *N* hydrochloric acid at 94° and measuring the rate of evolution of hydrogen. Iron powders of particle size 0.1–0.2 mm were ground and heated at 950° for different times to remove the structural distortions. The results plotted in Fig. 8 show that the chemical activity of mechanically deformed iron is several times greater than that of the undeformed metal. The effect of the mechanical processing then disappears only after heating at 950° for 100–120 h.

7. SOME ASPECTS OF THE PRACTICAL APPLICATION OF FINELY GROUND MATERIALS; RATIONAL DEGREE OF GRINDING

The increase in the rate of heterogeneous processes involving highly disperse solids, the considerable rise in their specific reactivity (per unit surface), and the lowering of phase transformation temperatures are responsible for the wide application of fine grinding in various branches of industry: chemical technology, the production of building materials, metallurgy, powder metallurgy, etc.[66-90]

The milling of solids has an especially strong effect on those technological processes involving them which go very slowly with ordinary materials. Thus practically no reaction occurs between unground quartz sand and lime in a moist medium at room temperature and atmospheric pressure. The use of vibro-ground sand, however, so activates its reaction with lime that lime–sand mixtures are used as binding materials. The rate of bonding by quartz of lime from aqueous solution rises rapidly with increase in its degree of dispersion[71,76,77]. The ratio of bonding rate to the specific surface then increases with growth in the latter, in agreement with views on the decisive role of the solubility of the sand grains, which increases with decrease in particle size and with increasing imperfection of structure of the surface layers. The strength of specimens made from a mixture of lime and unground sand is extremely low. However, the use of finely ground sand under ordinary conditions enables considerable strengths to be obtained, reaching 240 kg cm^{-2}.[71,72,74,76,78-81] The longer period of grinding the quartz corresponds to a high rate of interaction with lime, with the formation of monocalcium hydrosilicate. Since hydrosilicates govern the hardening process, the strength of the specimens and the rate of hardening increase with the degree of dispersion[78,79]. The strength of lime–sand products on hydrothermal processing is also appreciably increased by increase in the degree of dispersion of the sand. The setting time is thereby shortened, and the optimum temperature and pressure are lowered[83].

Fine grinding accelerates chemical processes also in the setting of cement, and increase in degree of dispersion improving its reaction with gypsum[82]. The use of finely ground cement in the production of reinforced concrete allows a smaller amount to be used, shortens the period of setting, and increases the strength of the concrete[75,88].

Treatment of powdered dolomite in a vibro-mill makes it possible to lower the sintering temperature by 100°–300° in the making of refractories and to obtain particles having improved mechanical properties[66,86-88]. With the relatively high firing temperatures of refractories, such a reduction in the temperature is of great practical value. The fine grinding of quartz and of feldspar shortens the time required for the sintering of glazes. The strength is thereby increased from 251 to 492 kg cm^{-1}, and the firing temperature lowered by 80°. Similar technological results are obtained by the vibro-milling of porcelain paste[89]. The use of finely ground materials improves the tendency of specimens to sinter, lowers the water absorption from 5.6% to 0.9%, and increases the quantity of cristobalite from 4% to 15%.[90]

The fine subdivision of oxides considerably improves the quality of parts made from them by powder metallurgy, and enables the temperature and duration of their firing to be diminished. Thus grinding allows Fe_2O_3 and SiO_2 powders to yield, on sintering at 1150° for 4 h, parts which are about ten times as strong as those obtained from the unground powders. In other cases grinding allows the sintering temperature, required to achieve a given strength, to be lowered from 1500° to 1300°.[66]

The temperature at which oxides are reduced is also considerably lowered as a result of fine grinding. The strength of this factor is shown by the reduction of Fe_2O_3 to Fe_3O_4 when Fe_2O_3 is ground in a vibro-mill at room temperature. The temperature at which Fe_2O_3 is reduced to Fe_3O_4 in a current of hydrogen is lowered by ~80° as a result of grinding. The effect of grinding disappears only when the oxides are heated to 900°. A similar lowering of the reduction temperature is observed also with NiO, MoO_3, and WO_3. Ground chromic oxide is completely reduced in a current of hydrogen at 1250°, whereas the unground powder is not reduced under these conditions[66].

In all cases of the industrial production and use of highly disperse materials, the question arises of the rational degree of grinding, which is governed primarily by the fact that the expense of grinding should be paid for by the technological improvement achieved. In view of the considerable energy consumption of grinding, in which only a small fraction of the energy consumed is usefully expended on the dispersion and degradation of the materials, this question is of great practical importance.

The fraction of the energy which is usefully consumed changes in the course of grinding, and rapidly decreases at sufficiently high degrees of dispersion. From the data plotted in Fig. 9 it is seen that grinding increases the heat of dissolution of sugar in water at room temperature[43], its value changing from negative to positive. However, with increased duration of grinding, the rate of change in the heat of dissolution rapidly decreases, and then becomes practically zero.

A similar retardation of the growth of activity occurs in the case of quartz[65]. The rate of increase in the solubility of quartz in water falls with increase in time of vibro-milling. Furthermore, as is shown by the data plotted in Fig. 7, when the grinding of quartz is prolonged, the increase in its solubility in alkaline medium almost ceases, the kinetic curves for 16 and 32 min coinciding. A

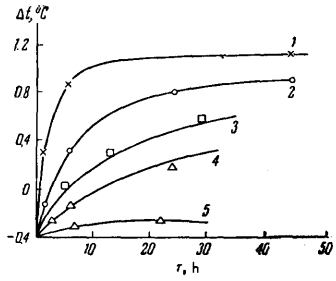


Fig. 9. Effect of duration of grinding of sugar on its heat of dissolution in water at 20° (11 g sugar in 200 cm^3 water). Curves 1–5 relate to various conditions of grinding [43].

slowing down of the yield of polymer with increasing duration of grinding is observed also in the mechanochemical polymerisation of methacrylamide in the solid state [93].

These phenomena probably result from the mechanical working producing not only increased dispersion, formation of free radicals, and destruction of the lattice, but also the reverse effects, as in the case of molecular aggregation. With a sufficient density of structural defects in the surface layers formed on dispersion, and with a given energy density produced by the ground material, a statistical balance is probably established between the formation and removal of defects. Increase in the energy intensity of the mechanical operations shifts the equilibrium towards an increased density of defects, and hence an increase in reactivity. As a result, the activity of the ground materials becomes greater, as has been shown in the cases of quartz [31] and sugar [43] (Fig. 9).

The growth in dispersion with time of grinding also slows down sharply. Sometimes this is due to dense aggregation of the particles, with their partial or complete reformation. However, this effect is observed also under conditions when aggregation is practically excluded: on grinding with water [34,94]. The decrease in the rate of dispersion is a consequence of the increasing specific consumption of energy in the limiting plastic deformation, which at a constant depth is proportional to the specific surface of the material. Therefore with the energy concentration, which the material can acquire in a single act of disintegration, limited for each mill, there is a limiting value of the dispersion, determined by the design of the grinder and the way in which it operates. The degree of dispersion increases, for example, with increasing amplitude of vibration in the vibro-mill. Hence the maximum dispersion which can be achieved also increases [94]. Similarly, the heat of dissolution of sugar in water and the solubility of quartz become greater as the action becomes more vigorous. It is characteristic that the increase in solubility ceases considerably earlier than the growth in dispersion or degree of amorphisation [65]. As has been mentioned, this is associated with the fact that the activity is determined by the state of extremely thin surface layers, which are constantly subject to mechanical constraints. In most cases the forces arising in the numerous contacts of particles and their rubbing against one another cannot cause disintegration, but are sufficient for deformation of the surface layers.

Another factor governing a rational degree of dispersion is the industrial desirability of speeding up the reactions. In several cases the use of highly disperse materials in ordinary technological layouts adapted for operation with comparatively coarse products leads to undesirable consequences. Thus, for example, very fine grinding of cement considerably shortens the time of hardening of concrete and could result in an increase in its strength. However, the cement solution then sets rapidly, becoming difficult to pack and transport. A rapidly hardening cement paste is therefore difficult to mix and set well, and the hardening process does not take place uniformly. The high water requirements of finely ground cement diminish the strength and density of the concrete. In production, therefore, a rational degree of grinding of cement is chosen experimentally on the basis of the optimum technological conditions for making it and utilising the equipment [92]. The optimum degree of grinding of quartz sand in the autoclave production of silicalcite is determined similarly [95].

Thus the use of highly disperse cement and sand proves inadvisable with the usual technological arrangements. However, the high activity of finely ground binders finds successful practical application in the technology of concrete development by Mikhailov and Rebinder [96,97] from the principles of physicochemical mechanics. The basis of this technology is the use of highly disperse cement and sands with a filler (readily available fine sand) with different frequencies of limiting vibration of the mixture at all stages of preparation of concrete from mixing to pouring and setting. This ensures a fuller utilisation of the bonding properties of cement, diminishes the consumption of the scarce coarse filler, and enables concrete of high strength, density, and durability to be obtained. Similarly, it would be useful to review the technological arrangements for other manufactures in which highly disperse materials are used.

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THE THIYLATION OF OLEFINS

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INTRODUCTION

A very large number of papers in the last 15–20 years have dealt with the reactions of substances containing thiyl (SH) groups (thiols, hydrogen sulphide, thio-acids) with various unsaturated compounds (we propose the name "thiylation" for these reactions). Thanks to the high reactivity of the thiyls, multiple C–C bonds can be readily thiylated in both heterolytic and homolytic conditions. This often gives crystalline adducts which are widely used in the study of the structural and steric direction of ionic and free-radical addition.

These reactions provide a convenient method of synthesising various thiols and sulphides with properties of practical interest: regulators for polymerisation processes, vulcanisation accelerators, insecticides, drugs, etc. Some of these syntheses have acquired industrial importance. The thiylation of unsaturated compounds is also of interest, since these reactions can be regarded as models for certain processes of physiological importance, taking place in living organisms, particularly the synthesis of natural mercapto-amino-acids. A knowledge of the features of these reactions is necessary for the control of

processes of technical importance, such as the processing of petroleum, the vulcanisation of rubber, the regulation of emulsion copolymerisation by means of thiols, and many others.

Interest in this problem has led to the appearance of a number of reviews. The most complete, for its time, was a review of the addition of thiyl compounds to olefins[1]. Other reviews deal with specific topics: the addition of thiols to alkenes[2], methods of synthesising sulphides from H_2S or thiols and various olefins[3], and the homolytic addition of thiyls to olefins[4,5]. An extensive bibliography covering the literature up to 1954–1955 is given in the appropriate chapters of Reid's monograph[6].

Up to the present time, however, no attempt has been made to analyse all the available data from the viewpoint of the dependence of the structural direction of these reactions on the mechanism of addition and the structure of the unsaturated compound and addend. In the present review the thiylation of ethylenic compounds has been systematised according to this principle. The literature has been reviewed up to and including 1960 and some data published in 1961–1962 have been used.

I. THE HETEROLYTIC THIYLATION OF DOUBLE BONDS IN COMPOUNDS CONTAINING ELECTRON-DONOR GROUPS

1. Electrophilic Reactions without Catalysts; "Competition" with Free-Radical Addition

The mode of addition of electrophilic reagents to unsaturated compounds containing electron-donating substituents is governed by Markovnikov's rule. It has been suggested that these reactions either are ionic processes involving carbonium ions $CH_3\overset{+}{C}HX$ [7] or — and this is now accepted as more probable — involve preliminary formation of π-complexes[8] or 5–7-membered cyclic activated complexes[9] with addend, catalyst, and solvent. In the case where the substituent contains a hetero-atom capable of undergoing complex formation, an important part is played by "onium" complexes involving this atom[10].

Since the thiols are weak acids, we should expect that they would add on to alk-1-enes in accordance with Markovnikov's rule, but the first experimental studies gave the opposite result.

Posner studied the reactions of thiophenol and toluene-ω-thiol with a number of unsaturated ketones[11,12] and unsymmetrical hydrocarbons[13]. The reaction products, without being isolated, were converted to the sulphones, whose structure was proved by synthesis by an alternative route. Posner found that irrespective of the structure of the olefin and the reaction conditions (without catalyst, in acetic and sulphuric acids), the RS residue always appears to be attached to a terminal carbon atom. This rule for the thiols was accepted for a number of years, since it appeared to be confirmed by new experimental data. Thus, for example, it was found that thioglycollic[14] and thioacetic[15] acids react with styrene to form β-carboxymethylthio- and β-acetylthio-ethylbenzene respectively; the addition of p-thiocresol to the double bonds of divinylacetylene in accordance with this rule was used to prove the structure of the latter[16]. In 1928 it was suggested for the first time that the mechanism of the "anomalous" addition of thiophenol to styrene must differ from that of the addition to styrene of other acidic reagents which takes place in accordance with Markovnikov's rule[17]. In 1938 Posner's data were subjected to thorough examination and it was shown[18] that some of his results were erroneous. Thus thiophenol reacts with lower unsymmetrical alkenes in the presence of sulphuric acid in accordance with Markovnikov's rule. In particular, trimethylethylene gives t-pentyl phenyl sulphide and not isopentyl phenyl sulphide as reported erroneously by Posner[13]. In the absence of catalyst and with heating, the course of the addition of thiophenol to the same olefins is indeed anomalous, but it was shown simultaneously that this reaction of thiols is due to the presence of peroxy-compounds[19,20], is retarded by antioxidants, and is thus a free-radical reaction, like the anomalous hydrobromination of olefins[21,22]. Unlike the case of the reactions involving HBr, however, the free-radical addition of thiols is initiated by the smallest traces of peroxides and even by oxygen, and their normal addition to olefins usually takes place at a very low rate, due to their low acidity.

In Table 1 we have arranged the most frequently used thiyls in order of increasing acidic dissociation constant K_a, measured in aqueous or aqueous-alcoholic media[23–25]. The lowest acidity is shown by t-alkanethiols. The acidity increases, while still remaining low, for primary alkanethiols, particularly those containing β-substituents, and then increases by three orders of magnitude for thiols with α-keto- or α-alkoxycarbonyl groups and by four orders of magnitude for arenethiols and H_2S. Thioacetic acid is an acid of moderate strength, and the values of K_a for dialkylphosphinodithioic and *OO*-dialkyl phosphorothiolothionic acids are comparable to that of the second dissociation constant of sulphuric acid. The values of K_a in alcoholic medium are smaller by approximately two orders of magnitude than those in aqueous medium. Substances containing thiyl groups thus include acids with dissociation constants covering a range of about ten orders of magnitude, and it might seem that for some of these we should expect successful competition between heterolytic and homolytic addition, particularly if the process is carried out in the presence of an antioxidant. The competition between these two mechanisms is complicated, however, by the fact that the most acidic thiols, as will be shown below, are also the best suppliers of free radicals, particularly those radicals most reactive towards olefins.

Nevertheless, in recent years, particularly as a result of studies carried out in our laboratory, a number of examples have been found of the autocatalytic electrophilic thiylation of ethylenic compounds having a nucleophilic double bond.

The normal addition of alkane- and arene-thiols to alkenes without catalyst requires severe conditions. Thus in the presence of 5 mole % of hydroquinone, which eliminates the homolytic reaction, no addition of thioglycollic acid to styrene or isobutene is observed at room temperature[20]. When ethanthiol and propene, or thiocresol and tridecene, free from peroxides but containing no antioxidants, are subjected to prolonged heating at 150°, a mixture of normal and anomalous products is obtained[19]. When heated in an autoclave to 150°–200°, hydrogen sulphide adds on slowly to lower alkenes in accordance with Markovnikov's rule[36]. This reaction, however, possibly involves catalysis by metal sulphides formed on the walls of the autoclave; it has been shown that such sulphides lead, for example, to the preferential formation of propane-2-thiol from propene and H_2S.[37] Dialkylphosphinodithioic and *OO*-dialkyl phosphorothiolothionic acids, which have a

TABLE 1. Acid dissociation constants of thiyl compounds RSH

R	K_a	Solution	Temperature, °C	Method of measuring pH*	References
t-C_5H_{11}—	$6.2\cdot10^{-12}$	aqueous	20±1	a	23
t-C_4H_9—	$8.9\cdot10^{-12}$; $7.3\cdot10^{-12}$	»	20±1	b; a	23
	$0.2\cdot10^{-12}$	80% aqueous alcohol	20±1	c	24
iso-C_3H_7—	$2.5\cdot10^{-11}$	aqueous	20±1	c	25
n-C_4H_9—	$2.21\cdot10^{-11}$; $1.65\cdot10^{-11}$	»	20±1	b; a	23
	$0.4\cdot10^{-12}$	80% aqueous alcohol	20±1	c	24
n-C_3H_7	$2.26\cdot10^{-11}$; $1.50\cdot10^{-11}$	aqueous	20±1	b; a	23
	$2.52\cdot10^{-11}$; $2.30\cdot10^{-11}$	»	20±1	b; a	23
C_2H_5—	~$1.30\cdot10^{-11}$	»	20±1	d	26
	$3.16\cdot10^{-11}$	»	20±1	a	27
	$1.10\cdot10^{-12}$	80% aqueous alcohol	20±1	b	24
HOOCCH$_2$**	$3.98\cdot10^{-11}$	aqueous	—	c	25
	$3.71\cdot10^{-11}$; $3.98\cdot10^{-11}$	»	20±1	a; c	27
CH_2=CH—CH_2—	$1.1\pm0.4\cdot10^{-10}$	»	25±1	d	26
HOCH_2CH(OH)CH_3	$2.2\cdot10^{-10}$	—	—	a	28
	$3.09\pm0.05\cdot10^{-10}$	aqueous	25±1	a	26
	$3.02\cdot10^{-10}$	»	25±1	a	29
	$3.74\cdot10^{-10}$	»	25±1	a	26
HOCH_2CH_2—	$3.31\cdot10^{-10}$; $2\cdot10^{-10}$	»	20±1	c; a	27
	$2.32\cdot10^{-10}$	»	—	c	25
C_6H_5OCH_2CH_2—	$4.15\cdot10^{-10}$	»	25±1	a	26
	$3.75\pm0.18\cdot10^{-10}$	»	25±1	c	26
C_6H_5CH_2—	$1.58\cdot10^{-12}$	80% aqueous alcohol	20±1	c	24
	$4.47\cdot10^{-9}$; $7.97\cdot10^{-9}$	aqueous	20±1	c; a	27
$NH_2CH_2CH_2$—	$2.52\cdot10^{-9}$	»	25±1	a	29
	$5.01\cdot10^{-9}$	»	23±1	c	30
	$5.01\cdot10^{-9}$	»	25±1	a	29
HOOCCHCH_2—	$2.95\cdot10^{-9}$	»	23±1	c	30
NH$_2$	$4.79\cdot10^{-9}$	»	20±1	c; a	27
	$1.6\cdot10^{-8}$	»	25±1	a	29
C_2H_5OCOCH_2—	$1.17\cdot10^{-8}$; $1.11\cdot10^{-8}$	»	25±1	c; a	26
	2.10^{-8}	»	20±1	a	27
CH_3OCOCH_2—	$1.58\cdot10^{-8}$	»	25±1	a	29
CH_3COCH$_2$—	$1.37\cdot10^{-8}$	»	25±1	a	26
H***	$9.5\cdot10^{-8}$	»	25±1	c	31
p-$CH_3C_6H_4$	$9.3\cdot10^{-8}$	48% aqueous alcohol	25±1	a	32,33
	$3.0\pm0.8\cdot10^{-7}$	aqueous	25±1	c	26
	$1.66\cdot10^{-8}$****	»	20±1	a	27
C_6H_5—	$3.2\cdot10^{-7}$	»	—	c	25
	$1.76\cdot10^{-8}$	48% aqueous alcohol	25±1	a	32,33
	$5.01\cdot10^{-9}$	80% aqueous alcohol	20±1	c	24
p-$CH_3SO_2C_6H_4$—	$2.69\cdot10^{-6}$	48% aqueous alcohol	25±1	a	32
p-$NO_2C_6H_4$—	$7.66\cdot10^{-6}$	ditto	25±1	a	32
CH_3CO—	$4.7\cdot10^{-4}$ *****	aqueous	25±1	a	34
$(C_2H_5O)_2P$(=S)—	$2.40\cdot10^{-2}$	7% aqueous alcohol	20±1	a	35
	$3.31\cdot10^{-3}$	80% aqueous alcohol	20±1	a	35
$(iso\text{-}C_4H_9)_2P$(=S)—	$1.00\cdot10^{-2}$	7% aqueous alcohol	20±1	a	35
	$1.55\cdot10^{-3}$	80% aqueous alcohol	20±1	a	35

* (*a*) Titrimetrically (with glass electrode); (*b*) calculated from data on the partition between aqueous and oil phases; (*c*) determined spectrophotometrically; (*d*) calculated from the gas solubility.

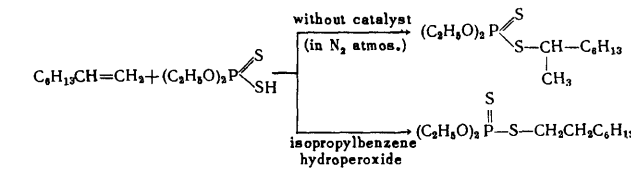
** Second acid dissociation constant, corresponding to the ionisation of the thiyl group.

*** First acid dissociation constant.

**** These data, although given in a recent paper[27], are probably erroneous since they are inconsistent with other values of K_a for this thiol.

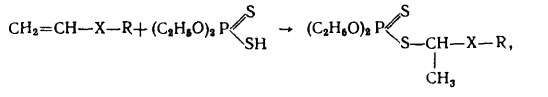
***** The only experimental data available for thioacetic acid are very old, so that the value of K_c, and not K_a, is given.

high acidity (Table 1), are still capable of undergoing exothermic electrophilic addition to olefins. Thus purified *OO*-diethyl phosphorothiolothionic acid results in an atmosphere of nitrogen with oct-1-ene, purified from peroxides, to give 87% of the normal product, whereas in the presence of isopropylbenzene hydroperoxide the anomalous product is formed exclusively, in high yield[38,39]. Olefins containing peroxides formed during storage give a mixture of the two types of product:



The addition of undistilled *OO*-dialkyl phosphorothiolothionic acids to alkenes always takes place in the normal way, due to the catalytic action of traces of sulphur–phosphorus compounds present (of the type P_4S_3)[39,40]. It is possible that analogous impurities were responsible for the normal addition of dialkyl phosphorotetrathioates $(RS)_2PSSH$ to alkenes[41].

The electrophilic thiylation of $\alpha\beta$-unsaturated sulphides and ethers is even more vigorous than that of alkenes[42-46]. Thanks to the combination of the high acidity of the addend and the marked nucleophilic character of the double bone, *OO*-dialkyl phosphorothiolothionic acids undergo quantitative exothermic addition to vinyl sulphides and ethers to give the normal adducts when the reagents are mixed in air[42-44]:



where X = O or S and R = alkyl or aryl. Adducts for which X = S and R = Ar have an acaricidic action and comparatively low toxicity towards warm-blooded animals[44,46]. Exclusively anomalous addition cannot be achieved in this case, even in the presence of free-radical initiators. Thus vinyl ethyl sulphides and *OO*-diethyl phosphorothiolothionic acid in the presence of benzoyl peroxide, azoisobutyrodinitrile, or isopropylbenzene hydroperoxide gives mixtures of 1- and *S*-(2-ethylthioethyl) *OO*-diethyl phosphorothiolothionates[43]. In this connection, the synthesis of the 2-ethylthio-derivative "M-74" and its analogues, which have a high insecticidal activity, has been found to be more conveniently carried out by alkylating salts of *OO*-dialkyl phosphorothiolothionic acids with bis-2-chloroethyl sulphide[47,48]. In the absence of atmospheric oxygen, vinyl alkyl ethers add on thioacetic acid chiefly in accordance with Markovnikov's rule[49]. The reaction is exothermic, confirming again the highly nucleophilic character of the double bond influenced by an alkoxy-group. Recently, the first example of the ready electrophilic reaction of thiophenol was discovered: its addition to vinyl lactams takes place with the exclusive formation of α-phenylthioethyl lactams, is accelerated by HCl, and, strangely, is retarded by the addition of azoisobutyrodinitrile[50].

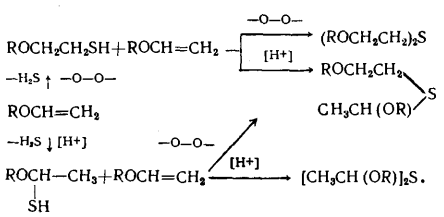
2. Thiylation in the Presence of Catalytic Quantities of Acidic Reagents

The ionic electrophilic addition of less acidic thiyls takes place in the presence of catalytic quantities of strong acids: this possibility was questioned recently in a number of papers and reviews[3,4,51].

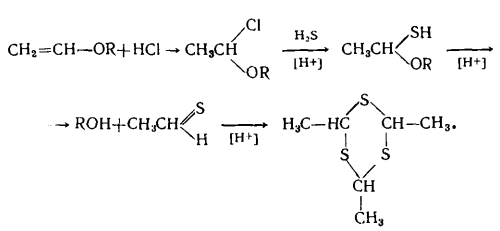
We found in our laboratory that traces of SO_2 bring about rapid and quantitative reaction between liquid H_2S and vinyl alkyl ethers with the formation of normal adducts[52-54]. In this case the true catalysts leading to the formation of the

$CH_3\overset{+}{C}HOR$ cation are apparently polythionic acids produced by the reaction between SO_2 and H_2S in the presence of traces of moisture[52,54]. The fact that SO_2 is an antioxidant and inhibits the competing free-radical reaction may also be significant. The addition of a small quantity of pyridine neutralises the action of SO_2 completely.

The competition between the ionic and free-radical addition of H_2S to a vinyl alkyl ether becomes particularly evident if this reaction is carried out in the presence of catalytic quantities of a saturated solution of HCl in anhydrous dioxan using gaseous[55,56] or liquid[54,57,58] H_2S. The dissolved HCl brings about normal addition and the traces of a peroxide of unknown structure present in the catalyst, even when the latter is prepared from thoroughly purified dioxan, bring about the anomalous reaction. As a result, all possible products were found in different proportions in the reaction mixture:

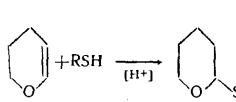


By varying the reaction conditions, particularly the quantity of catalyst, it is possible to obtain either exclusively the anomalous di-(2-alkoxyethyl) sulphides and 2-alkoxyethanethiols or mixtures of 2,2′- and 1,2′-isomeric sulphides or mixtures of all three of their isomers. The composition of the mixtures was determined titrimetrically, since it was found that sulphides and thiols containing α-alkoxy-groups, unlike ordinary sulphides and thiols, are decomposed quantitatively by mercuric chloride with the liberation of HCl.[54,59] When the reaction is carried out in a strongly acidic medium (for example by saturating the cooled vinyl ether first with HCl and then with H_2S), the chief product is 1,3,5-trimethyl-2,4,6-trithiane, whose formation is explained as follows[60,61]:



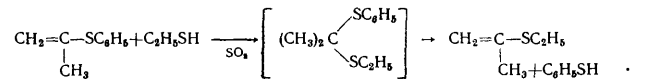
Traces of SO_2 also bring about the exothermic addition of alkanethiols[62] and thioacetic acid[49] to vinyl alkyl ethers with the formation of monothioacetals or thioacylals. The same catalyst has been used for the normal thiylation of vinyl aryl ethers, including ethers of halogenophenols[63-65].

The preparation of monothioacetals from vinyl ethers and thiols in the presence of $SOCl_2$ (0.1–0.2%)[66] or 1-chloroethyl methyl ether (1–2%)[67] has been recommended. Traces of HCl in an anhydrous medium bring about the formation of α-alkylthiotetrahydropyrans from dihydropyrans and thiols[68,69]:

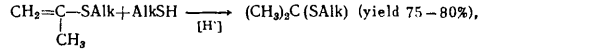


In the presence of trichloroacetic acid or 1-chloroethyl methyl ether, dithiols react with divinyl ethers to give polythioacetals[70]. Vinyl ethyl sulphide, which has a less nucleophilic double bond and slightly greater affinity for free radicals than vinyl ethyl ether[43,71], reacts with ethanethiol (traces of SO_2) to give a mixture of normal and anomalous adducts[43,72].

When 5% hydroquinone is added, the diethyl thioacetal is formed almost exclusively. When heated with ethanethiol in the presence of SO_2, 2-phenylthiopropene apparently reacts according to the equation:



The intermediate thioketal could not be isolated[73,74], whereas in the 2-alkylthiopropene series exothermic addition of thiols under the influence of traces of HCl has been observed[73,75]:



where Alk = C_2H_5, C_3H_7, or C_4H_9.

Other examples of this type of catalytic reaction include several processes, described chiefly in the patent literature, for the thiylation of branched alkenes in the presence of small quantities of HF, BF_3, etc. These are considered in the next section.

3. Thiylation in Strong Acids and in the Presence of Friedel–Crafts Catalysts

Electrophilic thiylation can be brought about by successive treatment of an alkene with a large amount of strong acid and a thiol. In this case the reaction apparently involves alkylation followed by exchange of the acid residue.

A method has been described for the synthesis of thiols and sulphides from alkanesulphonic acids[76]. In concentrated or aqueous H_2SO_4 or CH_2COOH unsymmetrical alkenes add on thiols in accordance with Markovnikov's rule, whereas H_3PO_4, because of its low acidity, does not prevent the anomalous addition[18]. Secondary and tertiary thiols and sulphides have been prepared many times from alkenes and cycloalkenes in H_2SO_4. Thus 1-methylcyclohexane-1-thiol and 2-methylpentane-2-thiol were prepared by treating the corresponding olefins with H_2SO_4 and toluene-ω-thiol, with subsequent removal of the benzyl group by the action of Na in liquid NH_3.[77]

The tertiary thiol from 2,6-dimethyloct-2-ene was prepared in analogous fashion[78]. The following additions take place in accordance with Markovnikov's rule in H_2SO_4: thioglycollic acid to a number of terpenoid hydrocarbons[79], thioglycollic acid and thiophenol to methylcyclohexene[80], and 3-oxopentane-1,5-dithiol to unsymmetrical alkenes[51].

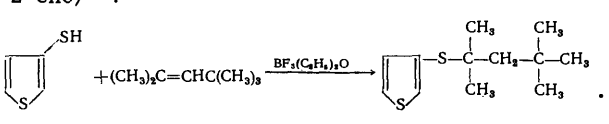
There are also a number of reports, chiefly in the patent literature, on the reaction of alkenes and terpenoid and other hydrocarbons with H_2S or thiols in the presence of H_2SO_4 and other acidic catalysts (P_2O_5, $ZnCl_2$, benzenesulphonic acid); in most cases the structure of the adducts was not proved[81-86]. Technical benzene[87] and petroleum cracking-distillates[88] are enriched with thiols during refining, as a result of reaction between the H_2S and olefins present catalysed by washing with H_2SO_4.

There are many patents† on reactions of branched alkenes with H_2S in the presence of various homogeneous and heterogeneous catalysts of the alkylating type. Tertiary thiols obtained in this way from cheap raw materials (the lower polymers of the propene–isobutene fraction from petroleum gases containing $C_{12}-C_{18}$) have been widely used as polymerisation regulators for styrene–butadiene rubber[89], corrosion inhibitors, and starting materials for the preparation of thioacetals, disulphides, etc., and used as vulcanisation accelerators, oil additives, and insecticides[90]. Reaction in a slight excess of H_2S (1.5 : 1 or 2 : 1 with respect to the alkene) gives chiefly the tertiary thiol, with almost no thioether formation. This is probably due to the marked difference in the acidities of the tertiary thiols and H_2S (Table 1).

H_2S reacts with alkenes to give secondary and tertiary thiols at comparatively low temperatures (from -70° to 0°) in the presence of HF, BF_3, and the chloride and fluorides of Al, Be, Zn, B, P, As, Sn, Ti, and Sb.[91,92] Thiols are formed when a mixture of liquid H_2S and triisobutylene in the ratio ~2 : 1, containing 1.7% BF_3, is passed through a steel coil at -30°;[93] BF_3 containing traces of HF brings about the formation of tertiary thiols from alkenes at -40° and below[94]. Tertiary thiols or their mixtures with sulphides are obtained by passing a mixture of H_2S and BF_3 through a column containing pumice, into which the alkene is introduced simultaneously[95], or by cooling their mixtures in a closed vessel. Substances recommended as catalysts include 80% aqueous HF (in this case a continuous process is described[96]) and BF_3 complexes such as $BF_3.(C_2H_5)_2O$, $BF_3.H_2O$, and $BF_3.H_3PO_4$.[97-101] H_2S adds on to propene tetramers at 0°–5° in the presence of 5–15% of $BF_3.(C_2H_5)_2O$, $BF_3.CH_3COOH$, or $BF_3.C_2H_5OH$ [102] (or in the presence of $BF_3.H_2O$ formed on introduction of moist H_2S [103]); thioglycollic acid or its esters undergo this addition in the presence of $ZnCl_2$, $AlCl_3$, or BF_3.[104] The reaction between alkenes and thiols on treatment with liquid HF has been proposed for the desulphurisation of petroleum fractions[105].

Other patents[106-115] recommend the use of various catalysts such as $AlCl_3$, $SnCl_4$, etc. The various factors influencing the reaction of H_2S with alkenes in the presence of $AlCl_3$ or a mixture of $AlCl_3$ and anhydrous HCl have been discussed in detail[106-108]. In the presence of this catalyst at 0°, H_2S and triisobutylene give t-dodecanethiol; at 50°–80°, as a result of depolymerisation, t-butanethiol and isooctanethiol are formed[109]. $AlCl_3$ in anhydrous medium completely inhibits the action of alkene peroxides, present in the reaction medium, in their reactions with H_2S and primary and secondary thiols[110].

$AlCl_3$, $BF_3.HF$, CuCl, etc. catalyse the formation of sulphides from alkenes and alkane- or arene-thiols, when equimolar quantities of the reagents are used, and the formation of alkanes if an excess of the thiol is used[111]. In the presence of $AlCl_3$ or BF_3 thiophenols or thiocresols add on to both double bonds of 2,5-dimethylhexa-2,6-diene according to Markovnikov's rule[112], whereas boron trifluoride-etherate brings about the following reaction between thiophene-3-thiol and diisobutylene (2,3-dimethylbut-2-ene)[113]:



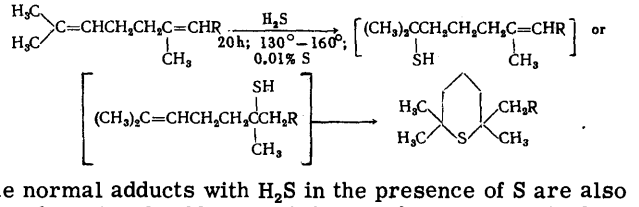
† Only the most important are cited here.

The thiylation of alkenes under the influence of strong Lewis acids takes place much more readily with branched alkenes than with normal primary alkenes, evidently due to the electron-donating effect of the alkyl groups. Thus ethylene, when passed with H_2S through a packed column (catalyst HF or BF_3), gives 17.7% C_2H_5SH and 1.3% $(C_2H_5)_2S$, whereas triisobutylene gives 75% $C_{12}H_{25}SH$.[116] These differences in reactivity make it possible to use the reaction of H_2S with mixtures of alkenes to separate tertiary alkenes, which form tertiary thiols, from primary and secondary alkenes, which do not react under the experimental conditions[117]. Thus $C_{12}-C_{18}$ sulphonic acids at 30°–60° bring about the formation of up to 98% tertiary thiols from H_2S and tertiary alkenes, whereas primary alkenes react only at 100°–120° and give the sulphides[118].

4. Thiylation in the Presence of Elementary Sulphur

Jones and Reid[19] showed that the addition of thiols and H_2S to alkenes takes place in accordance with Markovnikov's rule when the reagents are heated with elementary sulphur (150°–180°, 10–15% S). Even better results are obtained when ethyl tetrasulphide, which is readily miscible with organic substances, is used as sulphur donor. Under these conditions, the lower alkenes (ethylene and propene) reacted with H_2S to give chiefly sulphides and small amounts of thiols, isobutene and cyclohexene gave chiefly thiols, and the addition of thiophenol to all alkenes took place in accordance with Markovnikov's rule[19]. This method was subsequently used by many workers. Thus when ethanethiol was heated with allyl alcohol in a sealed tube (120°, 67 h, 2% S), the chief product was 2-hydroxyethyl isopropyl sulphide (59%); 5% of the anomalous 3-hydroxy-n-propyl ethyl sulphide was obtained simultaneously[119]. When the same alcohol was heated with monothioethylene glycol or thiophenol (3% S), however, the normal adducts were formed exclusively[120,121]. Mixtures of isomeric branched alkenes and H_2S (180°, 10–20 h, 2–3% S) gave the corresponding t-dodecanethiols, which are model regulators for polymerisation[122].

Sulphur does not, however, catalyse the addition of H_2S to the more highly branched dodecene (Butlerov's triisobutylene[99]). In the presence of S (or Al_2S_3), H_2S adds on to cyclohexene and the terpenes dihydromyrcene and geraniolene[123], the reaction in the latter case being accompanied by cyclisation of the adducts:



The normal adducts with H_2S in the presence of S are also given by natural rubber and this is of importance in determining the nature of the processes accompanying its vulcanisation[123].

The mechanism of the catalysis by sulphur in these reactions possibly resembles that of the action of iodine in processes of olefin hydrohalogenation[4]. An important part is undoubtedly played, however, by the ability of sulphur to inhibit radical processes and thus to suppress the anomalous addition.

To the reactions considered above we may add the thiylation of olefins catalysed by sulphur in the presence

of bases (ammonia, hydrazine, amines). According to the patent literature, this reaction can be used to prepare sulphur-containing polymeric products and also for the vulcanisation of rubbers[124]. It has been shown for the case of cyclohexene and 2-methylpentene that branched hydrocarbons react with sulphur and diethylamine to form tertiary sulphides and disulphides. It is suggested that the reaction proceeds *via* the polar complex $[NH_2(C_2H_5)_2]^+SH^-$, which is formed from the amine and the H_2S produced in the reaction[77]. The preferential addition of H_2S to branched olefins in accordance with Markovnikov's rule is the principal stage determining the course of the Willgerodt reaction (the preparation of amides from ketones, alcohols, aldehydes, and alkenes by the action of ammonium sulphide–polysulphide)[125].

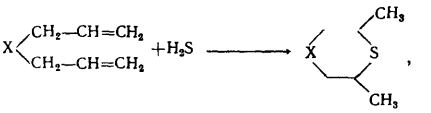
5. Thiylation in the Presence of Heterogeneous Catalysts

The mechanism of the reactions which will be considered in this section is even less clear. Interest in these compounds, which are dealt with chiefly in the patent literature, is due to the technical importance of a number of processes which have been developed. Catalysts which have been recommended at different times for the thiylation of alkenes include silica gel, fuller's earth[126-128], and metal sulphides (in conjunction with dehydrating agents[129]). Thiols react with alkenes over Ni, Fe, and Co sulphides at 35°–200° and increased pressure to form chiefly tertiary sulphides, which are converted to alkanes in excess thiol[130]. WS_2 and MoS_2 bring about the ready addition of H_2S and H_2Se to alkenes[131]. Studies have been made of the thermodynamics of the reaction of H_2S with ethylene and propene over NiS on silica gel, Ni on kieselguhr, and H_3PO_4 on kieselguhr in the range 200°–300°,[37] and the reaction of H_2S with diisobutylene in the presence of tungstosilicic acid at 230°–240°.[132] The reaction of H_2S with unsaturated cracking gases over a catalyst containing H_3PO_4 on kieselguhr at increased temperature and pressure is recommended for the removal of H_2S from these gases; valuable sulphur-containing compounds are obtained simultaneously[133]. The same catalyst brings about the reaction of considerable quantities of H_2S with mixtures of liquid unsaturated hydrocarbons, with the formation of thiols, sulphides, and other sulphur compounds; Tavtimanovskaya clay from the region of Vtoroi Baku has a slightly weaker effect. It has been suggested that these reactions are related to processes taking place in petroleum fields[134].

The reaction of H_2S with branched $C_{12}-C_{18}$ alkenes over heterogeneous catalysts forms the basis of the industrial production of polymerisation regulators of the t-dodecanethiol type[135]. It is stated in non-Soviet patents that the best catalyst is silica gel activated with a small quantity of alumina[97,136,137] or montmorillonite activated with acids[138]. The reaction can also be carried out in the presence of SiO_2 and small quantities of the oxides of metals in Groups III and IV.[136] Data have been given on the improvement of the process by decreasing the depolymerisation of the branched hydrocarbons and the improvement of methods for separating the thiols or purifying the original alkenes[136,137,139]. A continuous method for the synthesis of thiols from H_2S and homopolymers of propene with alumina–silica gel suspended in a liquid mixture of the reagents has been described[140]. Liquid H_2S adds on to the propene tetramer with the formation of up to 70% of dodecanethiol at 120°, in the presence of an aluminosilicate catalyst, which should contain not less than 9–11% Al_2O_3.[141] Under the influence of the catalyst Superfiltrol H_2S reacts with 3- and 4-vinylcyclohexenes to form monovinylcyclohexanethiols which are capable of undergoing polymerisation and copolymerisation. These compounds can also be used as regulators[142].

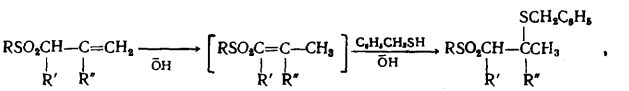
6. Thiylation in the Presence of Bases

There are comparatively few papers recommending that the thiylation of ethylenes with electron-donating substituents be carried out in the presence of bases. It has been shown that prolonged heating of allyl ether and H_2S with dibutylamine gives 2,6-dimethylthioxane in 43% yield, in addition to polymeric substances[143]. Under analogous conditions, the corresponding heterocyclic compounds are formed by the reaction of H_2S with methyl allyl ether, diallylamine[143], and diallyl sulphide[144]:



where X = O, S, NH.

In these examples the addition apparently takes place in accordance with Markovnikov's rule‡. Sulphones with allyl groups also react readily in alkaline medium, apparently in accordance with Markovnikov's rule, not only with thiols and H_2S but also with water and ammonia[145-147]. In this case, however, the action of alkali results first in allyl isomerisation to isopropenyl sulphones, which then add on nucleophilic reagents in the β-position to the electron-repelling sulphonyl group:



where R = $CH_2CH{=}CH_2$ or $C_6H_5CH_2$ and R′ and R″ = H or CH_3.

It has been stated that the thiylation of any olefinic compound appears to be catalysed by bases, irrespective of the nature of the substituent next to the double bond. Thus the addition of H_2S to various $R-CH{=}CH_2$ and $ROCH{=}CH_2$ compounds (where R = hydrogen, alkyl, aryl, alkoxycarbonyl, ether, nitrile, or heterocyclic groups) with heating and in the presence of alkalis, metal oxides, and other basic catalysts has been recommended[148,149]. Adducts of thiols with vinyl ketones, ethers, and esters ($RSCH_2CH_2OCOCH_3$, $C_6H_5SCH_2CH_2OR$, $RSCH_2CH_2COCH_3$) are obtained under analogous conditions[150]. It is stated that alkalis appear to accelerate the reaction between thiols and αβ-unsaturated sulphides with the formation of the compounds $RSCH_2CH_2SR'$.[151] The addition of H_2S [152] and thiophenols[153] to 2-vinylpyridines gives the corresponding β-(pyrid-2-yl)ethyl sulphides. The reaction proceeds spontaneously and is accelerated by the addition of piperidine or "Triton B". It is stated that Triton B is a universal catalyst for the addition of thiols to any olefin[154]. It has been shown that the reaction of allyl alcohol with toluene-ω-thiol in the presence of benzoyl peroxide or Triton B gives the same anomalous adduct, 3-benzylthiopropanol[155]. Allyl chloride also reacts in anomalous fashion with 3-oxopentane-1,5-dithiol in the presence of K_2CO_3.[156]

In all these examples, irrespective of the structure of the olefin, the thiyl adds on to the terminal carbon atom

‡ These papers, however, give no rigorous proof of the structure of the adducts.

of the double bond in the presence of alkali. In the work cited, however, no attempt was made to free the reagents from peroxides or to exclude oxygen from the reaction medium. It is therefore very probable that although true catalysis by alkalis took place in the case of unsaturated compounds containing electron-accepting groups, free-radical addition, catalysed by peroxides and unaffected by the presence of alkali, took place when electron-donating substituents were present. Direct proof of this is provided by our work on the free-radical addition of H_2S and thiols to vinyl ethers and sulphides. This will be considered in more detail below.

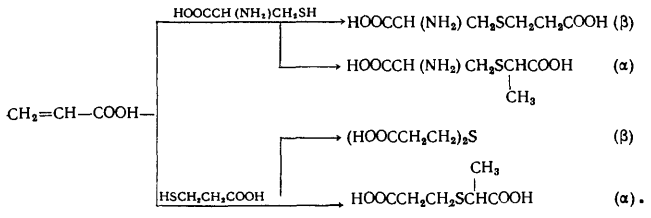
There are thus no confirmed data indicating that alkalis are universal catalysts for the thiylation of olefins.

II. THE HETEROLYTIC THIYLATION OF DOUBLE BONDS IN COMPOUNDS CONTAINING ELECTRON-ACCEPTOR GROUPS

1. General Conditions and Reaction Mechanism

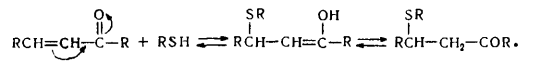
Electron-attracting groups activate a double bond towards nucleophilic attack, so that thiyls readily add on to compounds containing such groups, for the most part in the presence of basic catalysts, but sometimes in the presence of acidic catalysts if X contains carbonyl, carboxy, or alkoxycarbonyl groups. Bases which have been used include the alkalis NaOH or KOH, amines (most frequently piperidine, triethylamine, and diethylamine), trimethylbenzylammonium hydroxide (Triton B), sodium alcoholates, thiolates, and acetate, and anhydrous potassium carbonate. The acids most frequently used are HCl or a mixture of HCl and CH_3COOH. In some cases neutral substances, for example CuS, have been used. The highly nucleophilic character of the thiyl ions favours rapid thiylation, which can usually be carried out quantitatively in water or alcohol, no hydration or addition of alcohol to the double bond being observed. Thus the reaction of excess dodecanethiol in dilute alcoholic solutions with acrylonitrile, $\alpha\beta$-unsaturated esters, aldehydes, and ketones in the presence of Triton B has been proposed for the quantitative determination of these compounds; the back titration of the thiol is carried out iodometrically or amperometrically[157].

In the reactions with these olefins the thiyl residue usually enters the β-position relative to the substituent, with the formation of $RSCH_2CH_2X$, *i.e.* the order of the addition is controlled by the direction of polarisation of the double bond§. Methacrylic acid, however, reacts with cysteine, thioglycollic acid, and thiohydracrylic acids to give exclusively the β-adducts[159] only at pH > 7; in acid medium (pH ~5) a small quantity of isomers containing the thiyl in the α-position is produced[160,161].



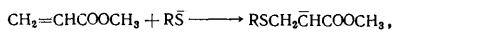
§ For substances with an "activated" C=C bond, the expression "contrary to Markovnikov's rule" is meaningless, since the rule is applicable only to olefins with electron-donating substituents[158].

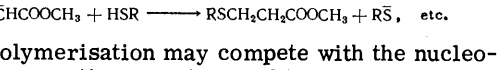
It is assumed that this is due to a decrease in the selectivity of addition on going from the strongly polar acrylate ion (alkaline medium) to the much less highly dissociated carboxy-group (acid medium)[160,161]. Other analogous examples will possibly be found in the future. No deviation from the β-addition rule is to be expected in alkaline medium, however. The thiylation of $\alpha\beta$-unsaturated carbonyl compounds apparently involves reversible 1,4-addition with participation of their enolic forms[12,162]:



The corresponding adducts are capable of redissociating into their components in strongly alkaline media[162]. These theories have been extended to other groups of compounds — $\alpha\beta$-unsaturated nitro-compounds, nitriles, and sulphones — for which the reverse reaction, dissociation of the adducts, has also been observed in alkaline media.

Later it was suggested that nucleophilic addition of thiols involves an anionic chain mechanism, for example[163]:





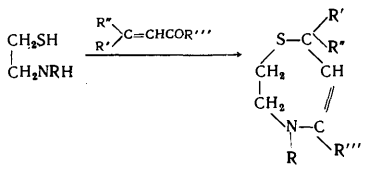
Anionic polymerisation may compete with the nucleophilic addition reaction, as observed in the reaction of excess vinyl ethyl sulphone with thiophenol in the presence of Triton B.[164]

These compounds usually give the same products $RSCH_2CH_2X$ on thiylation in both heterolytic and homolytic conditions. The ionic reactions, particularly in alkaline media, however, are exothermic and give adducts in high yield, whereas the free-radical reactions require more severe conditions and are often complicated by the formation of telomers. For the purposes of synthesis, therefore, reactions in the presence of ionic catalysts are usually employed. These will be examined below.

2. Thiylation of $\alpha\beta$-Unsaturated Ketones

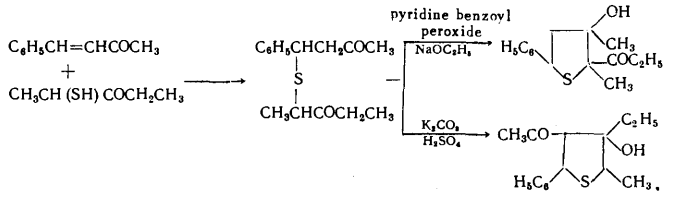
Posner showed that in a current of dry HCl in acetic acid thiols readily add on to the C=C bonds of conjugated ketones. At the same time the tendency to form thioacetals is decreased, particularly if an aryl group is present next to the keto-group[11,12]. It is much more convenient to carry out the addition of thiols to the double bond of unsaturated ketones using the basic catalysts Na ethoxide or piperidine, since under these conditions no thioacetals are formed[165]. High yields have been obtained for the adducts from thiols and substituted vinyl ketones; the substituted divinyl ketones gave di- and mono-adducts[165]. Various β-alkyl(aryl)thioketones obtained from vinyl methyl ketone, mesityl oxide, benzylidene- and dibenzylidene-acetone, benzylideneacetophenone, phorone, and various thiols with catalysis by piperidine have been proposed for use as a new type of antioxidant for fats, oils, and hydrocarbons[152,166,167]. H_2S and dithioethylene glycol add on to vinyl methyl ketone[152]. It has been shown that primary thiols, particularly those containing polar groups, react much more readily than tertiary thiols. Exothermic addition reactions take place between mesityl oxide and toluene-ω-thiol[146], vinyl methyl ketone or vinyl phenyl ketone and ethanethiol[168], and between vinyl methyl ketone and thien-2-ylmethanethiol[169] (catalyst metallic Na). Vinyl methyl ketone adds on thiols quantitatively in the presence of Triton B.[154] n-Dodecanethiol undergoes an exothermic reaction with mesityl oxide

under the influence of a current of dry HCl.[170] β-Aminoethanethiol and its derivatives add on to substances of the mesityl oxide type without catalysts, the reaction being followed by cyclisation of the adducts[171,172]:



where R = H, CH_3, C_6H_5; R′, R″, R‴ = C_2H_5 or CH_3.

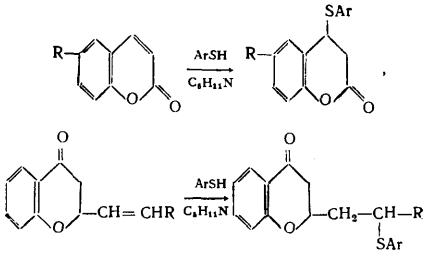
Thioglycollic acid and *p*-thiocresol react with benzylideneacetone and benzylideneacetophenone under the influence of $NaOC_2H_5$ [162] and 3-oxopentane-1,5-dithiol reacts with benzylideneacetone to give various products of the cyclisation of the primary adduct, depending on the catalyst used[173]:



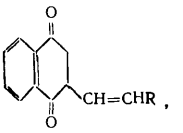
Some of the adducts obtained from substituted chalcones $R'C_6H_4CH{=}CHCOC_6H_4R'$ and alkane- or arene-thiols have an anti-tuberculosis action (catalysts $NaOC_2H_5$ [174], piperidine[175], pyridine, or diethylamine[176]; no reaction took place in the presence of HCl). The aminothiols $(C_2H_5)_2N(CH_2)_nSH$ (n = 2, 3) reacted in the form of the hydrochlorides on boiling[175]. 4-Dimethylamino-4-chlorochalcone added on *p*-thiocresol in the presence of piperidine, but no reaction took place between the chalcone and quinoline-2-thiol, since the more basic character of the addend displaced the equilibrium away from the formation of the adduct[177,178].

Protection of the thiyl group of thiophenols by addition to a 3-nitrochalcone, followed by the introduction of electrophilic groups into the nucleus and fission with $Pb(OCOCH_3)_2$ trihydrate, has been used to synthesise brominated and acylated thiophenols which could not be prepared by other methods[179]. This method of protection is not applicable to *o*-aminothiophenol, since its adduct with the chalcone readily undergoes cyclisation[180]. The method has been used to prepare various heterocyclic compounds from the thiophene analogues of the chalcones[181].

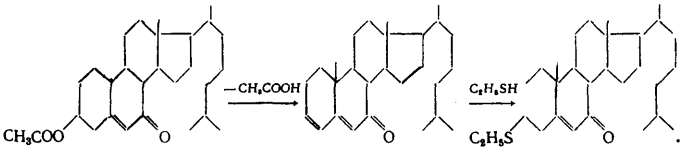
Hexamethylenedithiol and dibenzylideneacetone in benzene solution, with catalysis by piperidine or under emulsion conditions, give macromolecular products with the repeat unit $[-S(CH_2)_6SCH(C_6H_5)CH_2COCH_2CH(C_6H_5)-]$.[182,183] Arenethiols form physiologically active adducts with 6-methylcoumarin and also with 2-styrylchromone, which is a vinylogue of the chalcones:



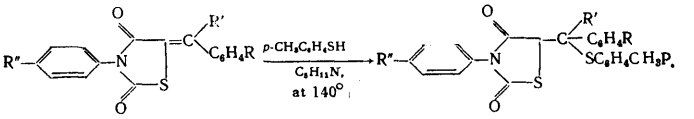
where R = H or CH_3, but do not add on to the ketone



which is a vinylogue of $ArCOCH_3$.[184] In a mixture of acetic and hydrochloric acids ethanethiol adds on to the conjugated steroid ketones 7-oxocholesteryl acetate and cholesta-3,5-dien-7-one in the 1,6-position; the expected thioacetal was not formed[185]:

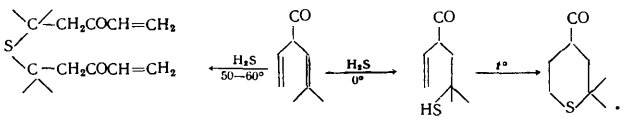


The exocyclic double bond of substituted thiazolidine-2,4-diones reacts readily with thiocresol[186]:



The addition of H_2S to carvone in the presence of ammonia in an alcoholic medium with the formation of a crystalline "hydrosulphide" was observed as early as 1849 [187] and was later used to isolate this and related unsaturated terpenoid ketones from essential oils[187-191]. The resulting crystalline ketosulphides gave the original ketone when boiled with alcoholic or aqueous alkali.

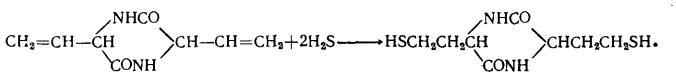
Nazarov *et al.* added H_2S to mesityl oxide and methoxyketones $CH_3OCH_2CH_2COCH{=}C(Alk){-}CH_3$ with catalysis by Na acetate in an alcoholic medium; β-ketothiols were obtained in 10–50% yield, and no ketosulphides were formed[192]. 3-Oxopentane-1,5-dithiol has been prepared by condensing H_2S into a cooled ethereal solution of mesityl oxide containing $N(C_2H_5)_3$.[193] An even simpler method involves the passage of H_2S into an alkaline aqueous-alcoholic or chloroform solution of mesityl oxide containing $N(C_2H_5)_3$,[196] at the boil[194] or with cooling to -15°.[195] In the addition of H_2S to dibenzylideneacetone[197], benzylidenemesityl oxide[198], or phorone[194] in the presence of sodium acetate or NH_3, the formation of cyclisation products of the substituted tetrahydro-γ-thiopyranone type was observed. Nazarov and Kuznetsova showed that H_2S adds on to bis-2-methylvinyl ketone only at the substituted vinyl group (with catalysis by sodium acetate in aqueous ethanol; no reaction takes place in anhydrous media); the products, depending on the reaction conditions, are the unsaturated ketothiol, its cyclisation product, or the unsaturated ketosulphide[199]:



Under analogous conditions homologues of divinyl ketone of general formula $R{-}CH{=}C(R)COCH{=}CHCH_3$ gave a range of tetrahydrothiopyranones, including the dicyclic compounds, whose stereoisomerism has been studied[200]¶.

¶ In this work[200] the original ketones were regarded as homologues of vinyl allyl ketone; later it was shown that they have the structure of substituted divinyl ketones[201].

Vinyl methyl ketone gave a mixture of the β-ketothiol and the β-ketosulphide in the presence of pyridine or 1% $NaOCH_3$ below 10°.[202] The dioxopiperazine ring causes such strong polarisation of the adjoining bonds that divinyldioxopiperazine reacts with H_2S at 0° in an alcoholic solution containing 1% CH_3COOH, according to the equation[203]:

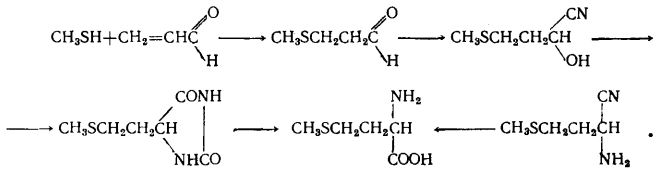


The reaction is undoubtedly heterolytic, since not only H_2S and HBr but also HCl add on in the same way.

3. Thiylation of αβ-Unsaturated Aldehydes

It was found that acrolein reacts with ethanethiol under the influence of $ZnCl_2$ in CH_3COOH to give 1,1,3-triethylthiopropane, together with a small quantity of 2-ethylthiopropanal[204].

Later, the addition of thiols to acrolein attracted the attention of many workers as one of the simplest methods of synthesising thioamino-acids, which are similar to the decomposition products of penicillin. (±)-Methionine, which is used as a beneficial additive to the food of young cattle and birds, was prepared as follows[205,206]:

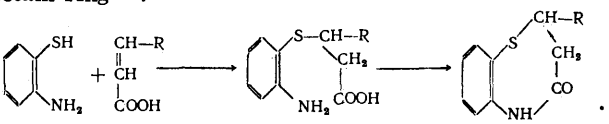


The addition of methanethiol was carried out in the presence of traces of $N(C_2H_5)_3$,[205] $Cu(OCOCH_3)_2$,[206] hydroperoxides, peroxides, polymerisation inhibitors[207], and dimethylaniline[208]. 3-Methylthiopropanal was also prepared in the vapour phase by a continuous method[209]. An analogous scheme using acrolein and the appropriate thiol [catalyst $N(C_2H_5)_3$] gave ethionine and *S*-benzylhomocysteine[210]. The reaction of acrolein with thiols is also catalysed by Amberlite IRA-400 resin in the basic form[211], piperidine[212], dimethylaniline[213], or a mixture of piperidine and organic acids[214]. Analogous syntheses were carried out using crotonaldehyde and 2-methylcrotonaldehyde, leading finally to the formation of the corresponding α-aminobenzylthio-acids[210]. Toluene-ω-thiol adds on spontaneously to crotonaldehyde at +50°, but between -50° and 0° basic catalysts are used[215]. A recommended general method involves the gradual addition of the unsaturated compound (αβ-unsaturated aldehyde, ketone, nitrile, or halogeno-derivative) to a solvent containing the thiol and catalyst [$N(C_2H_5)_3$, pyridine, piperidine] at such a rate that the temperature does not rise above 10°–20°.[216] Triton B has also been used as catalyst for the reaction of thiols with acrolein and crotonaldehyde[154,217]. The reaction of crotonaldehyde and ethanethiol under the influence of $N(C_2H_5)_3$ gives 3-ethylthiobutanal (yield 60%; exothermic reaction), whereas in CCl_4, in the presence of anhydrous HCl, the product is 1,1-diethylthiobut-2-ene, *i.e.* no addition at the double bond takes place[218]. Alkane- and arene--thiols react with crotonaldehyde and cinnamaldehyde under the influence of a small quantity of sodium dissolved in the thiol[219], and 3-oxopentane-1,5-dithiol reacts in the presence of K_2CO_3; in the latter case the adducts undergo cyclisation with the formation of 2,5-disubstituted 2-propionyltetrahydrothiophenes[173]. Crotonaldehyde slowly adds on H_2S in the presence of Triton B to give chiefly 2-thiodibutyraldehyde[220].

4. Thiylation of αβ-Unsaturated Acids and Their Esters

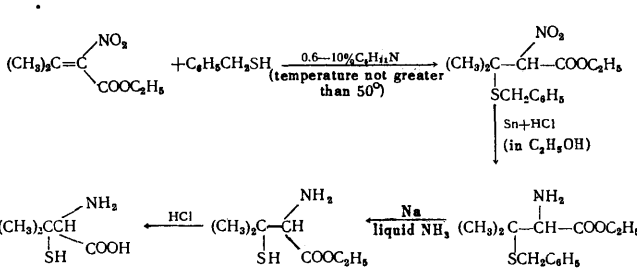
Thiophenol and ethanethiol react with acrylic, cinnamic, and α-phenyl- and *o*-, *m*-, and *p*-nitrocinnamic acids when left to stand for many days in CH_3COOH solution. Under these conditions ethanethiol does not add on to furfuracrylic or α-methylcinnamic acids or to esters of cinnamic acid[221].

The nucleophilic reactions of thiols with αβ-unsaturated acids and esters take place much more readily than the reactions with ketones and aldehydes, but are still exothermic. Piperidine catalyses the addition of thiols to methyl cinnamate[222], and Triton B gives the best yields of β-alkylthiopropionates from ethyl acrylate; a lower yield is obtained in the presence of anhydrous Na_2CO_3 or 2-hydroxyethylammonium hydroxide[154]. Triton B,[163] sodium dissolved in the thiol[168], and $NaOC_2H_5$ [170] have been used for the quantitative addition of alkanethiols to methyl acrylate. 3-Oxopentane-1,5-dithiol reacts readily with aqueous solutions of salts of acrylic and crotonic acids, and with their esters in the presence of K_2CO_3, but does not add on to esters of cinnamic acid or free acids[173]. Adducts are formed by *o*-aminothiophenol with acrylic and other unsaturated acids when the reagents are heated in an atmosphere of CO_2. These readily split off water with the formation of a lactam ring[223]:

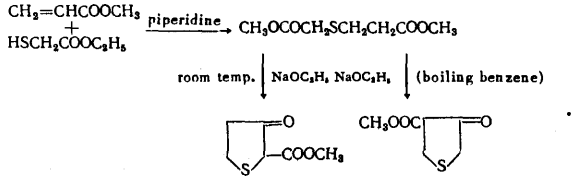


The crystalline dimethylphenylthiopropionic acids obtained in aqueous alkaline solutions from acrylic acid and isomeric thioxylenols[224], and also the 2-benzoyl-1-alkylthiopropionic acids formed under similar conditions from benzoylacrylic acid and various thiols[225], can be used for purposes of identification. β-Acetylacrylic acid reacts with thioglycollic acid in the presence of acidic or basic catalysts, or simply when the reagents are mixed, to give 2-carboxymethylthiolaevulinic acid[226].

The double bond in 2,2-dimethylacrylic acid is less reactive than that in acrylic acid. Thus H_2S reacts with the former to the extent of only 20% after 15 h at 120°, and toluene-ω-thiol to the extent of 50% after 8 h at 100°.[227] In the presence of $N(C_2H_5)_3$ neither the acid nor its esters add on H_2S or ethanethiol[193]. Esters of 1-nitro-2,2-dimethylacrylic acid are much more active in this reaction. The following methods of synthesising "penicillamine", an important intermediate in the synthesis of penicillin, and also a corrosion inhibitor, was described almost simultaneously by a number of workers[228,229]:

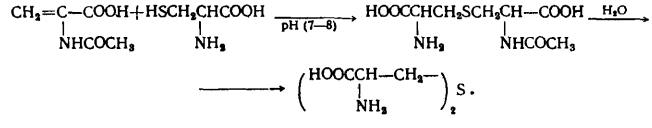


Penicillamine has also been prepared from 2,2-dimethyl--1-acetylaminoacrylic acid by the action of toluene-ω-thiol in the presence of sodium and pyridine (alcoholic medium) with subsequent removal of the benzyl and acetyl groups by sodium in liquid NH_3.[227] Keto-esters of the thiophane series are formed by the addition of esters of thioglycollic acid to esters of acrylic or substituted acrylic acids (catalyst piperidine) with subsequent cyclisation by Dieckmann's method[230,231] or directly, without isolation of the non-cyclic products, by carrying out the reaction in the presence of C_2H_5ONa.[232] The mode of the cyclisation depends on the conditions:

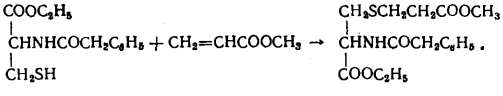


These reactions have been used for the synthesis of biotin[233]. The analogous addition of esters of thioglycollic acid to maleates and fumarates gives esters of thiophane--2,5-dicarboxylic acid[233].

Cysteine adds on to 1-*N*-acetylaminoacrylic acid in boiling aqueous solution at pH 7–8 to form lanthionine:



In this connection it has been suggested that analogous reactions are also possible during the alkaline treatment of wool, where one of the products is lanthionine. Under the same conditions, thioglycollic and thiohydracrylic acids add on quantitatively to acrylic acid[159]. The adducts formed by cysteine with methyl acrylate and benzyloxycarbonylaminoacrylic acid were obtained in an aqueous alkaline medium at pH 7–8 in an atmosphere of H_2.[234] Acylated α-amino-acids and their esters (cysteine hydrochloride and *N*-phenylacetylcysteine) add on instantaneously and quantitatively to esters of acrylic acid in a triethylamine medium which acts simultaneously as catalyst[235]:

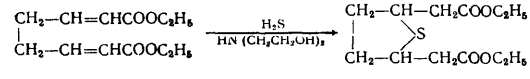


1-Nitro-2,2-dimethylacrylate gives adducts in lower yield under these conditions.

H_2S reacts readily and quantitatively with methyl acrylate in the presence of Triton B to give dimethyl 2-thiodipropionate; the reaction is strongly exothermic[220]. Methyl methacrylate does not add on H_2S, even in the presence of Triton B at 80°–90°, evidently due to steric hindrance by the methyl group[220]. H_2S reacts with butyl crotonate and other esters of αβ-unsaturated acids in the presence of anhydrous alkali metal sulphides to form chiefly the thio--diester and a small quantity of the ester thiol[236].

A number of papers have dealt with the reactions of H_2S and thiols with polybasic αβ-unsaturated acids and their esters. The kinetics of the reaction of maleic acid with thiglycollic acid, cysteine, and glutathione in aqueous alkaline solution at pH 7.4 have been studied[273]. Various esters of carboxymethylmercaptosuccinic acid have been prepared[238].

The reaction of disodium fumarate with other thiols gives crystalline alkyl(aryl)thiosuccinic acids[239]. The addition of RSH (R = alkyl or aryl) to esters of itaconic and aconitic acids is catalysed by anhydrous potassium carbonate at 30°–45°, whereas no addition is observed in the presence of benzoyl peroxide[240]. H_2S reacts smoothly with isopropylidenemalonic acid and its esters[193] with the formation, after decarboxylation, of thioloisovaleric acid. H_2S adds on readily to esters of maleic and fumaric acids at -10° in pyridine[241] or at 70°–80° with catalysis by $N(C_2H_5)_3$, piperidine, and Triton B.[242] The thiopolycarboxylic esters formed are excellent plasticisers for polymers and copolymers based on vinyl chloride. An ester of thiophane-2,5--diacetic acid has been synthesised as follows[243]:



The thiylation of vinylphosphonic acids in the presence of $NaOC_2H_5$ with the formation of the thiols $(RO)_2P(O)CH_2CH_2SH$ and sulphides $(RO)_2P(O)CH_2CH_2SR'$ [244] is a particular case of the more general reaction of "phosphonethylation"[245]. The analogous addition of RSH (R = C_4H_9, $C_{12}H_{25}$) under the influence of metallic sodium has been described[246].

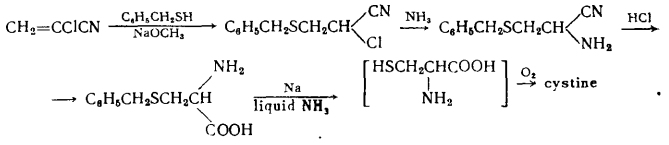
5. Thiylation of αβ-Unsaturated Nitriles†

The cyanoethylation of sulphur compounds also requires catalysis by bases. H_2S is cyanoethylated in the presence of KCN or Na_2S at 60°–80° in butanol[149], but with catalysis by $NaOCH_3$ or quaternary ammonium bases the reaction becomes exothermic[220]. The exclusive product is the dinitrile of thiodipropionic acid, from which plasticisers are readily obtained by hydrolysis followed by esterification. Alkane- and arene-thiols are quantitatively cyanoethylated in the presence of $NaOCH_3$ in dioxan[248]. Thiols, mercaptobenzothiazole, and esters of dithiocarbonic acid react in an aqueous solution of alkali, which acts simultaneously as catalyst and solvent[249], thien-2-ylmethanethiol adds on in the presence of metallic sodium[169], and 3-oxopentane-1,5-dithiol reacts in the presence of K_2CO_3.[173] With catalysis by Triton B, β-thionaphthol gives β-(2-naphthylthio)propionitrile which on saponification readily undergoes cyclisation to benzothiochromanone[250]. The reaction of diethylaminoethanethiol is exothermic and proceeds without catalyst[251]. The cyanoethylation of higher thiols in the presence of $NaOC_2H_5$ has been carried out with the aim of synthesising anti-tuberculosis compounds[252]. Under these conditions, diphenylphosphinodithioic acid gives the physiologically active $(C_6H_5)_2P(S)SCH_2CH_2CN$.[253] β-Alkylthio-acids of the type $RSCH_2CH_2COOH$ and $RSCH_2CH(CH_3)COOH$, which are active antioxidants, are prepared *via* a stage involving cyanoethylation of thiols in the presence of piperidine[254]. In the study of the comparative efficiency of different catalysts with respect to the cyanoethylation of thiophenol by the nitriles R–CH=CHCN [R = CH_3, $(CH_3)_2CH$, $(CH_3)_3C$] the best results were obtained using piperidine (or rather its salt with thiophenol) or a mixture of piperidine and Triton B. The

† Reactions of acrylonitrile described up to 1949 have already been reviewed[247].

latter by itself is a poor catalyst for the addition of thiols to substituted acrylonitriles[255]; this is confirmed by study of the reaction of 1-cyanocyclohexene with thiophenol and toluene-ω-thiol[256]. The yield of adducts obtained from acrylonitrile and various thiols in the presence of piperidine decreases in the order: RS = $C_6H_5S > C_6H_5CH_2S >$ $> HOCH_2CH_2S > t\text{-}C_4H_9S$.[257] The cyanoethylation of esters of thioglycollic acid by substituted acrylonitriles in the presence of $NaOC_2H_5$ has been used in the synthesis of biotin[232]. With catalysis by Triton B, thiols give adducts not only with ω-cyanostyrene[258] but also with *o*- and *p*-cyanostyrenes, which can be regarded as vinylogues of acrylonitrile[259]. Thiols with trialkylsilyl groups in the α-, β-, and γ-positions are readily cyanoethylated with catalysis by traces of $NaOC_2H_5$.[260]

A simple method for the synthesis of (±)-cystine from 1-chloroacrylonitrile and toluene-ω-thiol has been proposed[261]:



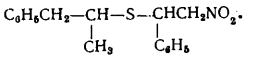
1-Chloro- and 1-bromo-acrylonitriles also react (exothermic reaction) with other alkane- and arene-thiols in the presence of sodium alcoholate in dry benzene[262].

6. Thiylation of $\alpha\beta$-Unsaturated Nitro-Derivatives

Thiols react with α-nitro-olefins in an alkaline medium more readily, and with higher yields, than their oxygen analogues, water and alcohols. Thiolates react with nitropropenes and ω-nitrostyrene in absolute alcohol with external cooling to give β-alkylthionitro-compounds in 50–80% yield, the reactivity decreasing in the order: $C_6H_5SH > C_4H_9SH > CH_3SH$.[263] The addition of thiols to these nitro-olefins proceeds to completion very rapidly in methanol or dioxan at 0°–5° in the presence of metallic sodium[264]. Dinitro-thioethers are formed by the reaction of thiols with an excess of nitro-olefins[265].

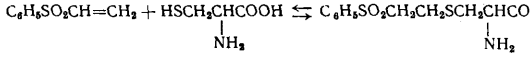
Various β-arylthiophenetylamines have been prepared with the aim of obtaining substances with antibacterial action[266] or substances for the treatment of rheumatoid arthritis and other inflammations[267]. For this purpose, use was made of the exothermic reaction between substituted thiophenols and ω-nitrostyrenes with various substituents in the ring, in the presence of piperidine: the nitro-group was then reduced to the amino-group. The adducts are stable in acid and neutral media but decompose in alkaline media to regenerate the original thiol and nitro-olefin. The passage of dry H_2S into a solution of a nitro-olefin in dioxan, cooled with ice [catalyst $N(C_2H_5)_3$], gives 2-nitroalkyl sulphides which are used as corrosion inhibitors, vulcanisation accelerators, and starting materials for the preparation of polymers of the nylon type[268]. Nitrostyrenes and nitro-olefins also add on H_2S without catalysts at moderate temperatures[264]. A convenient method for the synthesis of β-nitrosulphides related to biotin is based on the exothermic reaction between aldehydes, thiols, and nitroparaffins in the presence of piperidine; in the case of nitromethane and alkanethiols, the intermediate acyclic products are obtained in quantitative yield[269].

The reaction of the optically active 1-phenylpropanethiol or its racemate with ω-nitrostyrene in the presence of piperidine or ascaridole gives a mixture of various diastereoisomeric forms of the sulphide[270]:



7. Thiylation of $\alpha\beta$-Unsaturated Sulphoxides and Sulphones

The high reactivity of $\alpha\beta$-unsaturated sulphones towards thiyl ions was first observed in the case of divinyl sulphone. Kretov[271] ‡ first prepared this compound from bis-2-chloroethyl sulphone and showed that on boiling in the presence of traces of alkali it reacts with thiols to give various bis-2-alkyl(aryl)thioethyl sulphones. Their structure was confirmed by the fact that they were identical with the sulphones of substances previously prepared from bis-2-chloroethyl sulphide and thiolates[273]. Alexander and McCombie[272] showed that H_2S and thiophenol add on to divinyl sulphone in the presence of $NaOCH_3$. The reactivity of divinyl sulphone towards amino and thiyl groups was later studied in detail because of its genetic relationship to bis-2-chloroethyl sulphone, which for some time was considered to be the active metabolite responsible for the toxicity of bis-2-chloroethyl. Later, however, the formation of this sulphone *in vivo* was considered unlikely[274]. In the reactions of cysteins or its hydrochloride with divinyl and phenyl vinyl sulphone in aqueous $NaHCO_3$ solution, the addition involves the thiyl group[275]; at pH ~3, *i.e.* under conditions close to physiological conditions, the reaction is reversible[275,276] [this does not agree with the statements in the original papers (Ed. of Translation)]:



The crystalline adduct $SO_2[CH_2CH_2SCH_2CH(NH_2)COOH]_2$ is recommended for the quantitative determination of divinyl sulphone[274]. The reaction of divinyl sulphone with thiols depends greatly on the pH of the medium. Thus the rate of addition of cysteine is doubled when the pH is changed from 4.4 to 6.2 and the same increase in the rate of addition of 2-mercaptoethanol is observed when the pH is increased from 5.4 to 6.5.[274] In an aqueous solution of cellosolve without catalyst thiophenol adds on to divinyl sulphone at 22° to the extent of 73% in 90 min; when 0.018 mole of $N(C_2H_5)_3$ is added, the reaction becomes exothermic and is complete in 7 min. No reaction takes place without solvent and catalyst. In the presence of a drop of $N(C_2H_5)_3$, 2-mercaptoethanol adds on quantitatively and exothermally, the adduct $SO_2(CH_2CH_2SCH_2CH_2OH)_2$ being stable in alkaline solution[274].

The passage of H_2S into boiling *p*-tolyl vinyl sulphone in the presence of $NaOC_2H_5$ gives $(p\text{-}CH_3C_6H_4SO_2CH_2CH_2)_2S$, and various arenethiols in toluene give compounds of the $p\text{-}CH_3C_6H_4SO_2CH_2CH_2SAr$ series. The reaction of *o*-aminothiophenol involves the mercapto-group, the adduct being

‡ In non-Soviet literature Alexander and McCombie's paper[272], published more than a year later, is usually erroneously cited as the first example.

readily diazotised[151,277]. β-Phenylvinyl *p*-tolyl sulphone adds on thiocresolate at room temperature in ether–benzene solution to form $C_6H_5CH(SC_6H_4CH_3)CH_2SO_2C_6H_4CH_3$.[278] In the presence of traces of $N(C_2H_5)_3$ *p*-tolyl vinyl sulphone adds on thiophenol and *o*-mercaptobenzoic acid[279], and phenyl vinyl sulphone adds on thiocresol, *o*-mercaptobenzoic, and thioglycollic acids[276]. The unsaturated cyclic sulphones benzothiophen dioxide[280] and 2- or 3-sulpholenes (the latter with isomerisation to the 2-sulpholenes) are also thiylated in alkaline media with the formation of β-thiosulphones. The sulpholenes have been used to prepare insecticides, vulcanisation accelerators, etc.[281-283]

In the presence of traces of $N(C_2H_5)_3$ vinyl ethyl sulphone undergoes exothermic reaction with thiophenol, and on heating vinyl methyl sulphone and vinyl ethyl sulphone add on *OO*-dialkyl phosphorothiolothionates with the formation of $RSO_2CH_2CH_2SP(S)(OR)_2$,[284] which has insecticidal action. Thiols add on to methyl propenyl and benzyl propenyl sulphones when boiled with $N(C_2H_5)_3$ in tetrahydrofuran to form $RSO_2CH_2CH(SR'')CH_3$.[144-147] Substances with antibacterial action have been synthesised by the addition of butanethiol to vinyl methyl and vinyl phenyl sulphones by boiling with an alcoholic NaOH solution[285]. It has been shown in our laboratory that Triton B is a particularly convenient catalyst for the quantitative exothermic addition of nucleophilic reagents, especially thiols, to various αβ-unsaturated sulphones (vinyl ethyl sulphone, vinyl dicycloheptenyl sulphone, and 1,4-dialkylsulphonylbutadi-1,3-enes)[164,286,287]. Vinyl ethyl sulphone and liquid H_2S (in the presence of Triton B) in different proportions react to give mixtures of bis-2-ethylsulphonylethyl sulphide and β-ethylsulphonylethanethiol[287]. Also in the presence of Triton B vinyl ethyl and vinyl butyl sulphones give $(C_2H_5O)_2P(S)SCH_2CH_2SO_2R$, which are powerful acaricides[164,289]. Triton B has also been used for the addition of ethanethiol to vinyl ethyl sulphone with the aim of synthesising a new type of antioxidant[288].

There are many fewer data on nucleophilic reactions of thiols with αβ-unsaturated sulphoxides. These reactions are much less vigorous than those of the analogous sulphones. Thus divinyl sulphoxide does not react with thiophenol without catalyst; in the presence of $NaHCO_3$ in aqueous medium the reaction is slower than that of divinyl sulphone, and at high pH values the compound combines with 2-mercaptoethanol[272,274] or cysteine[274,290]. Vinyl ethyl, vinyl *p*-tolyl, and vinyl 8-chloronaphthyl sulphoxides add on *p*-thiocresol on prolonged boiling in the presence of $NaOCH_3$.[151,277] The yields were not given. Vinyl ethyl sulphoxide reacts with *o*-mercaptobenzoic acid in excess aqueous $NaHCO_3$, with cysteine in aqueous medium containing $N(C_2H_5)_3$, and with thioglycollic acid in the presence of $Ba(OH)_2$.[290] The comparative reactivity of unsaturated sulphones and sulphoxides towards thiols in the presence of Triton B was studied in our laboratory. Vinyl ethyl and vinyl butyl sulphoxides undergo exothermic reaction with alkanethiols and thiophenol, but the yield of adducts is lower than in the case of vinyl ethyl sulphone and the quantity of catalyst required and the duration of the reaction are greater, indicating that the nucleophilic character of the C=C bond decreases on going from the sulphone to the sulphoxide[287]. It has been shown that the reaction of ethanethiol with vinyl ethyl sulphoxide gives the β-adduct exclusively[287]. *OO*-Diethyl phosphorothiolothionic acid undergoes exothermic reaction with vinyl ethyl sulphoxide without catalyst, but the yield of acaricidal *OO*-diethyl *S*-(2-ethylsulphinylethyl)phosphorothiolothionate is low and is not increased by the addition of Triton B.[289]

8. Thiylation of Perhalogeno-olefins

Perfluoroethylene reacts readily with various alkane- and arene-thiols in the presence of sodium dioxane, dimethylformamide, or dimethylcellosolve[291]. Trifluorochloroethylene adds on alkanethiols quantitatively at room temperature with catalysis by 0.02% Triton B, 2% $N(C_2H_5)_3$, or 0.05% of the thiolate[292]. The structure of the adducts, with general formula RSC_2F_3ClH, was not proved. Knunyants and Fokin[293] have shown that the same olefin reacts with alkane- and arene-thiols when heated in an autoclave in the presence of powdered KOH for 6 h at 115°–120° to give 60–90% of $RSCF_2-CFClH$, whose structure was proved by the fact that the action of alkali gives $ClFC=CFSR$. Under the same conditions thiols readily add on to tetrafluoro- and *sym*-dichlorofluoro-ethylene[294], and perfluoropropene gives $CF_3CHF-CF_3SR$ in low yield[294]. Less extensively halogenated olefins also add on thiols in position β to the more extensively halogenated group. Thus 1,1,1-trichloropropene reacts with thiophenol, in the presence of elemental sulphur to eliminate the free-radical reaction, giving 1,1,1-trichloromethyl-3-phenylthiopropane[295]. No addition to the double bond takes place when perfluoro- and chlorofluoro--olefins are treated with thiols and excess K_2CO_3. Instead, halogen is partly replaced by SR groups with the formation of a range of monomers containing sulphur and halogen[296].

9. Thiylation of Vinylsilanes

A trialkylsilyl group next to a double bond has been assumed to acquire electron-accepting properties as a result of the interaction of the π electrons of the C=C bond and the *d*-level of the Si.[297] The nucleophilic character of the double bond of vinylsilanes is apparently low, however, since alkanethiols give 2-alkylthioethylsilanes only in low yield on prolonged boiling in the presence of the thiolate[298]. Electrophilic attack also gives β-alkylthio-compounds, for example in the reaction of vinylsilanes with *OO*-dialkyl phosphorothiolothionic acids[299]. On the other hand, allylsilanes add on *OO*-dialkyl phosphorothiolothionic acids in accordance with Markovnikov's rule[260].

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Despite the fact that the above data were obtained under the most varied conditions, so that comparison is difficult, analysis indicates that the ease of nucleophilic thiylation increases in the same sense as the electron-accepting power of the substituent. Thus it decreases on going from vinyl ketones to acids and their esters, and from αβ-unsaturated sulphones to the sulphoxides. The introduction of methyl groups in the position α to the electron--withdrawing group hinders the addition (compare the reactions of H_2S with methyl acrylate and methyl methacrylate), while the introduction of methyl groups in the β-position facilitates the reaction (for example, divinyl ketones add on H_2S chiefly at the alkylated double bond)§. Electron--withdrawing substituents in the α-position facilitate the reaction considerably (compare the reactivities of 2,2-dimethylacrylic acid and its 1-nitro-derivatives). The reactivity of the thiyl ions in these reactions apparently increases with increase in their nucleophilic character (compare the reactions with αβ-unsaturated ketones,

§ In view of this, it is difficult to understand the low reactivity of ββ-dimethylacrylic acid and its esters.

nitriles, and nitro-derivatives), but in this case it is difficult to establish definite correlations, since there are no confirmed data on the change in the nucleophilic character of these ions with change in structure[27]. The reactivity of thiols in these reactions is much higher than that of water or alcohols, in agreement with the nucleophilic character of the corresponding ions.

III. HOMOLYTIC THIYLATION

1. Mechanism and Properties of the Individual Stages of the Chain Process

From the time when Kharasch proposed a free-radical chain mechanism for the anomalous addition of first HBr [22] and then thiols[20], so many data have accumulated on these and other homolytic reactions of olefins in solution that their chain mechanism may be taken as proved, while many of their properties have been fairly well studied[5]. The homolytic addition of a thiyl to an olefin M can be broken down to the following stages:

1. Initiation $RSH \rightarrow RS^{\cdot}$, ($k_1$)
2. Attack $RS^{\cdot} + M \rightarrow A^{\cdot}$, ($k_2$)
3. Chain transfer $A^{\cdot} + RSH \rightarrow AH + RS^{\cdot}$, etc. ($k_3$)

Chain rupture is brought about by recombination

$$RS^{\cdot} + RS^{\cdot} \rightarrow RSSR; \quad A^{\cdot} + A^{\cdot} \rightarrow A_2; \quad A^{\cdot} + RS^{\cdot} \rightarrow ASR.$$

Calculation shows that reactions 2 and 3 are appreciably exothermic, and this leads to rapid propagation of the chain[5]. Its kinetic length is usually high, reaching 10^3 links and above, so that the process is characterised by steady-state kinetics. Successful kinetic studies have been carried out by the sector method[300-304], which makes it possible to find the absolute rate constants of the stages. The overall rate of the process is usually determined by the rate of chain transfer. Thus the values found for the reaction of butanethiol with pent-1-ene are $k_2 = 7 \times 10^6$ litre mole^{-1} $\times$ $\times$ sec^{-1} and $k_3 = 1.4 \times 10^6$ litre mole^{-1} sec^{-1}; [301] for the reaction of thiophenol with styrene, the values of k_2 and k_3 are 2×10^7 and 3×10^3 litre mole^{-1} sec^{-1} respectively[303].

Reactions 1 and 3 are similar in that they involve homolytic rupture of an S–H bond[5,300,305-307]. One method which has been used to compare the ease of this fission involves the reaction of different thiyl compounds with dinitropicrylhydrazyl. This method has shown that the rate of removal of H$^{\cdot}$ decreases by a factor of about 20 in the series n-$C_6H_{11}SH$ > n-C_4H_9SH > iso-C_4H_9SH > t-C_4H_9SH, whereas the activation energy remains almost unchanged[308]. The ease of removal of H$^{\cdot}$ from thiophenol is greater by a factor of several hundred than the ease of removal from butanethiol[303]. Another criterion which can be used to estimate the ease of homolytic rupture of an S–H bond is the rate of oxidation of different thiols under standard conditions. Different authors have obtained the following almost identical series of thiols arranged in decreasing order of rate of oxidation: ArSH > $HOCOCH_2SH$ > RCH_2SH > > RR'CHSH > RR'R"CSH¶; [306] C_6H_5SH > $HOCOCH_2SH$ > > CH_3SH, $C_{18}H_{37}SH$ > t-C_4H_9SH, t-$C_{12}H_{25}SH$; [307] ArSH (Ar = C_6H_5, $C_6H_5CH_2$) > RCH_2SH (R = CH_3, C_3H_7) > t-thiols (C_4H_9) > mercaptobenzothiazole[309].

¶ The rate of addition of thiols to styrene changes in the same order[306].

The acidity of the thiols changes in approximately the same order (Table 1), so that the most strongly acidic thiols are also the best donors of radicals. Similar relationships were also obtained by a method based on the determination of the constants for chain transfer by thiols in the polymerisation of styrene[5,310]: $C_6H_5SH \gg C_2H_5OCOCH_2SH >$ > primary n-AlkSH (Alk = C_4H_9, $C_2H_5OCH_2CH_2CH_2$, C_5H_{11}, $C_{12}H_{25}$, C_8H_{17}) > t-AlkSH (Alk = C_4H_9, C_8H_{17}) > mercaptobenzothiazole.

Although the overall rate of the addition reaction, as shown above, is determined by the rate of transfer, comparison of data on the reactions of different thiols with the same olefin, or of different olefins with the same thiol, can be used to estimate the comparative ease of attack, on which the possibility of combining with a radical depends. Interesting semiquantitative results were obtained by the method of competing reactions. The available data show good agreement with the theory of the electron-accepting character of the thiyl radical. Electron-donating groups in the radical itself decrease its reactivity towards a double bond (the reactivity decreases, for example, from primary to tertiary radicals[5]). On the other hand, the presence of electron-withdrawing groups in the thiol increases the reactivity of the radical†; the reactivity increases, for example, in the order iso-$C_5H_{11}SH$ < $HOCOCH_2SH$ < < C_6H_5SH < CH_3COSH < $CH_2ClCOSH$ < $CHCl_2COSH$ < < CCl_3COSH.[80,311] Thioglycollic acid, its esters, and thiols with β-substituents, such as 2-mercaptoethanol, ethanedithiol, and bis-2-mercaptoethyl sulphide[312] are very reactive. On the other hand, olefins with electron-withdrawing substituents have a low reactivity towards thiyl radicals; for example, vinyl ethyl sulphone and sulphoxide[164,237] add on thiophenol very slowly at 20°–60° in the presence of azoisobutyrodinitrile. The method of competing reactions has shown that the $\dot{S}CH_2COOH$ radical combines much more readily with α-methylstyrenes with electron-donating groups (p-CH_3O, CH_3) in the nucleus, than with unsubstituted α-methylstyrene or with p-fluoromethylstyrene[313]. The same method has been used to determine the relative reactivity of the dodecanethiyl radical towards various compounds containing a double bond, using oct-1-ene as standard[314]. The observed relationships (Table 2) in general confirmed the increase in the rate of reaction of radicals with olefins having electron-donating substituents and the decrease in the rate of reaction with olefins having electron-accepting substituents. The method of competing reactions has also shown that the C = C bond in the conjugated bicycloheptene is approximately 45 times more reactive towards the p-thiocresyl radical than the double bond in cyclohexene[315].

The thiyl radical, like other free radicals[316], always attacks the terminal carbon atom of a vinyl double bond. It is assumed that this mode of addition is due to the lower activation energy necessary for the formation of a secondary radical during attack[317]. Similar explanations have been put forward for the fact that the rate of attack by thiyl radicals on terminal C = C bonds is approximately 50 times that on internal double bonds, while the corresponding rate

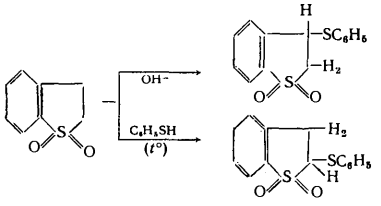
† Thiyls with electron-withdrawing groups are generally also stronger acids (Table 1), although there are exceptions to this rule: for example, the values of K_a for thioglycollic acid and alkanethiols are of the same order of magnitude. It is quite clear, however, that the high activity of these thiols in homolytic addition reactions cannot depend on the ease of removal of a proton, as was previously assumed[1,80,311].

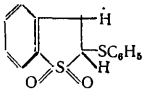
TABLE 2. The relative reactivity (a) of olefins towards dodecanethiol (60°, 0.2% azoisobutyrodinitrile)[314].

Olefin	a	Olefin	a
Styrene	17±3	Allylbenzene	0.99±0.08
β-Methylstyrene	5.5 ±0.4	Vinyl acetate	0.82±0.04
Vinyl butyl ether	3.9 ±0.4	Allyl chloride	0.72±0.04
Methyl methacrylate	2.4 ±0.2	Cyclopentene	0.64±0.04
Methyl acrylate	2.04±0.2	Allyl acetate	0.59±0.06
Allyl alcohol	1.5 ±0.15	Allyl cyanide	0.37±0.05
2-Methylbut-1-ene	1.2 ±0.08	Cyclohexene	0.25±0.15
Oct-1-ene	1.00 (stand.)	*cis*-Dichloroethylene	>0.2

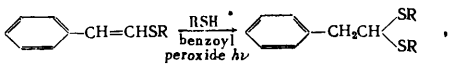
for conjugated double bonds (in styrene for example) is 100 times that for isolated and terminal double bonds[300]. According to other data[314], however, the factor is much smaller in the latter case, being about 20.

The question of the orientation of a radical in its reactions with compounds containing an internal double bond is much more complex. Thus thioacetic acid reacts with alkenes RCH=CHR′ to give an approximately equimolar mixture of adducts, whose composition is not influenced significantly by the structure of the alkyl groups[318]. In other examples, however, the orientation is determined by the possibility of formation of a more favourable radical. It has been found, for example, that the mode of addition of thiophenol to benzothiophen dioxide on heating is different from that for basic catalysis[319]:



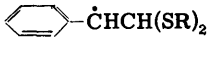
due to the greater stability of the radical  .

In this connection, however, it is difficult to understand why the addition of alkanethiols to benzothiophen dioxide and the addition of thiophenol to the sulphone $C_6H_5CH=CHSO_2C_6H_4CH_3$-*p* take place only in the position β to the sulphonyl group both with catalysis by alkali and on heating[319]. The homolytic addition of thioglycollic acid[320] and ethanethiol[321] to the corresponding 1-alkylthio-2-phenylethylenes obtained from phenylacetylene and a thiol takes place according to the equation



where R = C_2H_5 or CH_2COOH, whereas 1-alkylthio- and 3,3-dimethylbut-1-enes give adducts with 1,2-disposition of the thiyls[322]:

$$(CH_3)_3C{-}CH{=}CHSR \xrightarrow[\text{azoisobutyrodinitrile}]{RSH} (CH_3)_3CCH(SR){-}CH_2SR.$$

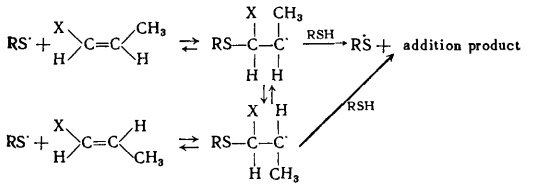
It is evident that as far as electron delocalisation is concerned, the radical  is more favourable in the first case and the radical $(CH_3)_3CCH(SR)\dot{C}HSR$ is more favourable in the second case.

Kinetic studies have revealed that attack on the C=C bond by thiyl radicals is reversible in both the gaseous and liquid phases[302-304].

This reversibility is possibly due to the formation of an unstable cyclic complex of the radical RS· with the C=C bond of the olefin[302]. Since, however, the stereochemical data (see below) indicate that "classical" radicals, and not π-complexes or cyclic complexes, take part in the homolytic reaction, it appears more correct to assume that equilibrium is established between the formation and dissociation of a complex radical[5]:

$$R\dot{S} + CH_2{=}CHR' \rightleftarrows RSCH_2\dot{C}HR'.$$

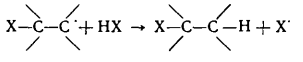
The reversibility of this reaction may be proved experimentally for systems for which the rate of transfer is comparatively low. Thus tihyl radicals produce rapid *cis–trans* isomerisation of but-2-enes[303,314] and 2-chlorobut-2-ene:[323]



where X = CH_3, Cl; R = CH_3, C_6H_5, CH_3CO. It has been found that in the reaction of methanethiol with but-2-ene (initiator azoisobutyrodinitrile) the rate constant for the formation of *trans*-butene from the complex radical is 80 times greater, and that for *cis*-butene 20 times greater, than the rate constant for the conversion of this radical to the addition product[314]. A method has been proposed for the modification of rubbers, based on the *cis–trans* isomerisation of polyisoprene chains by treatment with thiols or thio-acids on the rollers[324].

2. Stereochemical Data

The formation of the C–H bond in the act of chain transfer usually takes place in the *trans*-position relative to the C–X bond produced previously in attack by the radical X:

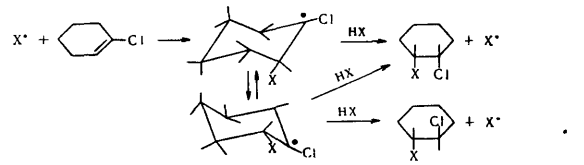


(the "*trans*-addition" rule).

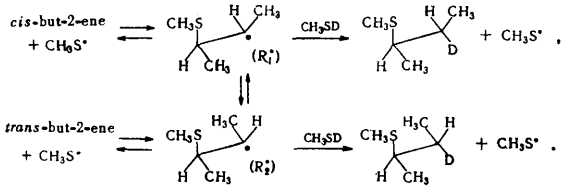
Exclusive *trans*-addition (> 99.5%) was observed in the homolytic addition of HBr to 1-bromo- and 1-chloro-cyclohexenes[325,326], and the reaction remained stereoselective for other cyclohalogenoalk-1-enes and methylcycloalk-1-enes with five- and seven-membered rings[327,328]. The thiylation of 1-chlorocyclohexene, initiated photochemically or in the presence of peroxide, also yields predominantly the product of *trans*-addition (*i.e.* *cis*-2-chlorocyclohexyl sulphide or the thiol), but the stereoselectivity decreases in the order $C_6H_5SH > H_2S > CH_3COSH$.[329] With photochemical initiation, thioacetic acid adds on to 1-methylcyclohexene to give 85% of the *cis*-adduct and 15% of the *trans*-adduct, and in the case of addition to 1-methylcyclopentene the corresponding proportions are 70% and 30% respectively. The addition of thiophenol also takes place predominantly according to the *trans*-scheme[330]; on irradiation by ultraviolet light, thiophenol, *p*-chlorothiophenol, and *p*-thiocresol react with 1-chlorocyclohexene

to give *cis*-2-chlorocyclohexyl sulphides[331], and thioacetic acid and 1-acetoxycyclohexene react in sunlight to give *cis*-1-acetoxyacetylthiocyclohexene[332].

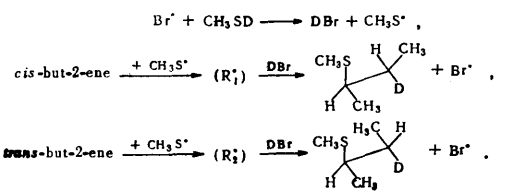
All these facts are readily explained if it is assumed that attack produces radicals in which the substituent lies in the axial position, creating conditions which are sterically more favourable for the formation of products with the *cis*-structure on collision with HX. For complete stereospecificity, however, the act of transfer should take place before conformational equilibrium is attained, since a radical with a second substituent in the equatorial position can form both isomeric products with equal probability[329].



A high stereoselectivity may be expected if the life-time of the intermediate radical is very low. For this the addend should either be a very effective carrier (this in the case with HBr) or be present in considerable excess, in order to accelerate the stabilisation of the radical as the final product. The free radicals formed in the reactions of olefins with an open chain are capable of even more rapid spatial isomerisation as a result of free rotation. Thus, although stereospecific *trans*-addition could be achieved in the photochemical hydrobromination of *cis*- and *trans*-1-halogenobut-2-enes at -80° [326,333], the addition of thiols, which are poorer carriers, to these compounds was found to be non-stereoselective. Thioacetic acid reacts with both *cis*- and *trans*-chlorobut-2-enes (on irradiation by a mercury lamp at -78° in the presence of t-butyl peroxide) to give a mixture of the *erythro*- and *threo*-forms of 2-acetylthio-3-chlorobutanes, with the latter predominating[334]. The photo-addition of CH_3SD to *cis*- and *trans*-but-2-enes at -70° also gives a mixture of *erythro*- and *threo*-3-deutero-2-methylthiobutanes. These facts, which are not understandable from the viewpoint of the theory of intermediate cyclic complex formation, can be explained if we assume the existence of an "open" radical capable of undergoing isomerisation before transfer can take place[334]:



Stereospecific addition in the latter system has been carried out in the presence of DBr, which is such an efficient carrier that it is able to react with radicals before they isomerise[334].

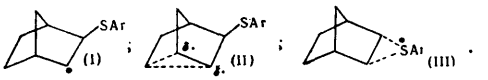


If transfer does not take place sufficiently rapidly, the radical A$^{\bullet}$ may undergo more extensive structural isomerisation. A characteristic example of this change is the transfer of halogen atoms along the chain of a polyhalogenoalkene during its photo-initiated reaction with a thiol, observed by Nesmeyanov *et al.*[295]:

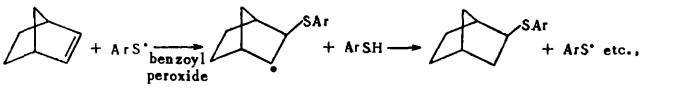
$$CCl_3CH{=}CH_2 + RS^{\bullet} \rightarrow CCl_3\dot{C}HCH_2SR \rightarrow \dot{C}Cl_2CHClCH_2SH \xrightarrow{RSH} \rightarrow CHCl_2CHClCH_2SR + RS^{\bullet}.$$

Isomerisation (with the transfer of phenyl) of the radical produced from 3,3-diphenylbutene does not take place during the addition of butanethiol or thioacetic acid to the compound, but is observed in the reaction with n-butyraldehyde; the removal of H$^{\bullet}$ from the latter is 4×10^4 times more difficult than its removal from a thiol[335].

The stereochemical data obtained for reactions involving bridged polycyclic hydrocarbons show that in this case also the reaction takes place *via* the formation of classical radicals (of type I) rather than "mesomeric" radicals (of type II) or cyclic complexes (of type III).[336]



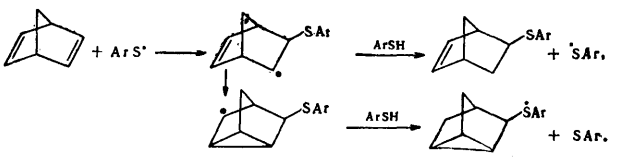
Homolytic addition to these systems therefore differs significantly from the heterolytic reactions, which are usually accompanied by nor-tricyclenic rearrangement of the cation[337]. Bicyclo[2,2,1]heptene undergoes exothermic reaction with *p*-thiocresol to give pure *exo*-*p*-tolyl nor-bornyl sulphide in 85% yield[315].



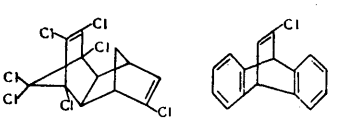
where Ar = *p*-$CH_3C_6H_4$.

Substituted bicycloheptenes react with thiophenol in analogous fashion[338].

The reaction of thiophenol or thiocresol with bicycloheptadiene gives mixtures of *exo*-5-nor-bornen-2-yl aryl sulphide and 3-nor-tricyclyl aryl sulphide, the relative yield of the products of the first type being greater, the higher the concentration of thiol in the reaction mixture[339]. From this it follows that the radical formed may (a) add on the hydrogen atom of the thiol in the act of transfer, or (b) isomerise to the nor-tricyclenyl radical, which is subsequently stabilised as the "homo-conjugate" addition product. Excess thiol favours process (a).



The thiocresyl radical has also been added on to more complex bridged systems: 6-chloroaldrin and 11-chloro-9,10-dihydro-9,10-ethenoanthracene[340].



It was found that the resulting adducts show chiefly *trans*-disposition of the halogen and thiyl, *i.e.* they are produced according to the *cis*-mechanism. This is due to the general tendency of bridged compounds to favour the *exo*-introduction of groups: chain transfer may take place predominantly when the thiol approaches the already-formed radical from the *exo*-direction.

3. Telomerisation in the Presence of Thiols

Thiylation accompanied by telomerisation, in the case of alkenes, is observed only under specially selected conditions. Thus a pressure of the order of 700–900 atm facilitates the formation of telomers from H_2S and ethylene[341]. Telomerisation is also favoured by the presence of excess alkene. At a very low thiol concentration the process observed is not addition but polymerisation, initiated or regulated by the thiol. Consideration of these very important processes is outside the scope of the present review.

Olefins with an activated double bond, which usually have a comparatively high reactivity towards their "own" free radical, may, however, give telomers even at equimolar reagent ratios, particularly in the presence of a slight excess of olefin. Esters of acrylic and 1-alkaneacrylic acids in mixtures with arenethiols react on irradiation by a mercury lamp to give, in addition to the 1 : 1 adducts, dimeric acrylates containing one molecule of thiol. These compounds have been recommended for use as plasticisers[342]. Kharasch and Fuchs[163] studied the reaction of methyl acrylate with thiols in the presence of ascaridol and isolated a number of telomeric adducts containing two, three, and more molecules of acrylate:

$$CH_2{=}CHCOOCH_3 + RS^{\cdot} \rightarrow RSCH_2\dot{C}HCOOCH_3,$$
$$RSCH_2\dot{C}HCOOCH_3 + RSH \rightarrow RSCH_2CH_2COOCH_3 + RS^{\cdot},$$
$$RSCH_2\dot{C}HCOOCH_3 + CH_2{=}CHCOOCH_3 \rightarrow RSCH_2CH(CH_2\dot{C}HCOOCH_3)COOCH_3, \text{ etc.}$$

The reaction of butyl acrylate with alkanethiols containing 10–18 C atoms (at a ratio of 10 : 1) gives viscous polymeric adducts which can be used as oil additives[343]. Telomers are also obtained from ethyl acrylate and dodecanethiol under the influence of benzoyl peroxide at 100°–240° [344] and from vinyl methyl ketone and thiols on illumination (λ = 3600 Å), with or without azoisobutyronitrile[345]. In the reaction of various thiols with styrene the ratios of the quantities of the 1 : 1 adducts and telomers formed depend on the transfer constant for the given thiol. Thioglycollic acid and styrene in equimolar mixtures give chiefly the mono-adduct; propanethiol gives, in addition to the mono-adduct, considerable quantities of the 1 : 2, 1 : 3, and higher adducts; and t-butanethiol gives a small quantity of the mono-adduct, higher telomers predominating[305].

4. Coupled Addition of Thiols and Oxygen

A process which often competes with the transfer reaction is the reaction of $A^{\cdot}$ with peroxides or oxygen present in the reaction medium: $A^{\cdot} + O_2 \rightarrow A{-}O{-}O^{\cdot}$.

The formation of stable peroxide radicals explains the retardation of the addition of thiyls to oxygen and peroxides, observed in some systems, and also the inhibition of polymerisation processes initiated by a thiol[306]. Kharasch[306] has shown that if the reaction between olefin and thiol is carried out in the presence of excess oxygen, coupled addition takes place, leading finally to the formation of a mixture of the two racemic forms of the β-hydroxy sulphoxides:

$$RS^{\cdot} + R'CH{=}CH_2 \rightarrow RSCH_2\dot{C}HR',$$
$$RSCH_2\dot{C}HR' + O_2 \rightarrow RSCH_2CH(O{-}O^{\cdot})R',$$
$$RSCH_2CHR' + RSH \rightarrow RSCH_2CHR'(O{-}O^{\cdot}) + RS^{\cdot},$$
$$RSCH_2CHR'(O{-}O^{\cdot}) \rightarrow RSCH_2CHR'(OOH),$$

and (or):

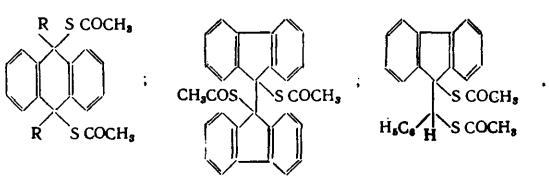
$$RSCH_2\dot{C}HR' \rightarrow RSCH_2CHR'(O{-}O^{\cdot}),$$
$$RSCH_2CHR'(O{-}O^{\cdot}) + RSH \rightarrow RSCH_2CHR'(OH) + RS^{\cdot}.$$

The coupled oxidation of styrene and primary thiols does not require additional catalysts: with t-butanethiol the reaction takes place only in the presence of a redox system (isopropylbenzene hydroperoxide–$FeCl_2$).[306]

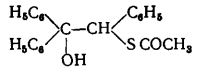
A number of examples of the oxidative addition of thiols to olefins have been given in patents[346,347]. Styrene and toluene-ω-thiol in the presence of benzoyl peroxide in an atmosphere of CO_2 give 85% of the mono-adduct and 15% of the di-adduct $C_6H_5(CH_2)_2(C_6H_5)CHCH_2SCH_2C_6H_5$, but in an atmosphere of oxygen $C_6H_5CH(OH)CH_2SOCH_2C_6H_5$ is formed[348].

Recently, Kharasch's mechanism has been confirmed by direct synthetic experiments in which the intermediate peroxides, previously hypothetical, were isolated. In the coupled oxidation of indene and thiophenol at room temperature, it has been possible to determine titrimetrically up to 70% of the hydroperoxide; however, this was not isolated[349]. In the action of air on mixtures of various arenethiols with such reactive olefins as styrene, methylstyrene, and indene dissolved in hydrocarbons at 0°, it has been possible to isolate the intermediate compounds ArSCH(R)CR'R"OOH and to study their rearrangement to the corresponding ArSOCH(R)CR'R"OH. The hydroperoxide obtained from indene and 2-thionaphthol was found to be so stable that it could be purified by recrystallisation (m.p. 70°). These reactions are responsible for the rapid peroxidation of cracking-distillates of the kerosene type containing thiols and olefins, and also for the loss of stability by motor fuels[350]. Reactions involving the oxidative addition of various alkane- and arene-thiols to styrene, *p*-substituted styrenes, methyl acrylate and crotonate, acrylo- and methacrylo-nitriles, methyl vinyl ketone, and cyclohexene have been described. These reactions are catalysed by Cl^- ions, usually provided by $(C_4H_9)_2NH.HCl$. A mechanism explaining this catalysis has been proposed[351,352].

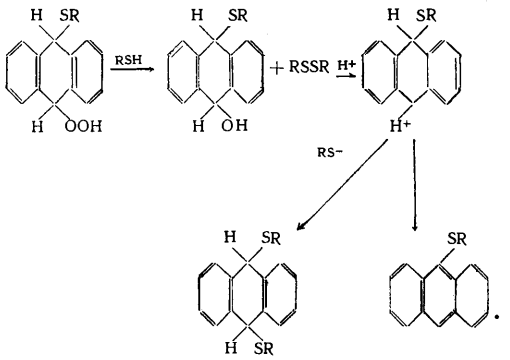
Coupled olefin oxidation reactions include the addition, discovered by Mikhailov and Blokhina, of thioacetic acid to anthracenes and certain polyarylated ethylenes. This reaction takes place only in an atmosphere of oxygen. Of the 9,10-disubstituted anthracenes[353], dibiphenylethylene [1,2-difluoren-9'-yl ethylene (Ed. of Translation)] and benzylidenefluorene[354] gave chiefly the dithioloacetates:



Triphenylethylene gave the hydroxy-thioloacetate:



Thiobenzoic acid reacts with anthracenes in analogous fashion[355]. It is suggested that these reactions take place, as in Kharasch's mechanism, *via* the formation of a hydroperoxide which reacts further as follows‡ [355]:



The biological importance of these reactions has been emphasised[355].

Examples of the coupled addition of thiyls and carbon monoxide to olefins are also known. Thiols R'SH and alkenes $CH_2=CHR$ under a CO pressure of up to 3000 atm in the presence of peroxides at 100°–110° gave chiefly the aldehydes $R'SCH_2CHRCHO$ by the reaction of the radical A• with CO. Under the same conditions H_2S and ethylene gave $C_2H_5SCH_2CH(SC_2H_5)_2$ and $(C_2H_5)_2S$. [356]

5. Application of Homolytic Thiylation Reactions in Organic Synthesis

Syntheses based on the use of homolytic thiylation cover almost all classes of olefinic compounds and thiyls. The number of papers devoted to these reactions is so great that it is difficult to guarantee an exhaustive review. In this section the material is grouped somewhat arbitrarily according to the reactions of the most widely used thiyls or definite groups of olefins and according to the methods of initiation. The addition of H_2S is considered in a separate paragraph.

a. Initiation conditions. Various methods are used for the initiation of free-radical thiylation. Sufficiently active thiols add on "spontaneously" with catalysis by the small quantities of peroxides present in the original materials or by atmospheric oxygen. Such reactions are often exothermic but sometimes require heat. The efficiency of thermal initiation is increased by adding catalytic quantities of peroxides, azo-compounds, and other initiators. In the presence of these additives the mechanism of initiation involves essentially oxidation:

$$R'OOR' \xrightarrow{t^\circ} 2R'O^\bullet;\quad R'O^\bullet + RSH \rightarrow RS^\bullet + R'OH,$$
$$(R'O^\bullet + CH_2=CHR'' \rightarrow R'OCH_2\dot{C}HR'' \xrightarrow{RSH} R'OCH_2CH_2R'' + RS^\bullet),$$
$$R'_3CN{=}NCR'_3 \xrightarrow[t^\circ]{} 2R'_3C^\bullet + N_2;\quad R'_3C^\bullet + RSH \rightarrow RS^\bullet + R'_3CH$$

(reaction between $R'_3\dot{C}$ and $CH_2=CHR''$ is also possible).

‡ A slightly different mechanism was proposed by Mikhailov and Blokhina[353,354].

Initially, the importance attached to the part played by peroxides was so great that the chief characteristic of a free-radical reaction was assumed to be its initiation by peroxides and inhibition by anti-oxidants. At the present time, however, there are many examples of free-radical addition reactions to which these criteria do not apply: organic peroxides have a low efficiency, or even bring about inhibition, and the same is true of oxygen. Detailed study of the process makes it possible to establish the reasons for these anomalies. Sometimes the peroxide combined rapidly with the olefin and is used up by a non-chain mechanism, and in other cases A• is apparently oxidised readily to a stable peroxy-radical A–O–O•, interrupting the normal course of the addition. In these cases, good results are obtained by using redox systems, removing oxygen or the undesirable peroxides from the reaction medium, and initiating with azo-compounds. Thus benzoyl peroxide, dihydroxypentane peroxide, and ascaridol do not bring about the addition of ethanethiol to cetene (hexadecene) (30°, 5 h), and the effect of diethyl peroxide, tetralin, or cetene itself is slight (yield of adduct 6–15%). Under the same conditions, however, a 94% yield is achieved by the combined action of ascaridol and $FeCl_2$. [357]

Oct-1-ene[358] and limonene[79] containing peroxides react with thioglycollic acid with difficulty, but after removal of the peroxides, exothermic addition takes place in the presence of atmospheric oxygen. The anomalous addition of H_2S to vinyl ethers is inhibited completely by atmospheric oxygen or benzoyl peroxide but can be carried out with good yield by catalysis with traces of oxygen or by the action of azoisobutyrodinitrile[54,57,58].

An unusual example of initiation is that described by Mikhailov and Tutorskaya[359] for the addition of thiols to allyl compounds of boron. This gives anomalous products, although the reaction appears to have been carried out in an oxygen-free medium:

$$CH_2=CH-CH_2B(SC_2H_5)_2 \xrightarrow{C_2H_5SH} C_2H_5SCH_2CH_2CH_2B(SC_2H_5)_2,$$
$$CH_2=CH-CH_2B(OC_4H_9)_2 \xrightarrow{C_2H_5SH} C_2H_5SCH_2CH_2CH_2B(OC_4H_9)_2.$$

In this case the initiators are apparently boron-containing free radicals, formed from trialkylboron and traces of O_2 present in the original materials. It is known that these radicals bring about the active polymerisation of many monomers in catalysis by boron compounds[360].

A particularly widespread method is that based on the photolysis of a thiyl compound[361]: $RSH \xrightarrow{h\nu} RS^\bullet + H^\bullet$, which can be carried out under very mild conditions, often at low temperatures of the order of -80°. In photo-addition oxygen can also play a double role as promoter and inhibitor. For example, the best yield of the adduct formed by methanethiol and allyl alcohol is obtained on illumination by sunlight in the presence of $Hg(SCH_3)_2$ and O_2, [362] whereas traces of O_2 inhibit the addition of thiols to olefins, brought about by illumination with ultraviolet light in the presence of azoisobutyrodinitrile[300,301] or initiated by X- or γ-rays[363].

b. Addition of thioacetic acid. In the reactions studied one of the most widely-used thiyls is thioacetic acid (TAA). This is due not only to its high reactivity, but also to the extensive synthetic possibilities opened up by its use. The β-acetylthio-compounds formed in the reaction of TAA with olefins readily undergo alcoholysis in alkaline or acid medium, and this is a convenient method for preparing substituted thiols[364]:

$$XCH{=}CH_2 + CH_3COSH \rightarrow XCH_2CH_2SCOCH_3 \rightarrow XCH_2CH_2SH.$$

TAA undergoes exothermic reaction with styrene[15] and adds on quantitatively to $\alpha\beta$-unsaturated monobasic and polybasic acids. Hydrolysis of the products gives various mercapto-acids or thio-lactones[365]. The reaction with styrene in the presence of atmospheric oxygen was so vigorous that it was not inhibited by diphenylamine and was even accelerated when hydroquinone was added[332]. The reaction with allyl chloride required heat[366]. A method has been developed for synthesising cyclohexanethiol, based on the exothermic addition of TAA or thiobenzoic acid to cyclohexene; from the preparative viewpoint, the synthesis *via* the acetylthio-derivatives is more convenient[367]. TAA and chlorothioacetic acid add on vigorously to model hydrocarbons and rubbers, the reactivity decreasing in the order: cyclohexene > methylcyclohexene > dihydromyrcene > > squalene > natural rubber, and increasing with increase in the degree of chlorination of the thio-acids[311,368]. The elastomers from natural rubber had an elementary unit with structure $(-CH_2CH(CH_3)CH(SCOR)CH_2-)$, gave the corresponding macromolecular thiol on hydrolysis, and, particularly in the case where R = CCl_3, had a high stability towards solvents, while retaining their elasticity[311,368].

The addition of TAA to $\alpha\beta$-unsaturated acids and aldehydes has been used as a stage in the synthesis of mercapto-amino-acids. Thus *NS*-diacetylcysteine is obtained from TAA and *N*-acetylaminoacrylic acid[369-372] and penicillamine is obtained from 2,2-dimethyl-1-acetylaminoacrylic acid[373].

TAA undergoes exothermic reaction with acrolein and its homologues[210], but this reaction has been found to be less convenient for the synthesis of *S*-substituted 1-amino--2-mercaptopropionic acid than the method described above (see Section II. 3)[210,215]. TAA reacts with a mixture of an unsaturated aldehyde and urea or acetamide[374]. TAA has also been used in the synthesis of water-soluble thiols[375] and dithiols of the BAL (2,3-dimercaptopropanol) type[376]:

$$CH_2{=}CHCOOCH_3 + CH_3COSH \xrightarrow[20\text{ h, room temp.}]{} CH_3COSCH_2CH_2COOCH_3 \rightarrow HSCH_2CH_2COOH,$$

$$\begin{matrix} CHCOOC_2H_5 \\ \| \\ CHCOOC_2H_5 \end{matrix} + CH_3COSH \xrightarrow[24\text{ h, }100^\circ]{} CH_3COSCHCOOC_2H_5 \longrightarrow \begin{matrix} HSCHCOOH, \\ | \\ CH_2COOH \end{matrix}$$
$$\qquad\qquad\qquad

The reaction of TGA with unsaturated acids and natural unsaturated oils[390,391] and mixtures of alkenes of the type present in petroleum fractions[358] or peat tar[392] have been studied with the aim of developing methods for the analysis of these substances. The *S*-alkylthioglycollic acids obtained from C_7-C_{11} alkenes, and the corresponding alkanesulphinyl(sulphonyl)acetic acids have been proposed for identification purposes[392]. The crystalline products of the addition of TGA to terpenoid hydrocarbons may be used for the same purpose[79].

Data on the reaction of TGA with natural rubber are contradictory. Holmberg[393] has stated that rubber slowly swells and dissolves in TGA, which is added on to the rubber; Japanese authors have prepared an adduct of composition $(C_5H_8)_{10}(HSCH_2COOH)_5$ by the action of TGA on a 5% solution of rubber in benzene[394]. Cunneen found, however, that TGA does not add on to rubber, either in the presence of peroxides or on prolonged irradiation with ultraviolet light[80,368,395]. The same author found that cyclohexene, dihydromyrcene, and 1-methylcyclohexene containing peroxides undergo exothermic reaction with TGA and that the adducts have exclusively the anomalous structure; this was proved rigorously for the case of methylcyclohexene[368]. The copper salt of the acid formed when TGA is mixed with dicyclopentadiene has fungicidal activity[85]. TGA adds on to unsaturated long-chain aliphatic acids and esters[396] in the presence of lauryl peroxide on irradiation by a mercury lamp. The reaction must be carried out with an excess of freshly-distilled TGA.[397] The reaction with thioglycollic acid proceeds smoothly in the presence of peroxide and is inhibited by hydroquinone[398].

$$CH_2{=}CHCH_2SCH_2COOH + HSCH_2COOH \rightarrow CH_2(CH_2CH_2SCH_2COOH)_2.$$

The anomalous addition of ethyl thioglycollate to vinyl and allyl lactams in the presence of azoisobutyrodinitrile was more vigorous than the same reaction with alkanethiols. The adducts showed considerable activity as precursors in the synthesis of penicillins when added to the culture medium of the fungus *Penicillium chrysogenum*[399].

d. Addition of arenethiols. Arenethiols and toluene-ω-thiol are among the most reactive thiyls. The spontaneous anomalous addition of thiophenol to styrene was noted by Posner[13]. The reaction is accelerated by the action of light[17]; for addition to lower alkenes, prolonged heating is required. Toluene-ω-thiol and toluene-*p*-thiol add on to αβ-unsaturated ketones at 100°.[222] The peroxide effect has been observed in the addition of thiophenol, thiocresol, thionaphthol, and higher thiols and dithiols to alkenes (propene, butene, and linear alkenes of the pentadecene type)[19]. An attempt to use the anomalous adducts formed by 4-mercaptobiphenyl with alkenes for identification purposes was unsuccessful, since the melting points of the alkyl biphenylyl sulphides and sulphones corresponding to homologous hydrocarbons were found to be too close[400]. In the study of the reactions of different thiols with cyclohexene it was established that the most reactive, after TAA and TGA, were thiophenol and toluene-ω-thiol, which after 25 h in sunlight gave 65% and 75% of adduct respectively, whereas to achieve the same yield with (±)-mercaptosuccinic acid, irradiation for 117 h by light with a wavelength of 3600 Å was required[367]. Analogous relationships were observed in the study of the reaction of thiols with cyclohexene, methylcyclohexene, dihydromyrcene, and rubber[80,311], and also with 2-vinylpyridine[401]. Thiocresol adds on to 2-methyl-5-vinylpyridine on heating[402], and the reaction of toluene-ω-thiol with crotonic acid, crotonaldehyde, and allyl alcohol with formation of the anomalous adducts takes place readily in the presence of ascaridol[155]. Arenethiols have been added on to the exocyclic double bond of 2-arylmethyleneindanediones[403] or 2-arylmethylene-3-(2*H*)-thianaphthenone 1,1-dioxides[404] on heating for a short time without catalyst; thiophenol reacts with benzylidenephenylmethylpyrazolone in the cold[405]. *p*-Thiocresol has been added on to 1-*p*-tolyl-1-phenylethylene in the presence of benzoyl peroxide[406], and thiophenol and toluene-ω-thiol have been added on to vinylsilanes with heating, to give the adducts $RS(CH_2)_2Si(OC_2H_5)_n(CH_3)_{3-n}$ (n = 1, 2, 3).[407] Indene reacts with various arenethiols in heptane solution to give adducts in up to 99% yield[408].

e. Addition of various thiols. This paragraph deals with work aimed for the most part at the synthesis of products with various useful properties.

Equimolar mixtures of thiols react with vinyl methyl ketone on boiling to give $RSCH_2CH_2COCH_3$ (R = C_3H_7, C_6H_5), which can be used as solvents, plasticisers, and intermediates in the synthesis of insecticides and flotation reagents[409], while benzylideneacetophenone and n-dodecanethiol under the same conditions give an adduct which has been tested as a regulator in emulsion polymerisation[410]. Thiols and H_2S add on when heated without catalyst to derivatives of abietic alcohol[411] and rosin[412], ore flotation reagents being obtained in the latter case. On standing in contact with styrene, thiophene-3-thiol forms 3-thienyl-2′-phenylethyl sulphide, which is a stabiliser for motor oils[113]. The addition of a wide variety of thiols to safrol and isosafrol in the presence of ascaridol has given more than one hundred new sulphides, some of which are active acaricides with a low toxicity towards warm-blooded animals[413,414]. *OO*-Dialkyl phosphorothiolothionic acids have been added on to various olefins with the aim of synthesising insecticides[415]. The adducts which are readily formed when dithiocarboxylic acids are heated with αβ-unsaturated aldehydes, ketones, acids, ethers, nitriles, sulphones, and sulphoxides can be used as antioxidants and intermediate products in the synthesis of drugs and poisons[416]. The passage of methanethiol through acrolein containing catalytic quantities of acetyl peroxide has been recommended for the synthesis of methionine[417].

In a number of cases thiylation gives polymeric substances. But-2-enethiol, 3-phenylbut-2-enethiol, and other thiols with double bonds in the βγ- or γδ-positions polymerise slowly on standing and rapidly on heating if the degree of screening of the C=C bond by neighbouring methyl groups is not too great[418,419]. Marvel and coworkers[385,386,420,421] prepared a very large number of polyalkylene sulphides with molecular weights up to 60 000, exhibiting rubber-like properties in a number of cases, by the reaction of various thiols (chiefly hexamethylenedithiol, but also various others, including silicon-containing thiols) with a variety of diolefins containing non-conjugated C=C bonds (diallyl, dibenzylideneacetone, diallylphenol, diallylmethanol, etc.). The reaction was studied in detail both in block and in emulsions. The preparation of a new class of elastomers by the addition of lower alkanethiols to the double bonds of butadiene rubbers in the latex stage has been described. A high degree of saturation is reached without rupture of the main chain of the polymer; the adducts have high thermal stability and resistance to the action of ozone and γ-rays[422,423]. For example, an adduct with up to 95% of the C=C bonds saturated with methanethiol resisted attack by ozone for 300 h under conditions

in which neoprene broke down in 1 h and butyl rubber in 20 h. [423]

f. Addition of thiols to $\alpha\beta$-unsaturated ethers and sulphides. These reactions are considered in a separate paragraph since they are fairly characteristic from the viewpoint of the conditions of their initiation and, more particularly, their inhibition. This has been shown by work in our laboratory.

Vinyl alkyl ethers undergo exothermic reaction when mixed in the presence of air with sufficiently active thiols [thiophenol, TAA, dithiols such as $O(CH_2CH_2SH_2)$, and even with butanethiol] to give high yields of adducts containing 95–98% of the anomalous addition product [62,424,425]:

$$ROCH{=}CH_2 + R'SH \longrightarrow ROCH_2CH_2SR'.$$

The reaction of ethanethiol, which has been studied in detail for vinyl butyl and vinyl ethyl ethers [62], is much less predictable. When mixed in air, these substances react slowly and always give a mixture of the anomalous and normal products. The peroxides formed when vinyl ethers are allowed to stand in air decrease the overall rate of the process and facilitate the normal addition. Purely anomalous reaction was observed between freshly-distilled reagents in the presence of the traces of oxygen remaining in the reagents after degassing by evacuation to 2–5 mm Hg (with preliminary freezing); quantitative reaction under these conditions required heating [62]. The reaction is accelerated slightly by the presence of 0.1–0.2% of azoisobutyrodinitrile and by traces of moisture present in the thiol [424]. In the presence of azoisobutyrodinitrile thiols add on contrary to Markovnikov's rule to the vinyl ester of phthalylglycine [426] and to vinyl aryl ethers, including halogenophenyl ethers [65]. The adducts formed by the latter have insecticidal properties. The adducts formed by thiols with vinyl butyl ether have been used for the laboratory synthesis of insecticidal *OO*-dialkyl *S*-(2-alkylthioethyl)phosphorothiolothionates [47].

$$RSCH_2CH_2OC_4H_9 \xrightarrow{HCl} RSCH_2\mathbf{CH_2Cl} \xrightarrow{NaSP(S)(OR')_2} RSCH_2CH_2SP(S)(OR')_2.$$

Ethers of 1,2-dithioglycol with different structures are formed by an exothermic reaction when various alkyl-(aryl)thioethylenes are mixed in air with excess alkane- or arene-thiol [427,428]:

$$RSCH{=}CH_2 + R'SH \longrightarrow RSCH_2CH_2SR'$$

(where R = R' = C_2H_5, C_3H_7, C_4H_9, iso-C_3H_7, C_6H_5, $AlkOCH_2CH_2$) and also when 1-alkylthiopropenes are mixed with alkanethiols [75]:

$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}S\,Alk + Alk\,SH \rightarrow Alk\,SCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HS\,Alk$$

(where Alk = C_2H_5, C_3H_7, C_4H_9).

These reactions, which always accompany the synthesis of $\alpha\beta$-unsaturated sulphides from thiols and acetylene in alkaline media, are homolytic in character, since they are inhibited by hydroquinone [72], are retarded when the quantity of oxygen in the reaction mixture is decreased [427], and are not catalysed by bases, as pointed out earlier [151]. Ethanethiol adds on to vinylmercaptobenzothiazole on heating; mercaptobenzothiazole does not react under these conditions [429].

The addition of thiols to 1- and 2-arylthiopropenes [74] and to 2-(2'-oxopyrrolidin-*N*-yl)ethyl vinyl sulphide [430] required heating in the presence of azoisobutyrodinitrile. 2-Hydroxyethyl vinyl sulphide reacts with ethanethiol on heating to give a mixture of normal and anomalous adducts, and with 2-mercaptoethanol to give only the anomalous 1-(hydroxyethylthio)-2-ethylthioethane [431].

g. Addition of H_2S in the presence of radical initiators. When lower alkenes and H_2S are heated in a steel autoclave without special precautions to eliminate oxygen, the addition takes place in accordance with Markovnikov's rule, but the resulting thiol reacts anomalously with a second molecule of alkene, so that, for example, H_2S and isobutene give finally $(CH_3)_3CSCH_2CH(CH_3)_2$. [36] Very severe conditions (high temperature and pressure) are recommended in patents for the addition of H_2S to olefins [432–434]. At first, therefore, a somewhat incorrect impression arose regarding the reaction of H_2S with olefins. It was considered that H_2S has a low reactivity and adds on to double bonds chiefly in accordance with Markovnikov's rule, peroxides and oxygen producing no change in the mode of addition [1,4]. It was pointed out, however, that in the presence of redox systems consisting of peroxides and salts of Fe, Mg, Mn, etc. with strong inorganic acids (chiefly HCl) not only thiols but also H_2S may add on in anomalous fashion to various hydrocarbons with C=C and C≡C bonds [435]. The addition of H_2S to alkenes in the synthesis of primary thiols can be carried out under pressure in the liquid phase using anhydrous $FeCl_2$ and 0.5–8% of the hydroperoxide or peroxide of an aldehyde, ketone, ester, or aromatic hydrocarbon [436]. H_2S and unsaturated compounds with powerful electron-donating substituents react by a homolytic mechanism under even milder conditions with catalysis by a trace of oxygen [57,58,72]. This gives almost exclusively the β-alkoxy(alkylthio)-ethanethiols and bis-2-alkoxy(alkylthio)ethyl sulphides in proportions depending on the ratio of reagents in the original mixture:

$$RX{-}CH{=}CH_2 + H_2S \longrightarrow RXCH_2CH_2SH \xrightarrow{RXCH=CH_2} (RXCH_2CH_2)_2S$$

(where X = O, S).

The initiation conditions were studied in detail for the case of the reaction of H_2S with vinyl butyl ether [57,58,437]. The anomalous reaction is catalysed by ascaridol and azoisobutyrodinitrile; benzoyl peroxide is ineffective, probably because it combines rapidly with the vinyl ether to form the acylal of benzoylacetaldehyde [438]. Inhibition of the anomalous addition leads to the appearance, in the reaction medium, of a large quantity of the unstable normal adducts. This inhibition is observed not only in the presence of hydroquinone but also under the influence of the peroxides formed by the vinyl ethers during storage and also under the influence of excess oxygen. Only the normal adducts are obtained when the reaction is carried out under a pressure of atmospheric oxygen. Inhibition by oxygen is not observed in the homolytic hydrobromination of olefins in the liquid phase [439] but is shown in the reaction with thiols (particularly in the case of vinyl ethers), and is especially marked in the case of reactions with H_2S. It may be concluded that the ease of the reaction $A^{\bullet} + O{-}A \rightarrow A{-}O{-}O^{\bullet}$, which competes with the chain transfer, increases in the order:

$$RCHCH_2Br < RCHCH_2SR < ROCHCH_2SR < ROCHCH_2SH.$$

The structure of $R^{\bullet}$ in the OR group of the vinyl ether also influences the oxidisability of the radical $A^{\bullet}$, since the inhibition effects are particularly marked for ethers with branched chains and are much less marked for ethers with long straight chains [58]. Vinyl aryl ethers add on H_2S much more slowly than vinyl alkyl ethers; the reaction requires prolonged heating in the presence of azoisobutyrodinitrile, and always gives the anomalous adducts [54,64,437].

Under the influence of azoisobutyrodinitrile, H_2S also adds on to divinyl ether with the formation of dithiols containing oxygen atoms and sulphide groups[426], and also to vinyl lactams. Vinylcaprolactam gives good yields of thiol and sulphide, and *N*-vinylpyrrolid-2-one, even in the presence of excess H_2S, gives exclusively bis-2-(2′-oxopyrrolidin--*N*-yl)ethyl sulphide[440]. The addition of H_2S to allylamine in the presence of azoisobutyrodinitrile takes place chiefly in accordance with Markovnikov's rule, due to the inhibiting action of the amino-group[441].

It is clear from the foregoing that the anomalous thiylation of *O*-, *S*-, and *N*-vinyl compounds described in patents must be regarded as homolytic, although the authors emphasise the catalysis by bases[151,442].

Recently it has been shown that azo-compounds (azoisobutyrodinitrile and others) or peroxides (benzoyl peroxide) can be used for the anomalous thiylation of various alkenes by hydrogen sulphide in the absence of air and with the addition of water[443].

All these results indicate that, when conditions ensuring the absence of inhibitors are observed, the ease of addition of H_2S to the ethylenic bond in the presence of free-radical initiators is no less than that for thiols.

The reaction of HS· radicals plays an important part in the sulphur vulcanisation of rubbers[444]. In this connection the thermal decomposition of hydrogen disulphide, which is a much better HS· radical donor than H_2S, has been studied in solution in various alkenes. It was found that styrene and α-alkenes are more active acceptors of HS· radicals than β-alkenes and cyclohexene[445].

h. Photochemical thiylation. When reactions of thiyl radicals are initiated photochemically, the addition is rapid and almost no differences between thiols and H_2S are observed.

The accelerating action of light on the anomalous addition of a thiol was first observed in 1928.[17] Japanese workers made a detailed study of the addition of CH_3SH to a number of olefins under the influence of sunlight and various promoters[362,446]. For the reaction with allyl alcohol in the presence of $Hg(SCH_3)_2$, light, and O_2, the yield was 93%, for that with light and O_2 it was 61%, for that with the salt and light 33%, and for that with the salt and O_2 22%; no reaction took place on illumination without promoters[362]. Analogous relationships were observed in the reaction of CH_3SH with acrylic acid, acrolein, maleic acid, and styrene[446]. On illumination by sunlight in a quartz apparatus, thiols add on to acetals of vinylacetaldehyde with the formation of adducts $R'SCH_2CH_2CH_2CH(OR)_2$, which have been used for the synthesis of drugs[447].

Initiation with ultraviolet light[361,448,450] was found to be most effective. On irradiation by light with a wavelength below 3000 Å in a quartz apparatus, photolysis of the S–H bond takes place readily and H_2S and thiols add on rapidly and quantitatively to alkenes in both gaseous and liquid phases with the exclusive formation of the anomalous adducts.

Quantitative addition of H_2S in the liquid phase to prop--1-ene, but-1-ene, vinyl chloride, and methyl acrylate is observed at 0°–20° on illumination in a quartz tube after only 4–10 min. With a twofold excess of H_2S, 15–30% of sulphides and 65–90% thiols are formed[361,448]. Diallyl (hexa-1,5-diene) and allyl ether form polymeric adducts with H_2S.[361] With promoters (sensitisers) undergoing photolysis on irradiation by light of longer wavelength (metal alkyls[361,451], aldehydes, ketones, or other carbonyl compounds[361,450]), the reaction can be carried out in a Pyrex vessel, which transmits light above 3200 Å; this method has been used, for example, for the addition of H_2S to halogenoalkenes to form halogenated thiols and sulphides[361,449]. Irradiation by a mercury lamp has been used for the addition of H_2S and thiols to higher alkenes such as cetene (hexadecene)[452], of β-mercaptoethanol to vinyl acetate[453] and vinyl chloride in the presence of benzoyl peroxide[454,455], of methanethiol to cyclohexene[456,457], and also to vinyl acetate, vinyl chloride, and allyl alcohol [in the presence of $Hg(SCH_3)_2$ and O_2].[458] Different thiols react with vinyl acetate on illumination in the presence of O_2, but azoisobutyrodinitrile or benzoyl peroxide must be added[459]. Disulphides (diphenyl, dianisyl) (0.5–1%) considerably accelerate the rate of the photochemical addition of propane- and dodecane-thiols to styrene[460]. With promotion by $(C_6H_5)_2S_2$, the reaction between vinyl chloride and dithioethylene glycol is rapid and quantitative under illumination in a Pyrex vessel by a tungsten lamp[461]. 2-Mercaptoethyl ethers of diols are prepared from H_2S and divinyl ethers $(CH_2=CHO)_2(CH_2)_n$ (n = 2, 3, 4) with irradiation by light having a wavelength of 3000–4000 Å in the presence of anthracene, fluorene, divinylbenzene, divinyltoluene, divinylxylene, and polychlorostyrenes[462]. In an atmosphere of O_2, with irradiation by ultraviolet light, thiophenol and toluene-ω-thiol add on quantitatively to vinyl butyl ether after 3 h; the less active butanethiol adds on to the extent of less than 30%. In an atmosphere of N_2 the reaction is most effectively promoted by azoisobutyrodinitrile slightly less effectively by benzoyl peroxide and $Hg(SCH_3)_2$.[463] The addition of alkanethiols to undecanoic acid required illumination in a quartz vessel for 3 h.[464] H_2S reacts with trifluorochloroethylene on irradiation by a 500 W filament lamp in the presence of benzoyl peroxide; HF splits off from the adduct and polymers containing S, F, and Cl are formed[465]. The photochemical addition of H_2S to allylamine hydrochloride, vinyl lactams, etc. is promoted by trialkyl phosphites[441].

In the present review an attempt has been made to reveal the extensive possibilities for theoretical and practical studies latent in the, at first sight simple, reaction of thiylation of the double bonds in olefinic compounds.

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THE CHEMICAL ACTION OF IONISING RADIATIONS ON INORGANIC CRYSTALS

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1. INTRODUCTION

Considerably greater interest has recently been taken in the study of the chemical changes occurring in solids under the influence of ionising radiations. The results of these investigations have especially great prospects of practical application in the search for radiation-resistant materials for the construction of atomic reactors and plant and for intensifying many solid-state reactions of practical importance. These problems are also encountered in developing the technology of the production of artificial radioactive isotopes by irradiating solids in a reactor. It will therefore be useful to reach, from accumulated data, some general conclusions concerning the chemical changes produced by radiations in solids and their influence on the physicochemical properties of the solids.

The experimental data which have accumulated are so extensive and diverse that it is impossible to cover them in a short review. Since fairly complete surveys have appeared[1-13] of the action of radiation on metals and on polymeric materials, we shall confine ourselves to an examination of work on the chemical changes produced by radiation in ionic crystals. The variation in physical properties under these conditions has been considered[14], and therefore we shall disregard this question, too, in the present paper.

2. ACTION OF HEAT, LIGHT, AND IONISING RADIATIONS ON MATTER

In contrast to heat and light quanta, the energy of which is less than, or at best comparable with, that of chemical bonds, the energy of γ-quanta, electrons, or heavy particles formed in radioactive disintegration or in artificial (instrument) sources of radiation — accelerators — is much larger, usually by several orders of magnitude, than the chemical bonding energy, and this governs many specific aspects of radiochemical processes in the solid phase, which distinguish them from photolysis and thermal decomposition.

The action of heat on a solid results in atomic vibrations in the lattice, caused by the greater number of heat quanta; only a few of them correspond to the high-energy limit of the Boltzmann distribution and can lead to rupture of the chemical bond. Under isothermal conditions heat quanta are distributed uniformly throughout the volume of the crystal, and if this alone governed the start of thermal decomposition, the latter could begin at any point in the crystal, and its kinetics would be represented by a first-order equation. But different positions in the crystal are not equivalent in reactivity. Therefore bond rupture takes place at those points in the lattice where at a given instant the bond is for some reason weaker than at other points, and it is this which causes the localisation of the initial centres of thermal decomposition at defects in the crystal.

In the decomposition of solids under the influence of visible light or ultraviolet radiation the energy of the quantum is comparable in magnitude with that of a chemical

bond, and this case should represent the simplest type of decomposition of the solid[15]. Since on exposure the light flux is incident primarily on the surface of the crystal, any chemical interaction between light and matter which does occur is localised mainly at the surface.

Jacobs *et al.*[16] showed, in a study of the kinetics of the photolysis of barium azide as an example, that, by varying the wavelength maximum of the radiation employed, portions of the crystal surface differing in activity can be made to react separately. Thus at $\lambda < 2600$ Å photolysis can occur over the whole surface of the crystal. When $2600 < \lambda < 3300$ Å, photolysis is localised mainly at lattice defects, and at $\lambda > 3300$ Å the photochemical process can take place only if crystal nuclei of metallic barium are already present in the barium azide crystal, the process being localised at the interface between the starting material and the photolysis product.

Photolysis usually ceases when the crystal surface has become covered with a layer of product, which protects the deeper layers of the crystal from the action of light (provided that further development of the reaction by a thermal mechanism, by conversion of the energy of the light quanta into heat energy[17], is excluded).

The rate of photolysis may depend both on the probability of transfer of an electron to the conduction band and on the possibility of its recombining with a positive hole.

The main features of the radiolysis of solids which distinguish it from thermal and photochemical decomposition processes result from the fact that the energy carried by each γ-quantum or high-energy charged particle far exceeds (usually by several orders of magnitude) the energy of a chemical bond in a solid. Therefore only a negligible fraction of the total energy of a γ-quantum or a heavy particle is expended on the initial expulsion or excitation of an electron. The remainder is transferred to the expelled electrons on ionisation, is emitted as a γ-quantum of longer wavelength by the Compton effect, or may even be used up in displacing the atoms or ions from the normal lattice points into the interstices.

The distribution of the portions of the lattice which have been affected by interaction between radiation and matter depends both on the energy and intensity and on the type of radiation. In the case of γ-rays, for example, exposure produces a uniform formation of radiation defects throughout the bulk of the substance[18]. Exposure to particles results in ionisation of the substance predominantly along the track of the particle, and therefore in a non-uniform distribution of radiolysis products both in the volume of the crystal and along the path traversed by the particle in the crystal[18]. The mean free path then depends firstly on the energy and secondly on the nature of the particle itself.

Since the principal chemical effects of the exposure of solids to high-energy radiation (especially γ-quanta and electrons) are produced not by the bombarding particles themselves but by secondary electrons whose energy may vary within extremely wide limits, the elucidation of quantitative relations is extremely complicated, even if the initial exposure is to monochromatic radiation.

In contrast to light, which produces mainly ionisation effects, high-energy rays may also cause ions to be displaced from the normal lattice points into the interstices. The relative proportions of ionisation and displacement effects depend both on the nature of the irradiated material and on the type of radiation and its energy.

At the end of the track the transfer of the energy of the particle to the lattice causes the formation of heat wedges, which represent local hot spots in the crystal, in which the temperature rises sharply for a brief period.

The possibility of a high concentration of energy in a small portion of the lattice on exposure to high-energy particles and ionising radiation was the basis of attempts to initiate the detonation of explosives by irradiation. However, in spite of a large number of investigations with both high explosives and detonators and with various types of radiation — γ-rays, electrons, neutrons, protons, α-rays, fission products[19-28] — attempts at radiation initiation of explosion were unsuccessful (except for cases of the detonation of nitrogen iodide under the influence of α-particles and fission products). According to Bowden[29], this may be because the centres of decomposition thus formed are too small for the production of the local hot spots necessary for conversion of slow thermal decomposition into detonation.

A general and fundamental characteristic of the radiolysis of solids is that the probability of a process occurring is determined not so much by the weakness of the chemical bonds at individual sites in the lattice, which is the case with thermal decomposition and the action of light, as by what conditions exist for restoration of a bond in the lattice after it has been broken. These determining factors may be extremely varied, ranging from the ionisation potential of the cation, in the case of reactions resulting from electron transfer from anion to cation, to the free volume in the lattice of an ionic salt. The latter is of particular importance when the primary stage of radiolysis is the rupture of bonds within a complex ion, as, for example, in the action of high-energy rays on alkali metal nitrates and permanganates[30-34]. In the first case the mechanism of radiolysis of the crystal will be analogous to thermal decomposition and the action of light, while in the second case it may be different.

3. EXPERIMENTAL TECHNIQUE FOR IRRADIATION

The experimental technique for irradiation and for studying the radiolysis products has much in common with that used for studying the photochemical and thermal breakdown of solids. On the other hand, the basic features of radiolytic changes in ionic crystals, which distinguish them from thermal and photochemical processes, require a special technique for the experimental study of the chemical changes produced in solids by irradiation.

For exposure to an external source of X-rays or γ-rays, the specimens are placed in glass or quartz tubes[35-42] or in special vessels which enable the composition and pressure of the gas over the substance to be controlled, and also permit irradiation at low temperatures[34,43-45]. Exposure to neutrons and mixed radiation in the channels of a reactor is effected in a similar manner[46-49].

If decomposition under the influence of the radiation from a radioactive isotope contained in the test salt itself is to be studied, the preparation is simply kept for a certain time in air or in a vacuum[50,51].

In the case of irradiation with electrons (β-rays) there is a possibility of considerable weakening of the electron flux by the walls of the vessel containing the specimen. Therefore either an open vessel is used[52] or, if irradiation in a vacuum or in an atmosphere of an inert gas is required,

a window is made in the vessel and is covered with a material whose absorption of electrons is a minimum (for example beryllium or aluminium foil).

With exposure to low-energy electrons, which are obtained by means of instrument sources, the substance is placed in the actual space of the source. In special equipment described by Groocock and Tompkins[53] an electromagnetic device enables the substance undergoing decomposition to be introduced into the low-energy electron beam between the cathode and the grid.

In contrast to irradiation with γ-rays, when electrons of low and intermediate energies are used allowance must be made firstly for the great probability of non-uniform distribution of radiolysis products between the bulk of the crystals and their surface, and secondly for the possibility of the preparation being heated up in the electron beam at high intensities of the electron flux. The latter may result in thermal decomposition of the specimen as well as radiolysis, which will considerably modify the experimental results. The effect of this source of error in investigations of radiolysis in an electron flux may be diminished to a considerable extent by using pulsed electron accelerators.

When bombardment with heavy particles — ions, protons, deuterons, and α-particles — is used, the same difficulties are encountered to a still greater extent. Moreover, the shortness of the range in air of heavy particles and ions obtained by radioactive disintegration, is an added difficulty, so that exposure must be made either in a vacuum or with the material to be irradiated in direct contact with the source[54-56].

The possibility of obtaining high-energy particles fluxes in artificial sources sometimes permits enclosed specimens to be irradiated through a foil window, but this involves considerable loss of intensity in the foil.

Another very important factor in the method is measurement of the dose absorbed by the specimen. A distinction must be made between measurement of the intensity of the radiation source and measurement of the radiation dose absorbed by the substance, the latter being defined as the energy ΔE absorbed by an element of mass m or volume v of the material[57].

The first of these determinations is extremely important in the design and manufacture of isotopic and instrument sources of radiation, and the second is especially valuable in the study of radiochemical processes.

The absorbed dose can be measured either directly or indirectly, the former often involving great experimental difficulty and sometimes being altogether impracticable. Direct determination of the absorbed dose is usually accomplished by measuring the attenuation of the energy flux in the substance or the quantity of energy absorbed, by means of a standard made of material having the same thickness and approximately the same density but not subject to radiolysis under the given conditions. Thus, for example, Heal[34,43-45] in his work on the action of X-rays on ionic salts used as such a standard a metal disc of the same thickness as the irradiated crystal. This disc was placed in a calorimeter, and the absorbed dose was calculated from measurements of the temperature of the disc during exposure.

The absorbed dose can be measured also by determining the intensity of the dose by means of a ferrous sulphate or a ceric sulphate dosimeter, and then calculating the dose absorbed by the test material, allowing for the difference in electron density of this material and the dosimetric solution[35-42].

With neutron irradiation, measurement of the absorbed dose is also preceded by determination of the neutron flux intensity, which involves measuring the specific activity, after fixed intervals of time, of a cobalt wire introduced into the irradiated space[54,55,58].

The intensity of an electron beam can usually be characterised by the current measured in a Faraday cylinder, or can even be measured with an ordinary ferrous sulphate dosimeter.

4. METHOD OF STUDYING CHEMICAL CHANGES PRODUCED IN SOLIDS BY RADIATION

The above peculiarities of radiolytic processes in solids compared with thermal and photochemical decomposition are responsible for the special features of the technique used to study the chemical changes occurring in solids on irradiation.

These are methods for the rapid determination of the extremely small amounts of the radiolysis product, which can usually constitute only a few hundredths or tenths of a per cent of the total weight of material, and only in rare instances, when high doses are absorbed, can reach a few per cent. Secondly, in the study of chemical radiation effects in solids account must be taken of the distribution of radiolysis products in the bulk of the crystal, which may differ with the type and energy of the radiation used. Thirdly, the possibility of displacement effects as well as ionisation effects during radiolysis must be borne in mind. Displacement effects, which do not usually lead to chemical changes in the crystal, may have a considerable influence both on the chemical changes associated with ionisation and excitation of electrons in a solid under the action of radiation and on the rates of other physicochemical processes involving irradiated solids (for example, thermal decomposition).

The methods employed to study radiochemical reactions should provide for the possibility of following these effects too.

Among the methods employed at the present time to study the products of radiolysis, we may note firstly dissolution of the irradiated crystals in water and determination of the radiolysis products in the aqueous solution by the usual methods of chemical analysis, *i.e.* by the normal procedures of volumetric microanalysis, or even by means of colorimetric, spectrophotometric, potentiometric, and polarographic methods.

If one of the products of radiolysis is a gas, the course of the process can be followed by measuring the quantity of gas evolved in the reaction.

In contrast to the thermal and photochemical breakdown of solids, in which decomposition starts at the surface and gaseous reaction products are evolved immediately, radiolysis occurs throughout the volume of the crystal, and with small degrees of decomposition the gaseous products

remain in the crystal[52]; in order to determine their amount, therefore, this gas must be liberated from the bulk of the crystal.

One of the methods usually employed for this purpose is to heat the irradiated specimens in a vacuum[46] to the melting point or a crystallographic transition point. However, this may yield results which are too high owing to the simultaneous occurrence of thermal decomposition of the salt, which would be accelerated in the presence of solid products of the radiolysis. In addition, the temperature at which appreciable thermal breakdown begins may be lowered[59-61].

The errors associated with the heating up of the specimens are to a considerable extent eliminated in a method for studying the kinetics of radiolysis based on determining the dependence of gas evolution on the degree of dispersion of the crystals being examined, and then extrapolating the gas evolution at a definite dose to zero crystal size. The method was developed in connection with the radiolysis of barium chloride, and then used to study the dynamics of radiolysis with several other inorganic salts[62-64].

Another method for determining the amount of gas formed in a crystal on radiolysis is the microgas-volumetric technique developed by Heal[65] and based on measuring under the microscope the size of the gas bubble liberated when a small, accurately weighed crystal dissolves. This method was used to study the radiolysis of alkali metal azides[34,43,45]. It follows from the principle of Heal's method that it is applicable only if the gas evolved on radiolysis neither reacts with nor dissolves in the solvent crystal. The quantity of gas evolved can be followed also from the change in weight[66] or density[46] of the crystals during radiolysis.

The composition of the gas evolved can be determined by the usual methods of gas analysis[37,46,52] or by mass spectrometry[41,46].

The course of radiolysis can be followed by checking the amount and condition of a solid reaction product. If the initial crystals are colourless or feebly coloured, while the resulting product absorbs light strongly in the visible or ultraviolet range, the dynamics of radiolysis can be studied, especially in the initial stage of the process, by colorimetry[67], photometry[68-70], and spectrophotometry of the irradiated crystals[44,71-73]. The quantity and structure of the new phase which accumulates during radiolysis, and also the accompanying change in degree of imperfection of the crystal, can be studied also by X-ray[18,56,59,74-78] and electron[79-81] diffraction methods.

Electron paramagnetic resonance has become especially important for investigating the nature of the initial centres formed on the radiolysis of ionic crystals by interaction of electrons and positive holes with ionic defects, and of the free radicals which are formed by the rupture of intracrystalline bonds as a result of radiolysis. This method has been used[51,60,82-92] to study the chemical changes caused by radiation in ionic crystals.

Among other physicochemical methods employed to investigate irradiated ionic crystals the following may be mentioned: measurement of heats of solution[38], thermographic and thermogravimetric examination of the crystals[42], determination of the change in ionic and electronic conduction in the crystals after irradiation[53], and the magnetic susceptibility[46,93,94] and mechanical properties of the crystals[74].

5. CHEMICAL CHANGES PRODUCED BY RADIATION IN INORGANIC IONIC CRYSTALS

The nature and extent of the chemical changes in solid ionic crystals depend on the type and energy of the radiation, and also on the nature of the substance undergoing radiolysis. Absorption of radiation results in ionisation and excitation of the electron shells of the ions forming the lattice, and in some cases in their displacement from their normal lattice points into interstices. Chemical changes result mainly from ionisation effects; displacement effects most often entail a change in physical properties.

With binary ionic salts of the alkali metal halide type the action of ionising radiation depends to a considerable extent on the ionisation potential of the cation, since this quantity determines the depth of the potential traps for the capture of electrons by anionic vacancies, which is the initial stage of the radiolysis of these salts. A consequence of the formation of F- and V-centres is the formation, inside the crystals, of metallic particles and halogen atoms, which are uniformly distributed throughout the volume of the crystal in the case of γ-rays or are located in the portions of the crystal adjacent to the surface under the action of particles and electrons of intermediate energy.

The occurrence of chemical changes when these crystals are irradiated is indicated by the solution becoming alkaline and gaseous halogen being formed on dissolution of the salt (a fact known from the earliest work[95]† on the action of radiation), owing to reaction of the primary products of radiolysis with water molecules:

$$e + H_2O \rightarrow OH^- + \tfrac{1}{2}H_2,$$
$$h + Cl^- \rightarrow Cl, \quad 2Cl \rightarrow Cl_2.$$

As a result of the reversibility of the defects, their rate of breakdown increases with rise in temperature and in their concentration, the chemical changes accompanying their formation usually being slight and according to Heal[98] not exceeding 0.1%.

Increases in the ionisation potential of the cation increases the irreversibility of radiolysis and the yield of products, as is the case, for example, in the radiolysis of silver halides[70] and cadmium halides[99] under the influence of X-rays, γ-rays, and electrons, during which far greater yields of reaction products are reached with the same dose absorbed.

In the case of ionic salts containing complex anions or cations specific effects may appear owing to rupture of chemical bonds within the complex ions under the influence of radiation, which may occur in these cases together with the electron transfer from anion to cation usually observed in binary ionic crystals. In this class of salts the radiolysis of azides, nitrates, and perchlorates has been most thoroughly studied.

Heal, Groocock and Tompkins, Sviridov, and Bowden have investigated the breakdown of these salts under the influence of X-rays, electron irradiation, and reactor radiation[18,20,29,43,53,72,74,100-104]. In all cases metallic crystal nuclei are formed, and free nitrogen is evolved in yields which may reach 1–2.5%. As with alkali metal halide crystals, dissolution of irradiated crystals of sodium

† [Refs. 96 and 97 are not indicated in the text. They deal with free Na and Cl in sodium chloride crystals containing colour centres (Ed. of Translation)].

azide makes the solution alkaline, while interaction between the free hydrogen evolved and the nitrogen of the azide ion yields ammonia and hydrazine[98].

Just as with simple binary salts, the radiation yield and the rate of radiolysis of azides become greater the higher the ionisation potential of the cation. The permanence and the irreversibility of the chemical changes produced in solids by the action of radiation also increase.

Nitrates form another group of salts changes in which under the influence of ionising radiation have been studied in some detail. Irradiation of nitrates by X-rays, γ-rays, and electrons as well as reactor radiation usually results in elimination of an oxygen atom from the nitrate ion with conversion of the latter into a nitrite[34-39,41,46,52,105,106]. The oxygen remains trapped in the crystals, and is liberated from them only when the salt is dissolved in water or is heated to its melting point or a polymorphic transition point[46]. Solutions of irradiated nitrates appear[52,98] to have one more alkaline (pH 9–10) than would be expected solely from hydrolysis of the resulting nitrite.

The radiation yield of the process depends on the possibility of recombination of the nitrite ion with oxygen, and is higher the more conditions favour removal of the oxygen atom from the sphere of action of the NO_2^- ion. The radiation yield of nitrites therefore depends, under otherwise identical conditions, on the free volume, which is the difference between the volume of a unit cell of the crystal lattice and that of the ions in it[30-32,46].

In the radiolysis of alkali metal nitrates the radiation yield has been shown[30,31,46] to be higher the greater this free volume (for cations ranging from sodium to caesium). A similar relation is observed also with the nitrates of the alkaline earth metals[32]. In both cases the sequence of chemical stability on radiolysis is the opposite to the order of thermal stability for the same series of salts[107,108]. This is probably because the thermal stability of the nitrates is determined by such factors as, for example, the polarising effect of the cation on the anion, which play a secondary part in radiolysis. A similar relation is observed with other salts too, for example permanganates[33] and bromates[109].

The free volume is usually the main factor when the variation in ionisation potential in a series of salts is slight. When the change in ionisation potential is considerable, its influence, associated firstly with the polarising action which the cation can exert on the anion and secondly with a change in stability of the centres of electron capture, may become predominant, and the radiation stability will then vary in the same sequence as the thermal stability. Thus, for example, the free volumes in silver and sodium nitrates are about the same, while the ionisation potentials of their cations differ strongly (7.54 and 5.1 eV respectively[110]). Therefore the radiation stability of silver nitrate is far less than that of sodium nitrate. The same relation is shown by a comparison of the radiation stability of strontium and lead nitrates[32].

When the radiation stability of complex ionic salts is being studied, account must be taken also of the strength of the bond, within the complex ion, which is ruptured under the influence of γ-quanta or secondary electrons. An example is provided by comparative data on the radiation yields of potassium chlorate and potassium nitrate under the same conditions of irradiation. The energy of the Cl–O bond in the chlorate is 2.38 eV, while that of the N–O bond in the nitrate is 3.65 eV, and hence the radiation yield of oxygen is 4 and 0.8 mole of O_2 per 100 eV in $KClO_3$ and KNO_3 respectively[46].

Results obtained by Proskurnin and Baberkin have shown that the presence of water of crystallisation in the nitrate results in an increase of the radiation yield, owing both to radiolysis of the water and to a diminished probability of recombination of the oxygen eliminated on radiolysis, as a result of interaction with the water molecules[39,40].

Radiolysis of a chlorate by various types of radiation yields oxygen, chloride, hypochlorite, and perchlorate[44,46,60,61]. The first three products are formed as a result of breakdown of the chlorate ion, and the perchlorate ion is produced by interaction of the chlorate ion with oxygen[44]. Radiolysis of solid potassium perchlorate gives chloride and chlorate[43]. During irradiation the chlorate ion may itself break down into the above products.

The decomposition of solid crystalline salts has been noted also when they are used as targets in the preparation of radioactive isotopes[111-114].

Heavy-metal oxalates evolve carbon monoxide and carbon dioxide on irradiation[49,50,56], the oxalate ion being converted into carbonate[50,56], while in several cases the solid product of radiolysis is the metal oxide[49].

In the radiolysis of solid salts of chromic acids by a neutron flux, it has been established that the ability to undergo radiation-induced reduction increases in the sequence $K_2CrO_4 < K_2Cr_2O_7 < K_2Cr_3O_{10} < CrO_3$.[115]

Interesting relations have been obtained for the radiolysis of complex compounds which break down in several stages owing to their complicated composition[116]. The extent of decomposition of complex compounds depends on the ions in both the inner and outer spheres. Thus it is greater for the crystalline hydrates of nitrates than for the anhydrous salts[36,39,40]. This phenomenon can be explained as a consequence of structural changes and of the influence of products from the radiolysis of water[39,40], and also because the field due to the water dipoles separating the nitrate ions from the cations is weaker than the field due to the latter[36]. A comparison of the radiation stability of various platinum complexes (tetra- and hexa-chloroplatinates[117]) showed that, with the same inner sphere, ammonium salts decompose more readily than the potassium salts. Complexes containing different ligands in the inner sphere decompose more rapidly than those with identical ligands; compounds of bivalent platinum are more readily decomposed than quadrivalent platinum compounds; and a *trans*-isomer breaks down more readily than the *cis*-isomer. In the case of oxalate complexes those of a quadrivalent metal prove to be more stable than those of bivalent metals[116].

The above data suggest that in some cases radiolysis may take place by a mechanism similar to that of thermal decomposition, while in other cases it may have a different mechanism.

When the laws governing radiolysis and thermal and photochemical decomposition are the same, as for example in the case of silver oxalate, the breakdown of which probably always involves capture by interstitial silver ions of electrons expelled by radiation, factors which increase the thermal stability will lead to an increase in the radiation stability too. If, however, the laws are different, methods of increasing — or diminishing — the radiochemical

stability must be sought in terms of factors which are specific to radiolysis. Therefore a clear knowledge of what is the mechanism of the radiolysis of solid ionic salts and what factors govern the radiochemical process is absolutely essential in the search for methods of controlling their radiochemical stability.

The rate of radiochemical processes and the yield of the products of radiolysis may be greatly affected by the actual structure of the crystal, involving the presence of both macro- and micro-defects (ionic vacancies, interstitial ions, impurity ions, dislocations, grain boundaries, etc.). The radiochemical stability of ionic crystals will therefore depend very greatly on their mode of preparation [118], their deformation [119-121], and the concentration and type of impurities which have entered the crystal during its preparation or processing [122,123].

The influence of defects in crystals on their radiation stability can be examined in greater detail in the effect of impurities. A change in radiation stability resulting from the introduction of impurities had already been noted in the early work on the action of radiation on ionic crystals (see for example, Refs. 124 and 125), and formed the subject of later investigations on the tendency of ionic crystals containing impurities to become coloured by radiation. It was shown in this work that impurities may influence the radiation stability in the first place owing to a change in the number of breaks in the distribution of dislocations in the crystals resulting from the lack of correspondence between radii and polarisation properties of the impurity ions and the lattice ions which they replace [126,127]. Secondly, impurity ions differing in charge from the lattice ions which they replace lead to the formation in the crystal of additional cationic or anionic vacancies or interstitial ions. This also entails a change in radiation stability, which increases or decreases depending on the type of vacancies and interstitial ions formed [70,128,129].

Finally, a change in the radiation stability of ionic crystals may result from the direct capture of electrons and positive holes by impurity ions, as is observed when certain impurities are introduced into the crystals of alkali metal halides [130,131].

Apart from the effect of defects due to impurities in crystals, which we have examined in detail, radiation stability depends also on the presence of other types of defects [98]. The radiation stability is usually diminished by the presence of defects in crystals, owing to the participation of point defects in the electronic and ionic processes sometimes involved in radiochemical decomposition, the greater probability of the destruction of excitons localised at defects and accompanied by rupture of chemical bonds within complex ions. In the defective regions, moreover, there is a higher probability that ions, atoms, or radicals split off in the initial stages of radiolysis will be removed from the site of primary bond rupture, and therefore the "cage effect", which leads to recombination and is especially important in the case of solids, is diminished [98].

By analogy with what occurs in thermal decomposition [132,133], it is to be expected that the same defects will affect the rate of radiolysis differently depending on the reaction mechanism. For example, it has been shown [69,134] that the addition of cadmium ions, which generate cationic vacancies in the lattice of silver salts, increases the radiation stability of silver oxalate, but diminishes the radiation stability of silver carbonate [68], the decomposition of which involves rupture of bonds within the carbonate ion.

6. EFFECT OF PRELIMINARY IRRADIATION OF SOLIDS ON THE RATE OF TOPOCHEMICAL REACTIONS

Since the accumulation of defects in crystals may lead to a change in the rate of topochemical reactions (as was noted long ago in the literature on topochemistry), the effects of different types of defect varying according to the reaction mechanism, preliminary high-energy irradiation of solids may be expected to exert an appreciable and specific influence on the rate of individual types of topochemical reactions.

Since the effect of preliminary irradiation has been studied most thoroughly in the case of thermal decomposition compared with other types of topochemical reactions, we shall confine our attention first of all to such reactions.

The effect of previous irradiation on the rate of subsequent thermal decomposition had already been noted in the earliest work on the kinetics of thermal decomposition. The facts which have now been accumulated enable some quite definite conclusions to be drawn concerning the nature of the effect.

Among the earliest work was that of Garner and Moon [135] who found that preliminary exposure of barium azide to γ-rays from radium accelerates the subsequent thermal decomposition of this salt. The same effect was shown in later work with preliminary exposure to various types of radiation in the decomposition of barium azide irradiated with X-rays [101,136], of lithium, cadmium [29,131], and lead [137] azides exposed to γ-rays and neutrons, and also of mercury [139,140], silver [101,118,140], lead [142], nickel, and copper [75] oxalates.

Preliminary exposure to γ-rays, X-rays, and neutrons accelerates the subsequent thermal decomposition of the permanganates of potassium [143], rubidium [144], caesium [145], barium [146], and silver [58,147,148], silver carbonate [68], potassium bromate [149], ammonium dichromate [150], and ammonium perchlorate [42,151,152].

Freeman and Anderson [152] compared the formation of the initial reaction centres in the thermal decomposition of ammonium perchlorate crystals which had and which had not been exposed to X-rays. They discovered that, whereas in unirradiated crystals thermal decomposition involves formation of nuclei on the crystal surface and their further growth into the interior, in the thermal breakdown of irradiated crystals formation of nuclei is not confined to the surface, but takes place throughout the volume of the crystal.

This work established that preliminary exposure to ionising radiation may considerably diminish the time required for subsequent thermal decomposition. Exposure to γ- or X-rays causes mainly a shortening of the induction period [143-148]. For the thermal decomposition of the permanganates of potassium [143], rubidium [144], and caesium [145], it was found that the duration of the induction period t and the dose of ionising radiation absorbed in the substance, or the period of exposure τ, are linked by the simple and reproducible formula

$$\log \tau = kt + \text{const.}$$

A similar relation was observed for the shortening of the induction period in the thermal decomposition of barium azide which had been exposed to X-rays [136].

Neutron irradiation has a strong influence on the whole course of thermal decomposition [144,153], which is not confined

to the initial stage, and this is specific to the activation of thermal decomposition by neutron irradiation.

The effect of radiation on the rate of subsequent thermal decomposition by an ionic–electronic mechanism may be changed by the addition of heterovalent ions, which generate cationic or anionic vacancies, as has been shown for the addition of cadmium to irradiated silver oxalate[141].

A detailed study of the mechanism underlying the action of the additive showed[154] that, whereas with preliminary ultraviolet irradiation of the oxalate the additive affects both photolysis and thermal decomposition, with preliminary exposure to γ- and X-rays the diminution in the effect is due mainly to retardation of thermal decomposition in the presence of the additive.

Many questions still remain unanswered and obscure in the effect of radiation on the rate of subsequent thermal decomposition.

In some cases thermal decomposition is accelerated only by neutrons. Thus with lead styphnate monohydrate[153] the rate is unchanged on exposure to γ-rays and to a ^{60}Co source at doses of the order of 1.8×10^8 rad, but it is greatly increased by neutron irradiation in a reactor channel even at comparatively low doses.

The same occurs when manganese oxalate dihydrate is exposed to neutrons or γ-rays[155]. The causes of this phenomenon have been linked[155,156] with the fact that a great proportion of radiation-induced faults resulting in an increased rate of thermal breakdown of irradiated substances are due to displacement phenomena. In the case of lead styphnate, for example, these displacements may occur both as a result of elastic collisions between neutrons and carbon atoms in the styphnate ion and as a consequence of the reaction $^{14}N + n \rightarrow {}^{14}C + p$, which also leads to destruction of the styphnate ion.

It is not clear in what cases a diminution in activation energy can be expected to result from preliminary irradiation. A change in activation energy has been found[143-148] in the subsequent thermal decomposition of permanganates. In other cases, for example the thermal decomposition of silver oxalate exposed to ^{60}Co γ-rays, data have been obtained indicating the absence of such a phenomenon, the change in rate produced being linked mainly with a change in the pre-exponential factor in the Arrhenius equation[134].

The influence of the interval between the time during which irradiation is carried out and the time of thermal decomposition is not yet clear in all its details. With substances such as barium azide, on the one hand, it has been shown that the rate of subsequent thermal decomposition is affected by the length of this interval[101,136]. On the other hand, the length of the interval appears[143-147] to have no effect on the thermal breakdown of the irradiated permanganates of metals in Group I of the Periodic System, but it is extremely important when the interruption occurred — during the induction period, during the autocatalytic phase, or during the time of diminishing reaction velocity following the maximum.

In this connection it is of interest to study the rate of thermal decomposition directly at the instant of irradiation. It has been shown[157] by means of specially designed equipment[158] that exposure of barium azide to X-rays at the instant of thermal decomposition results in a greater increase in reaction velocity than with preliminary irradiation.

Besides the above data, according to which preliminary irradiation may strongly affect the rate of subsequent thermal decomposition, substances are known with which no such activating effect occurs, although their thermal breakdown takes place quite readily. An example is silver oxide, whose rate of subsequent thermal decomposition remains unchanged after preliminary exposure to γ-rays and neutrons over quite a wide range of doses[159]. The same applies to the thermal decomposition of potassium peroxochromate[101].

The criterion determining whether preliminary irradiation will affect the rate of subsequent thermal decomposition is still obscure, and different views are held concerning the mechanism by which the solid is activated.

According to one of these, the main part in the enhanced reactivity of solids resulting from preliminary irradiation is played by the excitation of electrons and ionisation, and ultimately by radiolysis of the solid. The products of radiolysis which appear in the lattice catalyse subsequent chemical reactions in which the irradiated solid is involved, including thermal decomposition processes.

According to another view, developed by Prout and his collaborators[142-147,159,160], the chief result of irradiation is the displacement of ions from normal lattice points into the interstices. In the course of subsequent thermal decomposition when the substance is heated, these defects are annealed, the interstitial ions returning to the lattice points which they had previoysly vacated. Owing to the accompanying evolution of heat, partial decomposition of the solid occurs even before the onset of general thermal decomposition. This decomposition is accelerated by deformation of the original lattice at the starting material–reaction product interface.

In his early papers Prout[160] suggested that this occurs as a result of elastic collisions of Compton electrons, formed in the primary acts of interaction between radiation and matter, with the lattice ions. This hypothesis, however, was not supported by the experimental data, either of other workers[33,136,148] or of Prout himself[161]. He therefore put forward a new hypothesis[161], according to which displacements can occur in the lattice not as a result of elastic collisions between electrons and ions but as a result of one of the possible displacement mechanisms associated with repeated ionisation of the anion in the ionic crystals. The possibility of displacements of this type, even when the energy of the radiation is low, has been shown[162-165] in the case of crystals of alkali metal halides. According to Prout's views, ionisation effects may appear in the rates of subsequent thermal decomposition mainly because of their being involved in processes resulting in displacement of ions from the normal lattice points into the interstitial space.

A critical comparison of these two points of view has shown[166,167] that the increased rate of thermal decomposition resulting from irradiation of solid salts cannot be reduced to displacement effects alone, but is associated to a considerable extent with the catalytic action of radiolysis products form by ionisation effects in the crystal lattice.

The principal objections to Prout's mechanism can be briefly summarised as follows.

1. According to Prout's mechanism in its original form, irradiation of a solid with γ-quanta and electrons of energy less than the threshold value should not produce displacements, and therefore will not accelerate subsequent thermal decomposition. This contradicts experimental results

indicating that irradiation may have a considerable kinetic effect in spite of its energy being far below the threshold value[33,136,148]. The concept of displacements resulting from repeated ionisation of the anion to some extent removes several objections to Prout's theory, but nevertheless does not eliminate them completely. If displacements resulting in activation of the solid are supposed to result from repeated ionisation of the anion and subsequent expulsion of the positively charged remnant from the lattice point, it must be assumed that those salts will be most sensitive to radiation in which the effective charge on the cation is greatest, or in other words the bond between cation and anion is most ionic in character. In compounds with a greater proportion of homopolar bond the probability of expulsion of an anion which has acquired a positive charge should be smaller, and the stability towards radiation therefore greater. If this were so, it would be expected, for example, that potassium permanganate would be more sensitive to irradiation than is silver permanganate. This contradicts experimental results; precisely the opposite is observed[33].

2. Similarly, doubt also arises concerning the validity of the other criterion which, in Prout's opinion, determines the sensitivity of a thermal decomposition to previous irradiation, namely the applicability of the Prout–Tompkins equation to the kinetics of the thermal breakdown. It is known that the applicability of a particular kinetic equation is not sufficient as a criterion of the occurrence of a chemical process in a solid by a given mechanism. Furthermore, direct experimental results are also known which indicate that a reaction which does not fit into the framework of a chain mechanism, and is not represented by the Prout–Tompkins equation, is nevertheless considerably speeded up by preliminary irradiation[68].

The fact that displacement effects play not the chief but a secondary part in the radiolysis of ionic salts is also indicated by results obtained by Henning *et al.*[46] These workers made a comparative study of the radiolysis of potassium nitrate on irradiation with fast neutrons, which lose a large part of their energy in the solid as a result of displacement effects, and with electrons, whose energy was below the threshold value required to produce displacement effects. The radiation yield was found to be about the same in the two cases.

This is confirmed also by calculations[54] showing that the number of displacements produced by each fission fragment of uranium in potassium nitrate crystals is smaller by two orders of magnitude than the number of nitrate ions decomposed per single fission fragment.

It is more likely that activation of the solid results from the appearance, in the crystal lattice after irradiation, of various defects and inclusions of radiolysis products, which catalyse the thermal decomposition. The formation of such inclusions in the lattice will result mainly from the capture of electrons, expelled by radiation into the conduction band, by anionic vacancies, by interstitial cations located at special points in the crystal (for example on dislocation lines), by impurity ions, etc., *i.e.* as a result of ionisation effects.

Displacement effects, which may change the concentration of ionic defects, also can influence the rate of subsequent thermal decomposition of irradiated materials. Sometimes they may even play the main part then, as is the case, for example, in the effect of preliminary neutron irradiation on the thermal breakdown of lead styphnate[156] and manganese oxalate dihydrate[155].

It can therefore be reckoned that in general both ionisation and displacement effects can be involved in the increased chemical reactivity of solids resulting from their preliminary irradiation. In most cases, especially when electromagnetic radiation and heavy corpuscular ionising radiation is used, the predominant part should probably be attributed to ionisation effects.

Apart from thermal decomposition, preliminary irradiation may substantially change the reaction velocity of ionic crystals in topochemical reactions of other types as well.

Preliminary exposure to protons increases the rate of reduction of nickel oxide by hydrogen[168,169] at low temperatures and the rate of dissolution of ferric oxide in hydrochloric acid[170]. Irradiation changes the adsorption capacity and other physicochemical properties of ionic crystals[171,172].

The mechanism of the change in reactivity produced in these substances by irradiation is probably analogous to that in the case of subsequent decomposition, and consists in the accumulation of defects in the crystals of the irradiated substance.

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STATUS OF THE THEORY OF ELECTRONIC ORBITALS IN MOLECULES AND SOME OF ITS PROBLEMS†

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Theoretical investigations of the electronic orbitals of molecules have developed during recent years in three main directions: (I) quantitative molecular calculations by means of electronic computers, (II) semiquantitative and semiempirical calculations of various properties and parameters of molecules, and (III) the search for new methods of calculation. This last line of research is, of course, interlinked with the other two, and therefore we shall not devote a special section to it.

I. PROBLEM OF QUANTITATIVE MOLECULAR CALCUTIONS

With improvement in automatic computing technique the number of publications in which calculations are made on molecules without using any experimental data on their properties has rapidly increased. Only the numbers of electrons and the nuclear charges of the atoms forming the molecules are assumed to be known. The ultimate aim of such calculations is to find the energy and wave functions of various states of the molecules; by means of these data complete information can in principle be obtained on the properties of the molecules. Up to the present such calculations have been carried out mainly for diatomic molecules.

In solving the problem, however, one comes up against serious mathematical difficulties. For the most part the calculations are based on the method of molecular orbitals (MO), which are set up in the form of linear combinations of specified atomic orbitals (LCAO). The coefficients in these molecular one-electron functions are chosen to make the best possible allowance for the field of the remaining electrons (introduction of self-consistent field according to Roothaan[1]). From the molecular orbitals thus obtained, the complete antisymmetric wave function of the molecule is constructed. If we then confine ourselves to the mode of distribution of the electrons among the molecular spin-orbitals which represent the lowest energy (which corresponds to representing the complete wave function as a single determinant), the results are not very satisfactory, being strongly dependent on the atomic wave functions initially chosen. If, for example, Slater functions are used, the relative error in the total energy is small (of the order of 1%), but the absolute error often amounts to 20–30 eV. In conformity with this, values are obtained for the dissociation energy which are less than the experimental value by a factor of 2–3, and sometimes are even negative (with F_2 for example)[2,3]. Errors of the same order of magnitude are obtained in the dipole moments of molecules[2–5].

There are several reasons for such a great divergence from the experimental data. Firstly, Slater functions are too approximate, and simply do not reproduce the properties of the atoms sufficiently well. Therefore the result is markedly improved when Hartree–Fok atomic functions are used. Thus for the HF molecule calculations with these two types of function give errors in the total energy of ~29 eV[6] and ~15 eV[7] respectively (the value obtained for the dissociation energy by means of Hartree–Fok functions was 2.11 eV compared with the experimental 6.08 eV).

The error in the latter case is partly due to the fact that molecular orbitals constructed from Hartree–Fok atomic orbitals are still not the best one-electron molecular functions. However, the maximum decrease in energy which can be achieved by complete self-consistency in the molecular orbitals is probably not large. Thus according to Allen and Karo's estimate[2] also for the HF molecule, this decrease can probably amount to 2–3 eV. The remaining 12–13 eV difference from the experimental value is due to correlation effects, *i.e* to interaction between the electrons.

Three methods have been worked out in the theory of the atom for taking account of electron correlation: calculation of interaction between configurations, explicit introduction of interelectronic distances into the wave function, and the method of open shells.

The calculations show that the configurational interaction method is very laborious and not very effective. For example, the introduction of seven configurations into the wave function for the HF molecule lowers the total energy by only 0.02% (less than 1 eV)[7]. Such a small effect is disappointing. Moreover, in several cases the use of a limited number of configurations makes the calculated values of various properties of the molecules worse instead of better (see, for example, Ref. 8). Probably the form in which the complete wave function is sought is a configurational series which converges very slowly; this calls into question the effectiveness of such a method when applied to molecules. With increase in the number of basic functions the number of multiply excited configurations grows very rapidly amounting to thousands, which makes the method unsuitable even for the best modern computers.

The method of introducing interelectronic distances into the molecular wave function was tried out for the hydrogen molecule[9] as early as 1933. During recent years Kolos and Roothaan[10] have found the most exact wave functions and energy of the ground state of H_2 by this method; their wave function contains fifty variational parameters, and their value for the bonding energy (4.7467 eV) shows excellent agreement with the experimental value[11] (4.7466 ± ± 0.0007 eV).

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The open-shell method consists in introducing different orbitals for electrons having different spins. As a result, electrons of opposite spins are somewhat separated from one another spatially, which produces a decrease in energy. The method has been used for calculations on the hydrogen molecule and several other diatomic molecules[12-17], and also for benzene[18,19]. It gives some decrease in energy, but nevertheless no decisive improvement is achieved.

Introduction of interelectronic distances into the wave function and introduction of different orbitals for different spins must probably be regarded not as independent methods for calculating the correlation of the electrons but as ways of improving the convergence of the expansion in configurations[20]. For example, a combination of these methods in calculations on the He atom to a one-determinant approximation reduces the error from 1.1 to 0.05 eV (three variational parameters were introduced: two effective charges on the nucleus to allow for radial correlation and the parameter α in the correlation factor $g = 1 + \alpha r_{12}$)[20].

However, it is difficult to expect that a combination of these methods could be applied with equal simplicity and success to many-electron atoms or molecules. With increase in the number of electrons the number of non-linear variational parameters grows in proportion, and the number of terms in the correlation factor increases very rapidly. As the number of variational parameters required for the H_2 molecule approaches fifty, it is easy to imagine how great this number will be for, say, the fluorine molecule. Until recently, however, the correlation factor method had not been worked out at all for many-electron systems. It was not clear to what extent complicated electronic correlations play a part in atoms and molecules: whether only pair correlations are important, or ternary, quaternary, etc. as well, and how they should be allowed for. It was also not clear what excited configurations must be considered in the first place.

Recently this problem has been examined in detail in a series of papers by Sinanoğlu[21,22]. First solving the problem by a perturbation method, he found that, for atoms and molecules not containing conjugated bonds, the principal contribution to the correlation is made by the pair interactions of electrons located in the same orbital. This is because in these systems the orbitals are separated spatially from one another, as a result of which the probability of "collision" between electrons in different orbitals and having antiparallel spins is very small. The long-range part of the electron interaction potential is allowed for by the self-consistent field, and therefore the potential causing the correlation is short-range; its value at points where the electron of another orbital is predominantly located is practically zero.

The significance of the correlation of electrons in the same orbital was discussed as early as 1940 by Fok *et al.*[23] They pointed out the necessity for taking account of the pair correlation in bivalent atoms.

Sinanoğlu showed further[22] that ternary correlations play practically no part, and the only quaternary correlations of importance are those corresponding to two independent pair interactions ("collisions"). As a result he found that the complete wave function ψ of a many-electron atom or molecule without conjugated bonds, taking into account all correlations of any degree of complexity, can be represented with sufficient accuracy by the pair correlation functions u_{ij} in the form of a sum of two terms: a one-determinant function Φ_0 made up of Hartree–Fok orbitals, and a function χ (orthogonal to Φ_0) which represents the correlation; the function χ is expressed in terms of the u_{ij} as a finite sum of terms having definite coefficients:

$$\chi = \hat{A}\left\{\frac{1}{\sqrt{2}}\sum_{i>j}^{N}(1\,2\,3\ldots N)\frac{u_{ij}}{(ij)} + \sum_{i>j}^{N}\sum_{k>l}^{N}(1\,2\,3\ldots N)\frac{u_{ij}u_{kl}}{(ijkl)} + \right.$$
$$\left. + \frac{1}{2\sqrt{2}}\sum_{i>j}^{N}\sum_{k>l}^{N}\sum_{m>n}^{N}(1\,2\,3\ldots N)\frac{u_{ij}u_{kl}u_{mn}}{(ijklmn)} + \cdots\right\}, \quad (1)$$

where $\hat{A}$ is the antisymmetrisation operator (1, 2, 3, ..., N), and $(ijklmn)$ the product of the spin-orbitals. The number of pair correlation functions required for the calculation is determined by the spatial and spin symmetry of the system and is approximately equal to the number N of electrons: *i.e.* with large N it is considerably smaller than the total number of pair interactions $\frac{1}{2}N(N-1)$. The functions u_{ij} can be determined by minimisation of a functional, which is expressed in terms of Hartree–Fok molecular orbitals[24]. This can be done either by a direct variational method or by solving the corresponding equation. In essence the problem of finding u_{ij} is analogous to finding the correlation factor in calculations on the He atom or the H_2 molecule.

A test of these conclusions in the case of the Be atom and the LiH molecule gave excellent results[22]. The coefficients of configurations representing quaternary excitations, found by Watson[25] for Be by successive solution of the four-electron variational problem (taking into account 37 configurations), agreed well with the coefficients obtained simply by multiplying corresponding coefficients of configurations with binary excitation in conformity with Eqn. (1). The contribution (found by Sinanoğlu) of the correlation energy to the total energy of the Be atom was approximately only 1% smaller than that found by the variational method. Similar results were obtained also for the LiH molecule.

According to Sinanoğlu[22] the total energy of an atom or a molecule can be written in the form

$$E \simeq E_0 + E_1 + \sum_{i>j}^{N}\tilde{\varepsilon}_{ij}, \quad (2)$$

where E_0 is the orbital energy, E_1 the Hartree–Fok energy of self-consistency, and the last term represents the correlation energy, which is to a good approximation the sum of the effective correlation energies of individual electron pairs, although actually it includes not only pair but also more complex correlations.

This result confirms in particular descriptive models of the atom and the molecule in which a many-electron system is regarded as a set of electron pairs located in separate orbitals (or bonds) and interacting feebly among themselves. These results provide also in justification for the π-electron approximation, since they show that the correlation of σ and π electrons, which are located in different orbitals, is small. The correlation of π electrons among themselves in conjugated systems, however, will be given special consideration, since owing to delocalisation of the correlation potential (just as in metals) it will no longer be a short-range effect (see below). In these cases other methods must be used to estimate the correlation; perhaps methods developed in the theory of the solid state[26,27] will prove effective here. It is also significant that Sinanoğlu's method has made it possible for the first time to calculate rigorously intramolecular interactions of atoms not directly linked together, which is especially important for the theory of internal rotation.

Thus Sinanoğlu's investigations probably open the way to quantitative calculations on atoms and on molecules not containing conjugated bonds. As yet it is difficult to say how far the method will prove effective in practical application to many-electron molecules. It is now clear that successful calculation requires exact self-consistent one-electron molecular functions as zero approximation. So far such functions are known only for atoms. For diatomic molecules this problem can probably be solved by means of electronic computers, and, as can be seen from the literature, is included in the work plans of several computing centres. In the case of polyatomic molecules the problem of finding exact self-consistent orbitals is very complicated. Perhaps self-consistency must be confined here within the framework of Roothaan's LCAO method[1]. The calculation[22] on the LiH molecule mentioned above shows that with Roothaan's molecular orbitals Sinanoğlu's method also gives comparatively good results. Perhaps practical calculations of correlation energy will prove necessary only for a series of typical examples, on the basis of which an additive scheme can be constructed by means of Eqn. (2), which will allow the energies of any molecules not containing conjugated bonds to be calculated if the energies of the self-consistent molecular orbitals are known for them.

Apart from the fundamental problems of finding self-consistent molecular orbitals and allowing for electron correlation, quantitative calculations on polyatomic molecules involve a serious problem of computation, which is the calculation of many-centre integrals. Estimates by approximate formulae give unsatisfactory results[28,29]. Attempts are now being made, both in the USSR and in the USA, to find a method for the numerical calculation of many-centre integrals on electronic computers. Another way of overcoming this difficulty, proposed by Boys as early as 1950, consists in replacing hydrogenlike atomic functions by gaussian functions, with which all integrals are obtained without difficulty[30]. In practice, however, this method involves a loss of accuracy, for the expansion of hydrogenlike functions in gaussian functions converges only over a finite range of change in the variable.

In quantitative calculations on molecules (and also atoms) a further problem arises, that of the relativistic corrections[31]. With atoms the relativistic correction to the electron energy increases rapidly with increase in nuclear charge. Thus whereas for the C^{4+} ion it is 0.35 eV, for Al^{3+} the correction is already 11 eV. With neonlike ions[31] the relativistic correction already exceeds the correlation energy for $Z > 13$, and exceeds the total energy of coulombic repulsion of the electrons for $Z > 65$. It is significant that with large atoms the relativistic correction is extremely sensitive to small perturbations of the electron shell, due, for example, to correlation.

II. SEMIQUANTITATIVE CALCULATIONS

The possibilities of quantitative calculations on many-electron systems are limited, of course, by their unwieldiness. Improvement of methods of calculation and computer technique may perhaps allow exact calculations to be made for molecules containing up to twenty electrons, but such calculations will hardly ever be undertaken for heavier molecules. Coulson[32] has commented facetiously that merely to write down a table of values, with a sufficiently small interval, of the wave functions for the uranium atom will require so much paper and ink that all the atoms in the whole solar system will not suffice for their production. And if it is borne in mind that the majority of the molecules of greatest interest to chemistry contain more than twenty electrons (for benzene the number is 42), it becomes clear that, for chemistry as a whole, those quantitative calculations which can actually be carried out do not present a task of primary importance. For the experimenter it is far more important that theory should give qualitative, descriptive explanations of facts and generalisations which so often puzzle him, and which for the most part require for their explanation not cumbersome calculations but simple, aptly chosen models. An approximate approach, representing a qualitative solution of the problems, is especially necessary in the case of large molecules, in particular those which are biologically active.

In chemistry there are, of course, many individual problems, solution of which requires quantitative calculations; an example is the exact calculation on the CO molecule, since it is impossible experimentally to determine unambiguously its dissociation energy D, the value of which plays a fundamental part in thermochemistry. Hurley's calculation[33] by the method of "atoms in molecules" enabled a correct choice to be made (the highest of three experimental values, D = 11.24 eV, proved to be the true one). Knowledge of fairly exact wave function remains important also in explaining new facts, for sometimes it is impossible to decide whether the failure of an explanation is due to an incorrect model or to the approximate character of the wave function. Solution of most qualitative problems of the structure and properties of molecules requires molecular wave functions of intermediate precision. Exact functions for the solution of such questions would only be unnecessarily complicated. Simplified functions, which are convenient for practical calculations, can always be readily obtained from them.

We shall now consider the main applications and most important successes of semiquantitative and semiempirical calculations of the electronic orbitals of molecules.

1. Theory of Conjugated Systems

This branch of the theory of the electronic structure of molecules, the foundations of which were laid by Hückel[34], has been developed by many workers. Important contributions to the theory were made in papers by Coulson[35-38], Lennard-Jones[39,40], Mulliken[41-43], Longuet-Higgins[44], and others. During recent years a series of interesting calculations on conjugated systems has been undertaken by Koutecký and his collaborators[45-51]. Recently Ruedenberg has published a series of papers[52] in which he has examined systematically, from a unitary viewpoint, the whole theory of π electrons in molecules containing conjugated bonds, within the framework of the LCAO-MO method taking into account the non-orthogonality integrals and electron interaction. He has found several new and interesting relations for quantities analogous to "bond order", and in some sense has summed up a definite stage in the evolution of the π-electron theory of conjugated systems.

At the present time fundamentally new results in the theory of conjugated systems can be expected from taking into account non-adiabatic conditions (*i.e.* interaction between the motion of electrons and of nuclei) and especially electron correlation. Both problems can be examined most successfully by a method of secondary quantisation, which

has been well developed and successfully applied in quantum field theory and in the theory of the solid state[26,27].

As noted above, owing to the delocalisation of electrons in conjugated systems, their correlation is not localised in electron pairs, and the correlation of each electron with all the others is important here. As a result, the estimation of correlation effects involves considerable difficulties. In general, self-consistent molecular orbitals for conjugated systems are no longer a sufficiently good zero approximation. Correlation effects are no longer as small as in light atoms and in molecules not containing conjugated bonds.

Conjugated molecules, like other many-electron systems, have energy levels representing "collective" states, which are not represented in the one-electron approximation. In three-dimensional systems (metals, heavy atoms) these collective levels are separated from the "one-electron" states, when the number of electrons N is sufficiently large, by an energy gap which remains finite as $N \to \infty$.[26,27] In the case of conjugated chains, the unidimensional character of the latter results in the collective levels merging with the main band, formed by the one-electron states, as $N \to \infty$.[53]

With finite N the collective levels in the molecular chains may appear in the electronic spectra. However, calculations of these spectra by existing methods cannot be regarded as completely satisfactory. Many workers[54-68] have made such calculations within the framework of the LCAO-MO method. Since in this work the electron correlation has been either completely disregarded or allowed for approximately (by taking into account a small number of configurations), satisfactory results have not usually been obtained, either for the levels or for the oscillator strengths.

For the planar cyclic molecule $C_{18}H_{18}$, for example, calculation gives[69] the following positions of the levels (in cm^{-1}): $^1B_{2u}$ 13 230, $^1B_{1u}$ 16 800, and $^1E_{1u}$ 33 920, whereas the corresponding experimental values are 20 350, 21 345, and 27 060. Discrepancies are obtained not only in the absolute but also in the relative magnitude of the terms (the relative values are 1 : 1.30 : 2.60 and 1 : 1.05 : 1.35 as calculated and measured respectively). It is surprising that discrepancies are obtained here in spite of the semi-empirical character of the calculation, which was based on values for several parameters found from data on the electronic spectrum of benzene. For the oscillator strength f of the transition to the $^1E_{1u}$ level (collective state) in the $C_{18}H_{18}$ molecule, experiment gives 1.7, whereas the calculated value[69] is $f = 6.8$.

Another example is provided by the polyenes, for which it was long ago noted that calculation by the LCAO-MO method (like that based on the potential box model) gives too strong a dependence of the position of maximum absorption in the electronic spectrum on the length of the conjugated chain[70-73].

In order to improve calculations on conjugated systems, we must learn to allow considerably more exactly for the correlation of electrons. This may apparently be done in two ways, by applying methods of secondary quantisation and by introducing various simple models.

Recently Nikitin[74] has suggested a simple model for the potential interaction of electrons in conjugated cyclic systems. He introduced the angle $\varphi_1 - \varphi_2$ instead of the distance between electrons, and expanded the interaction potential in a Fourier series, in which he retained only the first two terms. The wave equation can then be solved exactly, and therefore with this model the electron correlation can be assessed exactly. Nikitin found a series of excited collective states, which in the absence of electron interaction merge with the one-electron states, as they should. Allowance for the electron correlation was found to diminish the contribution of their mutual repulsion to the excitation energy of the collective states. For the $C_{18}H_{18}$ molecule, in particular, the ratios of the terms given above proved to be 1 : 1.00 : 1.95, *i.e.* considerably closer to the experimental values. The oscillator strength for the transition to the $^1E_{1u}$ level in the same model is $f = 3.4$, which is also far closer to the true value. In view of the crude model used by Nikitin, these results must be regarded as extremely encouraging. However, the reason for the discrepancy in the absolute magnitude of the terms remains obscure.

Another very important line of advance in the theory of conjugated systems is to allow for the interaction of the motions of electrons and nuclei (non-adiabatic conditions). This interaction must be borne in mind in attempts to explain the above peculiarities of electronic spectra. Allowance for non-adiabatic conditions is in general necessary in cases in which the electronic excitation energy is comparable with the energy of a vibrational quantum. Such a situation occurs, for example, when an electronic term which is degenerate as a result of molecular symmetry is split on destruction of this symmetry by molecular vibrations. Then the adiabatic approximation for electrons and nuclei is not applicable. Electrons and nuclei should be treated as a single system, the wave function of which can be written in the superposition form:

$$\Psi = \sum_n \varphi_n(X)\,\psi_n(x, X), \qquad (3)$$

where $\psi_n(x,X)$ is the eigenfunction of the whole set of coordinates x of the electrons at specified values of the coordinates X of the nuclei, and $\varphi_n(X)$ is the wave function of the nuclei relating to the n-th electronic state. As a result of the interaction of electronic and nuclear motions, the equilibrium configuration of the nuclei differs from that in the absence of such interaction; in particular, the original symmetry is destroyed, and the degeneracy eliminated. This effect, which has been termed the dynamic Jahn–Teller effect[75-82], is encountered in cyclic systems, in ion-radicals, in complex compounds, and in several other cases.

The Jahn–Teller effect is closely linked with the hypothesis of the alternation of bond lengths in long conjugated chains[70-73,83]. The reason for this alternation is simply that it is energetically advantageous: with alternating long and short bonds the band of electronic energy levels is split into two equal parts, the lower (filled) band being somewhat depressed, which produces a gain in energy. The extent of the alternation is, of course, limited by the forced shortening of some and lengthening of other σ bonds. It is difficult to calculate the resulting effect exactly, and nothing final can yet be said concerning its magnitude. Until now the influence of alternation only on the electronic spectra and on the magnetic screening of protons in nuclear magnetic resonance has been considered.

Longuet-Higgins and Salem[83] used alternation to explain the spectral peculiarities of cyclic polyenes $C_{4n+2}H_{4n+2}$, in particular of $C_{18}H_{18}$. However, according to Gouterman[69], new, more precise data on the spectrum of the $C_{18}H_{18}$ molecule cannot be explained on this hypothesis: the vibrational

structure of the spectrum, which would be expected theoretically, is not observed, the term ratios (1 : 1.4 : 1.58) do not correspond to the experimental values (see above), and the smallest possible oscillator strength is $f = 4.5$; in order to obtain this value, however, it is necessary to assume maximum alternation of bond lengths (1.33 and 1.52), which is intrinsically unlikely and above all gives poor results for the magnetic screening of protons. The negative result in the case of the $C_{18}H_{18}$ molecule is not surprising, since according to Longuet-Higgins and Salem[83], alternation should occur when the number of links in the chain exceeds 30. Whether it does actually occur in such long chains will be shown by future investigations. At the present time it seems quite probable that several features of shorter conjugated systems are to a considerable extent due to electron correlation. Nevertheless, it is quite possible that interaction between electronic and nuclear motions also plays some (as yet not entirely clear) part.

In this connection we may note that, when the non-adiabatic nature of the system is taken into account, the wave function is substantially many-electron in character even in those cases in which terms representing interaction of the electrons have been omitted from the original Hamiltonian. Actually, as can be seen from Eqn. (3), the wave function ψ can be regarded as broken down into configurations, which allows for electron correlation. Such interaction of electrons through the motion of the nuclei is equivalent in the method of secondary quantisation to interaction of the electrons with virtual phonons. It would be very interesting to apply to the treatment of non-adiabatic conditions and electron correlation in conjugated systems the method developed by Bogolyubov[26,27] in connection with the theory of superconductivity. It may be hoped in this way to erect a many-electron theory of the optical, electrical, and magnetic properties of conjugated systems.

2. Dependence of the Energy of the Ground State of Molecules and Radicals on Their Structure

This problem is very important for chemistry, since it is linked with finding the way in which the energy of bond rupture depends on molecular structure. An extensive literature has been devoted to this question, but it cannot be said that sufficient clarity has been achieved or a method found for estimating bond energies even semiempirically.

For a long time it was accepted in chemistry that the difference in energy between isomeric molecules and so-called deviations from the additive scheme of organic chemistry were due to conjugation and hyperconjugation. As calculations improved, however, it became increasingly clear that an important role belongs here also to such factors as the type of hybridisation of the orbitals, the length and polarity of the bonds, etc.[84,85] Nevertheless, numerical calculations of these effects made no appreciable progress.

As noted above, calculations by the molecular orbital method have so far usually given unsatisfactory results for bond energies, whether or not the interaction of configurations was taken into account. Apart from a series of diatomic molecules and radicals, this method has been used for calculations on the molecules[86,87] H_2O, O_3, NH_3, CH_4, HCN, CO_2, SiH_4, Be_4, and HCHO, and the radicals[88-91] CH_3, CH_2, and NH_2 (summary table in Ref. 2). Owing to the complexity of the calculations and the different degrees of approximation in different papers, these calculations shed no light on the problem of the dependence of dissociation energy on molecular structure. On the other hand, similar calculations on electronic computers do not yet have such an aim.

One elegant method for approximate calculations on unconjugated molecules, which was worked out by Mamotenko[92] in the Karpov Institute of Physical Chemistry even before the Second World War, has unfortunately been undeservedly forgotten (and among non-Soviet scientists it is probably simply unknown). The basic idea of this method is to utilise the invariance of the determinantal wave function of the molecule with respect to linear transformations of the basic one-electron functions, and to choose as the latter those for which the mean energy of coulombic repulsion of the electrons would become a minimum and could to a first approximation be neglected. This method probably gives correct relative values for the energies of the initial molecules (for example hydrocarbons). Mamotenko obtained a value of 104 kcal (experimental 102 kcal) for the energy of rupture of the C–H bond in methane, and 48 kcal for the height of the barrier to internal rotation in ethylene.

In our opinion Mamotenko's method is worthy of thorough study and development. If allowance were made in it for interaction between configurations, the method could be extended to conjugated molecules.

One result of Mamotenko's calculations[92] has been to establish the strong dependence of the bond energy on the type of hybridisation. Thus, for example, the energy of the C–C bond diminishes by 18 kcal on passing from sp^2-hybridisation to sp^3-hybridisation when the bond length (1.30 Å) is unchanged, but by 39 kcal when the simultaneous lengthening of the bond to 1.52 Å is taken into account. This probably means that change in the type of hybridisation is the main cause of breakdown in additivity in organic chemistry, while conjugation plays a subordinate part here. Recently Dewar[93] reached the same conclusion. However, his arguments cannot be regarded as completely convincing, since they were based only on experimental data in which the effects of hybridisation and of conjugation (or hyperconjugation) operate at the same time, and it is impossible to separate them.

Mention must be made of a semiempirical method for calculating the energy of molecules, proposed by Moffitt[94] in 1951 and termed the "atoms in molecules" method. The main idea of the method is to make maximum use, in molecular calculations, of experimental data on various atomic parameters (ionisation potentials, electronic terms, etc.). Although several difficulties[95-98] arise here, it is possible that with further improvement this method will achieve success[33,99-102].

3. Geometry of Molecules

One of the traditional tasks of quantum chemistry is to explain and predict the shape and size of molecules. The theoretical prediction of the equilibrium configuration of atoms is especially important for electronically excited molecules and for labile intermediate structures (for example activated complexes, radicals, carbonium ions, etc.).

It is significant that the electron correlation varies comparatively little with change in valence angles and slight

changes in bond lengths. This follows directly from Sinanoğlu's results[22], since changes in valence angles do not involve breakdown of the bonding electron pairs which make the main contribution to the correlation. The change in correlation will then be slight, since it will depend solely on the pair correlation of "foreign" electrons and on quaternary and higher correlations. Probably these effects mainly govern the difference in energy between rotational isomers, since it is most likely that self-consistent orbitals for different isomers differ little. It is therefore not surprising that the one-electron treatment of the geometry of simple molecules proposed by Walsh[103] possesses great predictive power. Starting from a few postulates and knowing only the number of electrons in a molecule, Walsh was able to explain and predict the shape of triatomic and several other molecules both in the ground and in excited states. Walsh's method is very important for analysing the vibrational structure of electronic spectra. Recently his starting postulates were analysed by calculating molecules of the type HAH by the molecular-orbital method with different basic atomic functions[104]. This work showed that Slater functions reproduce Walsh diagrams quite well, but it was observed that his first postulate, that with a valence angle of 90° the s function of the A atom does not combine with other functions, is usually satisfied only very approximately.

In some cases, of course, the geometry of the molecules is governed by the Jahn–Teller effect. Relevant calculations have been carried out for a relatively small number of molecules and complexes[76-82,105-108], although this is one of the very important problems of quantum chemistry.

Until now, unfortunately, still fewer calculations have been made on the geometry of labile species. Here we can mention only calculations on the radicals mentioned above[88-91], CH_3, CH_2, and NH_2, and also the complexes[109-115] H_3, H_3^+, and H_4. Nevertheless, a theoretical examination of the configuration of unstable intermediate structures is extremely important for chemical kinetics. The present level of computing technique obviously does not make it possible to calculate the absolute value of the energy, but it will probably permit calculations on the basis of which conclusions can be drawn concerning the energetically most favourable configurations of molecules and complexes.

4. Excited States of Molecules. Probabilities of Optical Transitions

Interest has greatly increased recently in excited, especially triplet, states of molecules. This is because the latter play an important part in processses involving energy transfer in condensed media, in chemical reactions, in luminescence, and above all in quantum multipliers and generators. Here theory has developed mainly in the direction of determining the position of electronic levels, their dependence on internuclear distances, and the probabilities of transitions between them. To some extent these questions have already been touched on above.

Quantitative calculations of the energy of the excited levels of molecules as a whole depend on the state of computing methods in the theory of many-electron systems. Apart from a few of the simplest examples, calculations which have been made up to the present are semiquantitative in character. They are very useful for the classification of energy levels, and also for testing different methods of calculation. In several cases semiempirical approximate calculations enabled the qualitative dependence of absorption frequencies and band intensities on molecular structure to be found, and in this lies, of course, one of the most important contributions of quantum mechanics to molecular spectroscopy[54-68].

One of the most important problems of the theory of electronic orbitals of molecules consists in finding the dependence of excited levels on interatomic distances. The absence of such data imposes marked limitations on many investigations.

This problem was partly solved for simple polyatomic molecules by Walsh[103] — semiempirically, as stated above. For diatomic molecules Vanderslice and Mason proposed in a series of papers[116-118] a semiempirical method of finding the dependence of the energy of excited states on the internuclear distance. They used for this purpose Dirac's expression for the energy operator[119]

$$\hat{\mathbf{H}} = \Sigma J_{ij}\,\vec{S}_i\vec{S}_j\,, \qquad (4)$$

where J_{ij} is the exchange integral between the i-th and the j-th orbitals. With diatomic molecules the energy of the levels can be expressed by means of two exchange integrals (for $p\sigma$ and for $p\pi$ orbitals), values of which can be determined, depending on the internuclear distance, from any two known potential energy curves for the given molecule. This yields self-consistent results, agreeing well with available data‡, for a series of excited states of O–O, O–N, N–N, and several other molecules. At first sight, however, such success seems surprising, for Dirac's formula (4) takes no account of non-orthogonality integrals, and hence would appear to have no claim to be a quantitative description.

The question of the applicability of Dirac's vector model has been discussed recently by Mattheiss[120]. Instead of the usual atomic functions he used as bases semilocalised orbitals orthogonal to the orbitals of neighbouring atoms. Taking into account all ionic structures having one atomic orbital filled twice, as well as the ordinary covalent structures, he showed that Eqn. (4) is valid provided that the exchange integral J in it is replaced by the effective quantity

$$J_1' = J_1 + \frac{2M^2}{E - H_1}\,,$$

where J_1 is the exchange integral between neighbouring semilocalised orbitals ($J_1 > 0$), E the energy of the system, and H_1 the diagonal matrix element for the corresponding ionic state. The sign of J_1' may be either positive or negative.

The result obtained by Mattheiss is significant not only in connection with the work of Vanderslice and Mason, since formula (4) can be conveniently used also for other purposes, for example in calculations of spin–orbital interaction.

The probabilities of optical transitions (oscillator strengths) are extraordinarily sensitive to the choice of wave functions, and therefore the corresponding calculations are usually very approximate. This problem cannot be regarded as solved, either for molecules or even for atoms. In this connection a method of calculating oscillator strengths proposed by Vetchinkin[121] merits attention.

‡ For calculations of excited states of several diatomic molecules, see also Ref. 8.

The basic idea is to find optimum wave functions for calculating the given matrix element. For this purpose the wave function should satisfy several conditions, which can also be used to find the parameters which it contains. The energy calculated by means of these functions is, of course, somewhat higher than the minimum value reached with the given form of tentative function. The method was tested on the lithium atom and gave good results, not inferior to those calculated by the Hartree–Fok method. It is applicable with equal success to molecules. It is significant that a similar method can be suggested for calculation of matrix elements of other quantities, and also for finding values of ψ in the vicinity of the nucleus.

Apart from the problem of calculating oscillator strengths of "allowed" transitions, calculations of the probability of transitions between states of different symmetry are extremely important for electronic spectroscopy. These transitions occur because the vibrations of molecules somewhat disturb their symmetry; when this is taken into account, the corresponding matrix elements are non-zero (so-called vibronic transitions). Thus we have here the same problem of allowing for the interaction between electronic and vibrational motion as was discussed above. The Jahn–Teller effect and "forbidden" optical transitions in molecules are the principal manifestations of this interaction [122].

Theory gives fairly good results for the probabilities of "forbidden" transitions. Thus calculation gives 0.26 compared with an experimental value [123] of 0.1 for the oscillator strength of the transition $^1A_{1g} \rightarrow {}^1B_{1u}$ in benzene. The most probable cause of the discrepancy is the approximate character of the molecular orbital adopted. The effect of electron correlation on the probability of vibronic transitions has not been investigated.

Another important problem is the calculation of the probability of singlet–triplet transitions. Here it is most interesting to elucidate the role of paramagnetic impurities [124–126] and of complex formation [127].

5. Calculations of Weak Interactions

In comparison with the coulombic interaction of charges, many intramolecular interactions and interactions with external fields are characterised by very low energies (of the order of 10^{-4}–10^{-14} eV). These include spin–spin interaction of electrons and nuclei, spin–orbital interactions, interaction of magnetic moments of electrons and nuclei with external magnetic fields, interaction of quadrupole moments of nuclei with external electric fields, etc. The problems involved in calculating such interactions have become especially urgent in connection with the rapid development of microwave spectroscopy. The necessity for interpreting various data on electron and nuclear magnetic resonance, quadrupole resonance, and microwave spectroscopy made it essential to solve several new theoretical problems connected with the structure of molecules, radicals, and complex compounds. Furthermore, calculation of weak interactions makes it possible to assess the quality of approximate wave functions of molecules. This possibility is based on the fact that, with different weak interactions, the main contribution to the mean value is given by different regions of space. Thus, for example, the diamagnetic part of the susceptibility of molecules depends on $\langle r^2 \rangle$, the diamagnetic part of nuclear screening on $\langle r^{-1} \rangle$, spin–orbital interaction on $\langle r^{-3} \rangle$, hyperfine interaction of electron with nucleus on $\langle r^{-3} \sin^2 \Theta \rangle$ and $\langle r^{-3}(3\cos^2\Theta - 1) \rangle$, etc. In the case of the simplest molecules satisfactory results are obtained for these quantities [128–130], although they do differ from the true values by factors of 1.5–2.

More difficult calculations arise for the so-called paramagnetic parts of the suceptibility and nuclear screening, which occur in second-order perturbation theory. Calculation of these quantities by means of the formulae of the theory [131,132] requires knowledge of the eigenfunctions and eigenvalues of all excited states of the molecule. Since they are unknown, such a procedure is impossible in practice. Calculations based on formulae obtained by the variational method [133–135] require knowledge of the wave function of the ground state alone. Since, however, these quantities depend on the second derivatives of this function, calculations with approximate functions yield unsatisfactory results. Thus, for example, the Heitler–London function gives for the paramagnetic part of the susceptibility of the H_2 molecule 0.465×10^{-6}, whereas the experimental value [130] is 0.0846×10^{-6}. When a more versatile wave function is used, a value of 0.106×10^{-6} is obtained [130]. A very exact wave function is obviously required for complete agreement with experiment. Similar difficulties arise in calculating the paramagnetic part of nuclear screening. In both cases a method can be found for avoiding the main source of error — double differentiation with respect to the coordinates — if molecular functions are constructed from atomic functions in which (as was suggested by London [136]) account had already been taken of the precession of electrons in an external magnetic field. This procedure was originally used by Aleksandrov to calculate magnetic screening [137]. It is comparatively simple to obtain quite satisfactory results for the paramagnetic part of magnetic screening [137] and also the susceptibility [138].

Good agreement with experiment is also difficult to achieve for the value of the wave function in the vicinity of the nucleus $\psi(0)$, which is necessary for calculation of the "contact" term in the expression for the energy of spin–spin interaction of nuclei among themselves [139–140] and with electrons [141,142]. In the one-determinant approximation of the molecular orbital method $\psi(0)$ often vanishes; the experimental value can be approached by allowing for the interaction of configurations. Thus the calculation of $\psi(0)$ represents a fairly rare example of a considerable improvement in the calculated result produced by allowing for excited configurations [128,143]. Satisfactory results can be obtained for $\psi(0)$ also by the valence bond method [144].

Many interesting and important tasks arise in interpreting the hyperfine structure of electron paramagnetic resonance spectra. Here data are obtained for the distribution of electron spin density [145–149] which are extremely interesting from the point of view of the structure of radicals. In particular, it has been found that this quantity does not in general correlate with the effective charge.

Calculation of the electric field gradient q was one of the first applications of quantum mechanics to microwave spectroscopy [150]. Recent investigations have shown that the early conclusions concerning the relative part played by hybridisation and the ionic character of bonds in producing the electron field gradient in the vicinity of the nucleus [151] must be seriously revised. The main difference between calculated and experimental (obtained from quadrupole resonance) values of q has been shown to be due to the fact that simple Slater functions, with which these calculations are usually made, give a poor descrip-

tion of the electron distribution in a region of overlapping atomic orbitals[152]. The introduction of different effective charges for different spins ("open shells") and for different molecular orbitals ($2s$, $2p\sigma$, $2p\pi$) of the nitrogen molecule considerably improves the calculated results, good agreement with experiment being obtained for the quadrupole bonding constant[152].

In conclusion we may note an interesting new field of application of quantum mechanics which has been revealed in connection with the recently started investigations of triplet states of aromatic compounds by means of electron paramagnetic resonance[153]. Here in particular, the problem[153-155] of elucidating the role of electron correlation arises.

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We have dealt briefly with several lines of advance and problems in the calculation of electronic orbitals of molecules. Several other questions in this field, which we have not touched on, are no less urgent. Among these are, for example, the theory of the structure of complex compounds and electron-deficient compounds, ligand field theory, intermolecular interaction and the donor–acceptor bond, the theory of the hydrogen bond, etc. The theory of the electronic orbitals of molecules represents an important branch of quantum chemistry. Not only chemical sciences but also many branches of physics are concerned in developing this theory and perfecting the technique of calculations on many-electron systems.

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REACTIONS OF OLEFINS IN THE PRESENCE OF METAL OXIDES

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INTRODUCTION

Metal oxides are widely used as catalysts in organic chemistry. Of particular interest are the various reactions of olefins in the presence of oxide and aluminosilicate catalysts, especially the recently developed polymerisation over transition metal oxides to produce solid polymers. These oxides and those of Group II metals are usually semiconductors, while the oxides of Group III and IV metals and aluminosilicates are predominantly dielectrics.

This review deals with the literature and patent data on the chemical reactions of olefins (polymerisation, isomerisation, redistribution of hydrogen, cracking, hydrogenation, and deuterium exchange) in the presence of metal oxides. The catalysts fall into two groups, dielectrics and semiconductors, although in some cases this is an arbitrary distinction, since there is no sharp boundary between the two classes[1-4].

I. POLYMERISATION OF OLEFINS

1. Non-Conducting Metal Oxides

Aluminium oxide does not polymerise ethylene at pressures up to 70 atm and temperatures of 320°–380°,[5-10] propene at atmospheric pressure and 150°–200°,[11,12] isobutene at 600°,[13] normal C_{6-8} olefins at 350°, [14] or olefins of

pyrolysis gases at 500°–515°.[9] Ethylene polymerises at 260° and 300 mm pressure over Al_2O_3 activated at 460° in a vacuum[15]. There is slight polymerisation of normal butenes at 400°–450°, with simultaneous cracking and isomerisation[16,17], of pent-2-ene and 3-methylbut-1-ene at 400°, giving cyclic polymers[18], of hept-1-ene[19] and of certain C_{6-8} isoolefins[14] at the moment of their formation by the dehydration of alcohols. Marked activity is shown by Al_2O_3 activated with HCl,[20-22] HF,[23] $AlCl_3$,[24] or LiH.[25]

Silicon dioxide in the form of thermally activated silica gel[11,12,26,27] or obtained by the hydrolysis of ethyl orthosilicate[10,28,29] is inactive at temperatures up to 350°.[8,10-12,26-29] Over silica gel at 670°–700° olefins undergo partial decomposition, polymerisation, and aromatisation[30]. Literature references to the polymerising activity of silica gel[31-35] relate to technical samples containing oxides of Al, Fe, Ca, and Mg, *i.e.* essentially to aluminosilicates.

Aluminosilicates. *Floridin.* The polymerising activity of natural aluminosilicates towards olefins at room temperature was first shown by Gurvich[36-39], who used Floridin. Lebedev and coworkers showed[40-46] that Floridin activated at 275°–325° (with loss of 12–13% moisture) causes the polymerisation at room temperature of asymmetric di- and tri-substituted ethylenes, while ethylene and its mono- and symmetric di- and tetra-substituted derivatives do not react. However, propene and but-2-ene polymerise under pressure in sealed tubes[42,47] or at atmospheric pressure and 350° (to the extent of 6%),[28] and ethylene and other olefins from cracking gases polymerise at 340°–470° under pressure[6]. Floridin is activated by concentrated hydrochloric acid[28]. Isobutene polymerises between -80° and 200°,[43,45,46] and more vigorously the lower the temperature. Gaseous isobutene gave a complex mixture of dimer (~20%), trimer (~30%), and higher polymers; the liquid, sealed in a tube, gave after 3–24 days a mixture containing ~70% of higher polymers. Diisobutylene polymerises completely, and triisobutylene not at all. An isobutene polymer of average molecular weight up to 8000 was obtained at -65° over Floridin of low activity[43,48,49].

Clays. Isobutene is the most readily polymerised, butene and propene with more difficulty, and ethylene not at all[50]. C_{3-4} olefins are polymerised at atmospheric pressure[51-54] and under a pressure of 35–50 atm[55] at 50°–190°, producing dimers, trimers, and higher polymers. Clays are activated by air at 320°–500°; a yield of liquid polymerisate of ~80% has been obtained from isobutene[26,55-57]. Isobutene copolymerises with propene at 200°–300° and 10–25 atm over the Georgian clay gumbrine[58]. Isooctene is best polymerised at room temperature over clays of low silica content[59]. The dehydration of 2-ethylhexan-1-ol over gumbrine at 140°–164° is accompanied by polymerisation[60].

Kieselguhr. Kieselguhr from Kisatibi[61] is a highly active catalyst which does not require preliminary activation, and converts isobutene mainly to dimers; at 160° the yield of liquid polymers reaches 77%.

Over *bauxite*[31,57,62-64] activated at 665°–775° isobutene is 82–90% polymerised, but-1-ene 13–16%, and but-2-ene not at all.

Synthetic aluminosilicates. Silica gel containing 1% of alumina is an active catalyst for the polymerisation of propene[28] and isobutene[65-69]. Water vapour, traces of alkali, ammonia, oxygen, and sulphur compounds deactivate the catalyst. Iron and magnesium silicates are inactive in polymerisation reactions. The isobutene polymerisates obtained over synthetic aluminosilicate, Floridin, and "solid" phosphoric acid were very similar in composition.

The most active synthetic aluminosilicate catalyst contains 10–12.8% Al_2O_3.[11,12,29,70-74] At the optimum temperature of 160° isobutene gave a liquid product which was 97% di- and tri-isobutylenes[70]. n-Butenes and n-pentenes polymerise at 400°–450°.[75] The maximum yield of isobutene–propene copolymers (heptenes) is obtained at 250° and 25 atm,[58] and of isobutene–2-methylbut-2-ene copolymers at 110° and 35 atm;[76] regenerated catalyst was more active than fresh catalyst[10]. Similar results were obtained with a $ZrO_2-SiO_2-Al_2O_3$ cracking catalyst[77].

The patent literature describes aluminosilicate catalysts, containing 0.5–20% Al_2O_3, for the polymerisation of olefins[62,78-86] and catalysts containing Zn, Zr, Be, Mg, Mn, Ti, Cd, Fe, Cr, Cu, and Th (20–50%) as activators[10,87-92]. Zn and Tl deactivate an aluminosilicate catalyst for isobutene polymerisation[69].

2. Semiconducting Metal Oxides

Oxides of Group II metals. Over ZnO propyl chloride forms propene and its liquid polymers at 250° and 36 atm, apparently with intermediate formation of the biradical $CH_3\dot{C}H\dot{C}H_2$.[93] At 100° and 26–73 atm isobutyl chloride gave isobutene and its dimers and trimers[94]. Direct polymerisation of propene and but-1-ene in the presence of ZnO and CaO takes place at 150° under u.v. irradiation[95].

Oxides of Group III metals. Alumina containing 10% of rare-earth oxides (Ce, Nd, Gd, Sm, Dy, Er, Yb) has been used for the polymerisation of ethylene[96]. The most active oxides are those of Dy and Yb, the oxides of Nd and Gd being slightly less active. Cerium oxide is inactive. At 240° and 140 atm total pressure ethylene gave solid polymers when $LiAlH_4$ was added as activator. Only liquid polymers were obtained when triisobutylaluminium was added. TiH_4 did not activate the process at all. With these catalysts there was no polymerisation of propene.

Oxides of Group IV metals. The oxides of Ti,[21,25] Zr,[10,21,25] and Th[9,21] polymerise C_{3-5} olefins at 100°–600°; u.v. light promotes the reaction[95]. Ethylene polymerises at 140° and 70 atm in the presence of TiO_2 activated with LiH.[25] When hexan-1-ol and 2-ethylhexan-1-ol are dehydrated over ThO_2 at ~400°, the polymer is obtained in 10–15% yield; C_{6-8} olefins themselves are 3–4% polymerised[14].

Oxides of Group V metals. Solid polymers of α-olefins have been obtained[97-100] using oxides of V, Nb, and Ta on various carriers (γ-Al_2O_3, SiO_2,[97-101] MgO, TiO_2, ZrO_2, and aluminosilicate[101]) activated with hydrogen at 250°–350° or by addition of alkali and alkaline earth metals and their hydrides, hydroborates, or hydroaluminates. The oxides of V and Nb were the most active, and the oxide of Ta less so[102]. Ethylene and propene have

been polymerised at 75°–325° and 14–350 atm in a diluent (toluene, xylene, or decalin).

Oxides of Group VI metals. *Chromium oxide* alone is not very active in the polymerisation of gaseous olefins[9,103], but propene is vigorously polymerised to liquid hydrocarbons at 310° and 150 atm in the presence of Cr_2O_3 on Al_2O_3. Steam intensifies the reaction. At 185 atm there is ~95% reaction[104]. The liquid product contains a mixture of dimers[105]. A mixture of ethylene and higher olefins at 850° in the presence of aluminosilicate containing 3.4% Cr_2O_3 gave mainly benzine[73,106].

The industrial conversion of olefins to solid polymers[107-114] is of great interest. One of the catalysts used is chromium oxide on aluminosilicate[102,105,107,115-142], the optimum amount being 2–5%.[107,118,119,131-134] The best carrier is an industrial synthetic aluminosilicate catalyst with $SiO_2 : Al_2O_3 = 9 : 1$;[107,118,122] also useful are metallosilicates[123], natural aluminosilicates[118], activated carbon[120], and oxides of Si, Al, Zr, and Th.[103,105,118,126,129,134,139] Solid polymers are given by all α-olefins containing not more than 8 carbon atoms and in which there is no branching closer to the double bond that the fourth carbon atom[107,128,129,132]; an exception to this rule is 4-methylpent-1-ene, which gives a solid polymer[107]. Copolymerisation of olefins can also be accomplished[115]. Polymerisation can be effected both in the vapour phase at 83°–250° and atmospheric pressure[119,128,133] and in the liquid phase in a diluent at 55°–250° and pressures up to 42 atm[107,114-122,129,130,133-140,142] with a fixed or suspended catalyst. The olefin must be carefully freed from H_2O, O_2, CO_2, and CO. The yield and molecular weight of the polymer are greatly dependent on the composition, method of preparation and content of the catalyst in the solution, the temperature and duration of its activation, the reaction temperature and pressure, and the time of contact. Chromium oxide catalysts do not require preliminary reduction or addition of activators, although the latter improve their properties[102,143-153]. The activators may be alkali and alkaline earth metals[102,143-145,149,152] and their oxides[150], hydrides, and hydroborates[102,152,153], aluminium trialkyls[120], alkali metal hydroaluminates[102,143-145,152], alkaline earth metal carbides[151], sodium pentyl[148], and certain metals and their mixtures (La, Ce, Nd, Th, and U).[153] A catalyst prepared by impregnating synthetic aluminosilicate with CrO_3 solution and treating with air at > 300° contains mainly Cr^{VI} and is inactive[103]. At 350° the Cr^{VI} is partially converted to Cr^{III} and at 480°–500° the ratio $Cr^{VI} : Cr^{III}$ is 1.55–3.2[118] – these are the most active catalysts. Above 600° this ratio decreases and the activity again falls: increasing the activation temperature from 450° to 600° gives a polymer of lower molecular weight[118,154]. If the aluminosilicate is impregnated with chromium nitrate solution, the catalyst is activated at a higher temperature (550°–600°) and with a faster flow of air[103,118]. The optimum concentration of catalyst is 2–3%.

Electron paramagnetic resonance has shown that in aluminochrome catalysts [Al_2O_3–Cr_2O_3 (Ed. of Translation)] containing less than 3–4% of chromium oxide the Cr_2O_3 microcrystallites consist of 3 or 4 atomic layers bonded to the carrier, the surface layer of microcrystals containing a considerable number of Cr^{3+} ions[155].

The reaction temperature and the molecular weight of the polymer decrease with increasing molecular weight of the olefin. The optimum reaction temperature is 150°–180° for ethylene and 105° for propene[107,118-120]. When the reaction temperature for the polymerisation of ethylene was increased from 110° to 170°, the molecular weight of the polymeric product fell from 100 000 to ~25 000[107] and its yield decreased by a factor of 1.6.[118,154-159] The yield and molecular weight of the polymer increased with increasing pressure over the range 6–60 atm.[107,118,154]

Oxides of Mo and W deposited on Al_2O_3 and *tungsten oxide* on activated carbon are active in the conversion of propene to a mixture of isohexenes[73,105]. Isobutene is converted to dimers and trimers at 200° over MoO_3/Al_2O_3, and at 300°–450° polymerises with subsequent dehydrocyclisation of the reaction products[160]. Ethylene polymerises to solid polymers over a hydroforming catalyst or over MoO_3 deposited on γ-Al_2O_3 (1 : 4)[161-165], TiO_2, ZrO_2,[166] or on aluminosilicate[167]. Temperatures of 75°–325° and pressures up to 350 atm give polymers of molecular weight up to 50 000. Preliminary treatment of the Mo catalyst with acetylene prevents coke formation and increases the useful life of the catalyst[168]. Reaction takes place in the vapour phase or in a diluent[146]. Reduction of pressure in the range 55–70 atm and increase of temperature in the range 100°–400° increases the yield of liquid products. Even at 320° liquid polymers are formed almost exclusively[169]. Catalysts based on oxides of Mo, W, and U are treated with hydrogen and activated by adding Li, Na, CaH_2,[102] or CaC_2,[170] which reduce the catalyst, remove catalyst poisons[152], and also participate directly in the reaction[102,114].

Oxides of Group VIII metals. *Oxides of Pd and Fe.* Ethylene has been polymerised to high molecular weight polymers using Pd oxide on aluminosilicate activated by hydrogen above 600°[171] and Fe oxides on aluminosilicate activated by air at 510°.[172]

Nickel oxide does not polymerise ethylene[173,174] or but-1-ene[175] at 270°–300°. Ethylene decomposes explosively at 330° and 49 atm in the presence of a $4NiO–2Al_2O_3–CuO$ catalyst. At 500°–515° pyrolysis gas gave traces of liquid polymers; under these conditions the use of cobalt oxide produced soot, H_2, and CH_4.[9] Nickel oxide deposited on silica gel[176-178], silicate glass[179], kieselguhr[174,180-183], active carbon[174,184], thorium dioxide[185], and synthetic aluminosilicate[173,177,178,181,184,186-189] is active. The earliest studies in this field were by Sokolov and coworkers (see Kazanskii *et al.*[177]). The polymerisation of ethylene in the presence of NiO on various carriers was studied in detail by Eidus and Kazanskii and their coworkers[175,177,190-198]. The deposition of NiO on technical samples of silica gel by precipitation or impregnation with solutions of nickel salts gave inactive catalysts[177-190], with the exception of NiO on KSK silica gel, which produced 20–30% dimerisation of ethylene and 7–11% polymerisation to liquid products. Technical silica gels contain up to 1.5% Al_2O_3,[199,200] and this apparently causes the activity of the catalyst, which, however, rapidly declines[190]. In fact a small amount of Al_2O_3 has a strong promoting action on an NiO–KSK silica gel catalyst in the polymerisation reaction, both at atmospheric pressure[177,191] and at 135 atm.[176] The selective action of the NiO–KSK silica gel catalyst promoted with Al_2O_3 in respect of ethylene dimerisation is considerably increased by adding oxides of Cu, Ag, Zn, Ba, and Mn; the addition of oxides of Ag, Ca, and Ba reduced the total activity of the catalyst, and the addition of oxides of Ag, Ca, and Mg greatly reduced its stability. Addition of oxides of Cu, Zn, Mn, Mg, or Th did not affect the activity[176,192].

Nickel oxide on synthetic aluminosilicate is the most active and stable catalyst for the polymerisation and copolymerisation of olefins at temperatures from room temperature to 300° and pressures of 1–40 atm.[177,181,184,186,187,193,201] The optimum content of NiO is 4%.[173,177,201] Ethylene gives predominantly the dimer at 275°–300° and atmospheric pressure with a time of contact of 2.5 sec over this catalyst[194]. The rate of polymerisation decreases with increasing molecular weight of the olefin[181,187]. In the presence of an equal volume of H_2 ethylene is 97% converted to a mixture of true polymers, ranging from butenes to dodecenes and higher polymers, at 40° and 20 atm,[201] while at 70°–93° and 41 atm propene mixed with propane gives a liquid polymerisate in a yield directly proportional to the propene concentration. The life of the catalyst is increased several times by carrying out the polymerisation of olefins in the presence of diluents[201]. Hydrogen acts as a diluent only at comparatively low temperatures. At 260°–270° H_2 promotes polymerisation[186]. Over an impregnated NiO–aluminosilicate catalyst at the optimum temperature of 275° ethylene gives as the main product either the dimer (at atmospheric pressure) or liquid hydrocarbons (at 30 atm).[197] Increase of the pressure to 30 atm and of the temperature to 275° favours the formation of liquid hydrocarbons. The liquid polymerisate obtained from ethylene at 275° and elevated pressure comprises ~16–32% hexenes, ~18–23% octenes, 25–35% higher hydrocarbons, 12–24% "odd" polymers (C_5, C_7, and C_9 hydrocarbons), and 4–11% semi-solid residue boiling above 300°.[198] The main constituents were 3-methylalk-2-enes, with lesser amounts of 2-methylalkenes, dimethylalkenes, and the corresponding alkanes[198]. At atmospheric pressure the main product was the dimer but-2-ene, with lesser amounts of liquid hydrocarbons comprising ~45% hexenes, ~15% octenes, ~15% "odd" polymers, and ~25% higher hydrocarbons containing 2-methylalk-2-enes and a large quantity of α-olefins[196]. Gaseous olefins polymerise at 0°–140° and 1–45 atm over an NiO–kieselguhr catalyst[174,178–183,202–204]. The activity of this catalyst is due to dehydration during its activation. In the presence of a diluent ethylene polymerises to solid polymers at 100°–180° and 55–70 atm over an NiO catalyst on active carbon previously reduced by H_2 or activated by NaH or $LiBH_4$.[169,170,205,206].

Oxides of metals of Groups II–VIII are thus weak catalysts for the polymerisation of olefins; their deposition on carriers (metal oxides, aluminosilicates) produces active catalysts, and the polymerisation may produce either low- or high-molecular-weight polymers. Isoolefins (isobutene) are the most vigorously polymerised over natural and synthetic aluminosilicates, over a wide range of temperatures and pressures. Normal olefins require most severe conditions, and ethylene does not polymerise at all. The composition of the reaction products is similar to that of the polymerisates obtained in the presence of acids. Over transition metal oxide catalysts on aluminosilicates as carriers it is the normal olefins which are generally polymerised, and ethylene most vigorously of all. Low-molecular-weight polymerisation of olefins provides polymers which are multiples of the initial olefin. High-molecular-weight polymers are obtained from these catalysts after activation with hydrogen or special activators, at elevated temperatures and pressures, while in the presence of aluminosilicates high-molecular-weight polymerisation takes place at atmospheric pressure and ~ -80°. Over NiO catalysts the polymerisation of ethylene can be controlled so as to produce predominantly either the dimer or high-molecular-weight polymers.

II. ISOMERISATION OF OLEFINS

In the presence of metal oxides olefins may isomerise with shift of the double bond or change of the carbon skeleton, or they may undergo *cis–trans*-isomerisation. These processes are reversible, and depending on the conditions and the oxide used may proceed simultaneously or selectively[207].

1. Non-Conducting Metal Oxides

Aluminium oxide catalyses the shift of the double bond in the olefins produced by the dehydration of alcohols[27,208–214]. Over carefully purified Al_2O_3 butan-1-ol gives only but-1-ene[215]; but-2-ene is formed when the alumina contains acidic impurities and also when the temperature is raised[213,216,217], above 400° isobutene also being obtained[17,208,218–220]. At 150°–400° n-pentyl[221] and isopentyl[222–225] alcohols gave a mixture of pentenes differing in the position of the double bond. In the dehydration of a series of higher alcohols[14,226–229] some results indicated a displacement of the double bond and carbon-skeleton isomerisation, while according to others[19,224,229–231] there was no isomerisation or only a shift of the double bond. Over Al_2O_3 activated at 450° there is rapid isomerisation of n-butenes[16,17,232] and of pent-1-ene to pent-2-ene,[23,233] while over Al_2O_3 activated with HF there is carbon-skeleton isomerisation also[23,234]. The equilibrium composition of the isopentene mixture is reached in ~12 h at 250°–400°.[233,235–237] Shift of the double bond in hexenes of various structures takes place at 80°.[237] At 190°–440° there is also carbon-skeleton isomerisation, although equilibrium is not reached[14,226,238]. The calculated and experimental equilibrium compositions of hexenes at 100°–480° have been given[14,234,238,239]. Neohexene does not react at all[227]. Aluminium oxide treated with HCl or HF[22,207,234,238,240–242] or containing acidic additives (ammonium sulphate, kieselguhr)[226] caused the isomerisation of a series of C_{6-16} olefins at 190°–340°; cracking and polymerisation occurred to a marked degree. As a rule n-olefins are converted to the monomethyl-substituted isomers with the methyl group at the double bond, and then to dimethyl substituted isomers, the second methyl group being generally in position β with respect to the first. To a certain extent there is a shift of the double bond and the methyl group to the centre of the main carbon chain. In the case of C_{12-16} olefins the di- and tri-methyl substituted isomers are converted to monomethyl substituted isomers. Shift of the double bond in olefins to the centre of the molecule has been observed with Al_2O_3 on pumice at 330°–380°,[243] γ-Al_2O_3 containing metallic Na at 0°–100°,[244] and Al_2O_3 treated with HF at 300°–600°.[245] Under the same conditions Al_2O_3 can produce carbon-skeleton isomerisation of n-olefins[246,247].

Silicon dioxide in the form of technical silica gel can promote equilibration in the case of n-butenes even at 200°,[27,238] with partial formation of isobutene and pentenes[33]. Raising the temperature to 380° produces carbon-skeleton isomerisation. Hex-1-ene[22], *trans*-4-methylpent-2-ene, 3,3-dimethylbut-1-ene, 3-methylpent-2-ene, and 4-methylpent-1-ene[226] are not isomerised over silica gel at 300°–340°; however, silica gel becomes markedly active when treated with HCl[22] or irradiated with fast neutrons[248]. Equilibrium in the double bond displacement reaction with olefins of the type $RR'C{=}CH_2$ and $RCH{=}CR'R''$ is reached even at 25°, and the more rapidly the greater the ratio of silica gel to olefin[226,249]. Over

SiO_2 at 400° oct-1-ene is converted mainly to mixed methylheptenes[250].

Aluminosilicates. *Clays* produce isomerisation when isobutyl alcohol is dehydrated over them[251]. Butan-1-ol gives only but-2-ene over a clay–infusorial earth catalyst[252], a mixture of three butenes over gumbrine and askanite at 400°–450°,[253,254] and a mixture of n-butenes over bentonite and Uchkekensk clay†[255,256]. In the presence of Glukhov clay and Floridin n-butenes (diluted with steam to suppress polymerisation) are 6–7% converted to isobutene at 294°.[257] At 260°–335° hex-1-ene is converted to methylpentenes over activated clay[258,259]. The dehydration of 4-methylpentan-2-ol and heptan-2-ol over Floridin at 300°–385° gives mixed hexenes and heptenes respectively, differing in the position of the double bond[224]. At 160°–170° 3,3-dimethylbut-1-ene and 4,4-dimethylpent-2-ene undergo irreversible isomerisation to 2,3-dimethylbut-2-ene and 2,3-dimethylpent-2-ene respectively[260].

Permutite produces carbon-skeleton isomerisation of butenes and pentenes at 400°[261] and of hexenes at 335°.[22]

Andalusite converts pent-1-ene at 300°–550° mainly to pent-2-ene and only to a slight extent to methylbutenes[262].

Bauxite activated at 700° produces an equilibrium mixture of n-butenes at 250°–550° from mixtures of various composition[220,263-265].

Synthetic aluminosilicates produce isomerisation of olefins[29,75,77,263,266-270]. Shift of the double bond in n-butenes takes place at a rapid rate even at 100°–150°; equilibrium between the n-butenes is readily established at 270°–500°. At 400°–600° up to 40% of isobutene is formed, with simultaneous polymerisation and cracking[75,77,267]. Under the same conditions the reverse isomerisation of isobutene to n-butenes takes place, but without reaching equilibrium. A stereospecific isomerisation of but-1-ene to but-2-ene has been observed at 65°–66°; at low degrees of conversion the unstable *cis*-but-2-ene is the main product. Irradiation of the catalyst with γ-rays or neutrons reduces its activity, but does not affect the stereospecificity[271]. At 400° n-pentenes are more than 50% converted to methylbutenes[75]. The equilibrium compositions of pentenes[77,267,272] and hexenes[22,240] at various temperatures have been determined. As a result of hydrogen redistribution in the isomerisation of C_{6-8} olefins[207,241,273,274] the thermodynamically unstable as well as the stable isomers become saturated. The reactions of n-olefins over synthetic aluminosilicate catalysts have been studied by Naragon[240].

Among other metal silicates, those of magnesium ($2MgO.SiO_2$) and zinc ($2ZnO.SiO_2$) convert pent-1-ene at 300°–500° into a mixture of pent-2-ene and 2- and 3-methylbut-1-enes[262]; magnesium silicate is more active than zinc silicate, and the latter more active than andalusite.

2. Semiconducting Metal Oxides

Oxides of Group II metals. At 450° *beryllium oxide* produces shift of the double bond and carbon-skeleton isomerisation; hept-1-ene is converted predominantly into methylhexenes[250,275]. At 100° and 14 atm but-1-ene is 90–95% isomerised to but-2-ene in the presence of activated *magnesium hydroxide*, with simultaneous formation of liquid hydrocarbons. Pentenes are also isomerised under these conditions[276]. There is a shift of the double bond in butenes over *calcium oxide* at 600°.[232,264,265] *Zinc oxide* is inactive below 450°,[93,277-279] but at 450°–650° it produces shift of the double bond in olefins, and above 650° dehydrogenation and decomposition occur[279]. The addition of 1% Ga^{3+} to ZnO does not markedly affect its catalytic properties, but addition of 1% Li^+ completely suppresses them.

Oxides of Group IV metals. Over *thorium dioxide* at 385° but-1-ene, as such or at the moment of its formation from butan-1-ol, isomerises to but-2-ene, with some polymerisation and decomposition[232,233,280]. Hexenes and heptenes also isomerise[232,233]. n-Olefins are converted to isoolefins over thorium and zirconium oxides at 332°–555°.[246,281]

Oxides of Group V metals. Mutual interconversion of hept-1-ene and hept-2-ene without change of the carbon skeleton occurs at 400°–480° over *vanadium trioxide* deposited on Al_2O_3 (1 : 10).[282]

Oxides of Group VI metals. But-1-ene is about 80% converted to but-2-ene at 250°–260° over black *chromium oxide* (CrO_2).[283] In the production of aromatic hydrocarbons from isoolefins over Cr_2O_3 at 474° the isoolefins are first isomerised to n-olefins[14,284]. The chromium oxides may be deposited on an aluminosilicate carrier[232,233,285].

Molybdenum oxide produces shift of the double bond in hexenes at 400° and 140 atm; no carbon-skeleton isomerisation was observed[286,287].

Oxides of Group VII metals. Manganese oxide on Al_2O_3 shifts the double bond in isopentenes[233].

Oxides of Group VIII metals. *Nickel oxide* promotes polymerisation and decomposition to a considerable extent, and it is therefore not considered to be an effective catalyst for the isomerisation of olefins[9,233,278]. NiO on Al_2O_3[233] or aluminosilicate is an active catalyst for shift of the double bond in n-butenes at 270° and for carbon-skeleton isomerisation of ethylene polymers at 275°.[198] An NiO–glass catalyst does not isomerise butenes[175]. The activity of NiO containing Cr_2O_3 is directly proportional to the Cr_2O_3 content, and is due to the presence of nickel chromate as a new phase[278].

Cobalt and iron oxides on aluminium oxide produce shift of the double bond in isopentenes at 300°–370°.[233]

In the isomerisation of olefins the most active catalysts are thus the non-conducting oxides of metals of Groups II–VIII. Over these the reaction proceeds to equilibrium over a wide range of temperatures from room temperature to 500°. Below 150° there is only *cis–trans* isomerisation and shift of the double bond towards the centre of the molecule; this last reaction takes place most readily with isopentenes having a side chain at the double bond. At 250°–500° carbon-skeleton isomerisation also occurs. Over Al_2O_3 carbon-skeleton isomerisation of C_5 and higher olefins proceeds practically to equilibrium, but over aluminosilicates this does not happen, because redistribution of hydrogen produces some hydrogenation of the thermodynamically unstable olefins. Carbon-skeleton isomerisation over non-conducting metal oxides proceeds stepwise: normal olefins are converted to the monomethyl substituted isomers, predominantly with the methyl side chain at the double bond, and then the dimethyl substituted

† Chem. Abs. translates this as "bentonite", Chem. Abs., 42, 1562 h (1948) (Ed. of Translation).

isomers are produced. Typically, higher hydrocarbons undergo "straightening" of the carbon chain, but at a low velocity. 2- and 3-methylalkenes and 2,3- and 2,4-dimethylalkenes with the double bond at the "tertiary" carbon atom undergo isomeric conversions at a reduced rate.

Over semiconducting oxides of metals of Groups II–VIII only shift of the double bond of C_{4-8} olefins takes place at 300°–650°, sometimes under pressures of up to 140 atm. Oxides of Group II–IV metals can be used as isomerisation catalysts without a carrier, but oxides of Group VI–VIII metals require a carrier (Al_2O_3, aluminosilicates), since when used alone they produce vigorous decomposition and polymerisation of olefins.

III. DECOMPOSITION OF OLEFINS

The decomposition of olefins over metal oxides may proceed with rupture of C–C and C–H bonds simultaneously, and this is typical of the high-temperature decomposition when the composition of the final reaction products is little affected by the structure of the molecule (catalytic cracking). This type of reaction is used for the production of high-octane motor fuels[288,289] and C_{3-4} olefins employed as starting material for industrial petrochemical synthesis[290]. Another type of olefin decomposition reaction, which is used to obtain pure olefins, such as isobutene[291-295], occurs by rupture of C–C bonds and is formally the reverse of polymerisation, *i.e.* depolymerisation[287]. This is a low-temperature process, the nature of the products depending on the structure and molecular weight of the initial olefin. Lebedev and Koblyanskii have shown that the polymerisation of olefins over Floridin, which commences from ~200°, is complicated by depolymerisation of the resulting polymers[45,46].

A. CATALYTIC CRACKING

1. Non-Conducting Metal Oxides

Aluminium oxide and silicon dioxide separately are not very active in the cracking of olefins[23,296,297]. Treatment of aluminium oxide with HF [23] or HCl [242] or addition of even hundredths of a per cent of Al_2O_3 to SiO_2 [240,296,297] produces highly active cracking catalysts. Natural clays are also active[258,298].

Synthetic aluminosilicates. Over synthetic aluminosilicates olefins of various structures and molecular weights are cracked at 350°–450° to form C_{1-4} hydrocarbons and liquid products consisting of olefins and aromatic and saturated hydrocarbons[75,77,266,267-269,299-302]. Fig. 1 shows the conversion of normal olefins at 400° over a synthetic aluminosilicate catalyst as a function of the molecular weight.

2. Semiconducting Metal Oxides

But-1-ene undergoes vigorous dehydrogenation and decomposition at 615° over *zinc oxide* containing 1% Ga in a nitrogen atmosphere, producing C_4H_6, C_3H_6, and C_2H_4 in the ratio 2 : 2 : 1.[279] Isobutene is unchanged under these conditions, while 3-methylbut-1-ene and 2-methylbut-2-ene are dehydrogenated and lose the methyl group.

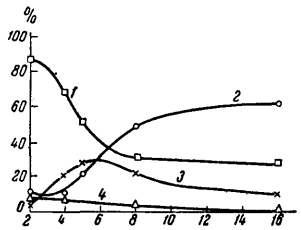


Fig. 1. Distribution of conversion products of n-olefins at 400° and space velocity 6.8 moles per litre of catalyst per hour, as a function of molecular weight:
1) unreacted olefins; 2) cracking products boiling below the initial olefin; 3) polymerisation products; 4) coke formation.
y axis: percentage conversion of olefin;
x axis: number of carbon atoms in the initial olefin.

At 500°–515° *nickel and cobalt oxides* degrade C_{2-4} olefins to methane and carbon[9].

B. LOW-TEMPERATURE DECOMPOSITION

Unlike catalytic cracking, low-temperature decomposition takes place at 150°–200°, but only with olefins of a certain structure and only over aluminosilicates[303].

Floridin and clays depolymerise olefin polymers at low temperatures[36-39,304] With polymers of isobutene and the isopentenes the reaction commences at a temperature as low as 50° and proceeds vigorously at 50°–250°;[41,43-46,305] polymerisation of the monomers and dimers takes place simultaneously, together with some redistribution of hydrogen. The depolymerisation is easier the higher the molecular weight: diisobutylene is the most stable, while triisobutylene decomposes practically completely into diisobutylene and isobutene[296,305,307]. Dimers of isobutene and its copolymers with n-butene are depolymerised over clay[308,309] and Volga kieselguhr (Volga opoka)[310], the yield of isobutene increasing with temperature over the range 200°–428°.

Synthetic aluminosilicates are sometimes more active[310] and sometimes less active[308,309] than natural clays in the depolymerisation of diisobutylene. At 367° triisobutylene is 70% depolymerised to isobutene[299]. Only olefins with two or more alkyl side chains in the β-position relative to one another undergo low-temperature decomposition[303,310].

Over aluminosilicates C_{2-12} olefins are cracked at 350°–500°, mainly with rupture of C–C bonds; isomerisation, aromatisation, polymerisation, and hydrogen redistribution take place at the same time. The ease of decomposition increases with the molecular weight of the olefin and the reaction temperature. Isoolefins react more readily than their normal isomers. At 150°–250° olefins with alkyl

side chains in the β-position relative to one another undergo decomposition, and the more readily the greater the number of such side chains in the molecule. Al_2O_3 and SiO_2 do not produce cracking of olefins even at 300°–450°, but they become active in this respect after treatment with mineral acids (HF, HCl). The semiconducting metal oxides which have been studied require higher temperatures (~500°–600°) to produce decomposition of olefins.

IV. REDISTRIBUTION OF HYDROGEN

The formation of saturated hydrocarbons takes place in the polymerisation[11,12,28,58,74], isomerisation[207,241,273,274], and cracking[75,77,258,262,266-269,298,299,301,311-313] of olefins over aluminosilicates. This reaction is sometimes used to improve the anti-detonation properties and stability of fuels[290,314-319].

1. Non-Conducting Metal Oxides

Aluminium oxide and silicon dioxide. Neither aluminium oxide nor silica gel is active in the redistribution of hydrogen in olefins. Al_2O_3 activated with HCl is an active catalyst for the refining of highly unsaturated petroleum fuels[320,321].

Aluminosilicates. Over *Floridin* saturated hydrocarbons are produced in the depolymerisation of dipentenes[41]. Alkanes are obtained from cracking petrol at 260° over activated clay[258,311,322-324]. Over *synthetic aluminosilicates* the reaction takes place with butenes at 300°–400°[320] and with oct-1-ene and 2-ethylhex-1-ene at 250°.[324] The reaction proceeds selectively[267,301,311,324] and most readily with olefins containing a "tertiary" carbon atom at the double bond, the hydrogen donors being either hydrocarbons [acyclic hydrocarbons? (Ed. of Translation)], which are converted to coke-like condensation products[207,301,311,325,326], or naphthenes[320]. Molecular hydrogen, like nitrogen, acts as a diluent[207,267]. The redistribution of hydrogen between naphthenes and olefins at 300°–400° is most vigorous on a catalyst containing 75% SiO_2.[320] Isoolefins become saturated considerably more readily than normal olefins. Coke is formed mainly from the olefin.

2. Semiconducting Metal Oxides

Up to 20–50% of ethane is produced in the dehydration of ethanol over *titanium dioxide* at 360°–400°.[327] *Chromium oxides* deposited on Al_2O_3 are inactive even at 400°.[267] The polymerisation product of ethylene at 275° and 1–30 atm over an NiO–aluminosilicate catalyst contains up to ~50% of saturated hydrocarbons, predominantly of iso-structure[198].

The data reviewed in this section show that the redistribution of hydrogen in olefins or between olefins and naphthenes occurs mainly in the presence of aluminosilicates. This reaction is important in the refining of unsaturated petroleum fuels and is best conducted at 250°–450° and 1–8 atm. Olefins with a tertiary carbon atom at the double bond are the most readily saturated, so that isoparaffins accumulate in the reaction products, and this improves the anti-detonation properties of the motor fuels.

V. HYDROGENATION OF OLEFINS, *ortho–para*-HYDROGEN CONVERSION AND DEUTERIUM–HYDROGEN EXCHANGE

Several reactions characteristic of metal catalysts also take place over metal oxides: hydrogenation, H–D exchange, and *o–p*-H_2 conversion. These reactions apparently take place on oxide films on the metals[328,329]. Hydrogenation over oxide catalysts proceeds at 250°–500°, when the oxide may be partially reduced to the metal, so that it is difficult to decide whether the hydrogenating activity is due to the metal or oxide. *o–p*-Hydrogen conversion and deuterium exchange over oxides take place at temperatures from -200° to 0°, when there can be no reduction of oxide to the metal.

A. HYDROGENATION OF OLEFINS

Oxides of Group I metals. Among these *copper oxide* possesses hydrogenating activity; in its presence ethylene and hydrogen produce ethane and a little methane at 180° and 60 atm. Trimethylethylene is almost completely converted to isopentane at 300° and 100 atm.[330]

Oxides of Group II metals. ZnO and MgO are inactive at 400° and atmospheric pressure[331]. ZnO is deactivated by small amounts of water and is activated by prolonged heating in a vacuum at 450°. Polymerisation and decomposition also occur in addition to the hydrogenation[332]. Irradiation of ZnO with γ-rays reduces its hydrogenating activity[333].

Oxides of Group III metals. Ethylene is ~80% hydrogenated to ethane at 500° over *aluminium oxide* activated at 400°–800°.[334] SiO_2 deactivates Al_2O_3. The hydrogenating activity of Al_2O_3 is due to deformation of its surface because of dehydration during the heating[335-341]. However, because of the high temperature used the hydrogenation may be only semi-catalytic, *i.e.* without activation by the hydrogen catalyst[339].

Oxides of Group IV metals. Ethylene is hydrogenated slowly over *titanium dioxide* at 300°–400°.[327,331]

Oxides of Group V metals. Isobutene, hex-1-ene, and oct-1-ene are 80–98% hydrogenated at 300°–400° over *vanadium trioxide* on Al_2O_3, this being accompanied by isomerisation[342-346].

Oxides of Group VI Metals. Olefins are hydrogenated at 350°–400° and 1–49 atm over amorphous *chromic oxide*[342,343,347], and at 200°–350° over thoroughly purified Cr_2O_3.[343] Crystalline Cr_2O_3 is inactive[348,349]. Addition of potassium and treatment with air reduce the activity of Cr_2O_3.[285] Its activation by treatment with hydrogen has been ascribed to partial reduction[350]:

$$Cr_2O_3 + H_2 \rightarrow Cr_2O_3 \cdot H_2 \rightarrow (CrO_2) \cdot H_2O. \quad (1)$$

Ethylene is hydrogenated at 184° over an $MnO–Cr_2O_3$ catalyst, with simultaneous vigorous decomposition[351]. Over a $Cr_2O_3–Al_2O_3$ catalyst hydrogenation proceeds to the extent of 94% at 200°;[334,352] the rate of hydrogenation of mixed n-butenes over this catalyst is given by the equation[353]:

$$W = kP_{H_2}P_{C_4H_8}^{0.5}. \quad (2)$$

An MoO_3 catalyst prepared from ammonium nickelomolybdate was very active, because of the formation of metallic

nickel; a catalyst prepared from ammonium phosphomolybdate and paramolybdate had a low activity[347]. The hydrogenation of ethylene over an MoO_3–aluminosilicate catalyst at 150°–350° and 50–400 mm Hg apparently proceeds by a radical–chain mechanism, and at high degrees of conversion its rate is reduced by the formation of ethylene polymers[354,355].

Oxides of Group VIII metals. The hydrogenation of ethylene to ethane at 130°–140° and 60 atm over *nickel oxide* is accompanied by considerable decomposition[330].

B. *ortho–para*-HYDROGEN CONVERSION

This reaction takes place at 20°–86°K and ~1.05 atm over Gd_2O_3, CeO_2, NiO, 2% paramagnetic Fe_2O_3 on porous glass, Fe_3O_4, 20% Cr_2O_3 on Al_2O_3, 15% paramagnetic Fe_3O_4 + 9.3% Cr_2O_3 on Al_2O_3, MnO_2,[356,357] and ZnO.[358-360] Of iron oxides the most active at -195° is the antiferromagnetic α-Fe_2O_3.[361] Even more active are the hydroxides of certain elements with an incomplete 4*f*-electron shell (hydroxides of Pr, Gd, Tb, and Dy) or 3*d*-electron shell (hydroxides of Cr, Mn, Fe, Co, and Ni);[362] this is ascribed to dilution of the paramagnetic ions. The concentration [high concentration? (Ed. of Translation)] of these ions in Cr_2O_3, NiO, and Fe_2O_3 is the cause of their antiferromagnetism and reduced catalytic activity.

C. DEUTERIUM–HYDROGEN EXCHANGE

1. Non-Conducting Metal Oxides

Aluminium oxide. Over heat-activated γ-Al_2O_3 H–D exchange takes place at temperatures from -124° to +200°,[334,337,362] the activity being determined by the degree of dehydration. Addition of sodium Al_2O_3 does not promote H–D exchange[363], but addition of NaH [364] or irradiation with γ-rays, α-particles, or neutrons[365] does favour the exchange. Adsorption and deuterium exchange take place when two molecules are present on one active centre[366].

Aluminosilicates. Deuterium exchange takes place at 150°–350° in the presence of *synthetic aluminosilicates*; its rate depends on the SiO_2 content and the activation and reaction temperatures[334,367,368] (Fig. 2). Above 350° there is considerable saturation, polymerisation, and cracking in addition to the deuterium exchange[367]. The activity of silica gel, quartz, and synthetic aluminosilicates in deuterium exchange at room temperature is greatly increased by irradiating them with γ-rays or neutrons[365].

2. Semiconducting Metal Oxides

In their activity in deuterium exchange the oxides of Group II–VIII metals lie in the series[4,350,358,359,369-371]:

$$WO_3 \gg FeO + Fe_3O_4 > ZnO > Al_2O_3 > ThO_2 > MgO > Cr_2O_3 > ZrO_2 > CeO_2 > > V_2O_5 > TiO_2, \quad (3)$$

and supported oxides in the series:

$$NiO + \text{kieselguhr} > Cr_2O_3 - Al_2O_3 > MoO_3 - Al_2O_3 > Cr_2O_3 - Fe_2O_3 - K_2CO_3 > WO_3 + + Al_2O_3 \gg \text{clay, bauxite} > \text{aluminosilicate}. \quad (4)$$

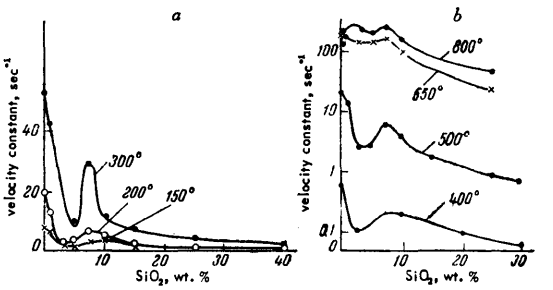


Fig. 2. Velocity constant of the deuterium–hydrogen exchange reaction as a function of the SiO_2 content of aluminosilicate and:
a) as a function of reaction temperature (activation temperature 500°); *b*) as a function of activation temperature.

The activity of oxides deposited on aluminosilicate decreases in the series:

$$ZnO > NiO > Cr_2O_3 > WO_3,\ UO_3,\ Fe_2O_3 > MoO_3\ . \quad (5)$$

Deuterium exchange over metal oxides is accelerated by raising the temperature to 350° and by treating the oxides with hydrogen. Traces of water completely deactivate them. The activity of ZnO when additives are present (Li_2O, Al_2O_3, and Ga_2O_3) changes in parallel with the conductivity[372-374].

At temperatures from -78° to 0° and 10 mm Hg the only active oxides are those of metals of approximately the same distance from the beginning and the end of the IVth Period (Cr_2O_3, Co_3O_4, and NiO) having some, but not too many, unpaired *d* electrons (Fig. 3)[375]. The low catalytic activity of oxides of metals at the beginning of the Period is due to the absence of *d* electrons; the oxides of metals in the centre of the Period have a stable $3d^5$ structure, while those of metals at the end of the Period have a full *d* shell. All these factors produce a slow rate of adsorption of hydrogen, and hence low catalytic activity.

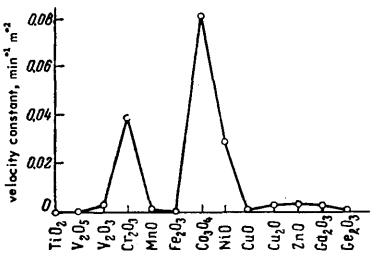


Fig. 3. Activity of the oxides of metals of the Fourth Period in deuterium–hydrogen exchange.

VI. NATURE OF THE CATALYTIC ACTIVITY AND THE MECHANISM OF THE REACTIONS OF OLEFINS IN THE PRESENCE OF METAL OXIDES

The difference in catalytic activity between non-conducting and semiconducting metal oxides in the olefin reactions reviewed reflects their differing abilities to activate C=C, C–H, and H–H bonds, and hence the mechanism of their catalytic activity is different. Thus over non-conducting oxides isoolefins are more readily polymerised than n-olefins, while with semiconducting oxides the reverse is true. The activity of semiconducting oxides in isomerisation, cracking, and disproportionation of hydrogen is less, but in hydrogenation, deuterium–hydrogen exchange, and *o*–*p*-hydrogen conversion it is greater than that of non-conducting oxides. This is seen from Fig. 4‡.

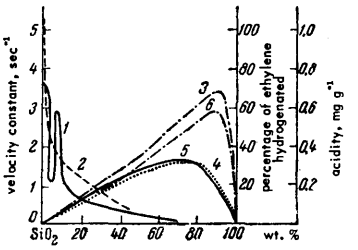


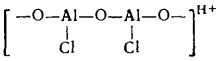
Fig. 4. Variation of velocity constants and acidity of the catalyst with SiO_2 content of a synthetic aluminosilicate:
1) hydrogenation of ethylene at 500°; [334] 2) deuterium exchange at 300° ($k \times 10$); [334] 3) polymerisation of propene at 200 ($k \times 10^3$); [376] 4) isomerisation of but-1-ene to isobutene at 340°; [320] 5) redistribution of hydrogen; 6) the acidity of the catalyst, as functions of the SiO_2 content of a synthetic aluminosilicate.

1. Non-Conducting Oxides

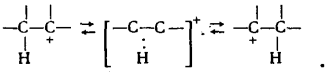
Aluminosilicates, aluminium oxide, and silicon dioxide have acidic properties [376-381] and a direct relationship exists between their catalytic activity and their acidity [28,29,297,381-387] determined by titration [29,388] with bases in non-aqueous solutions [376,377,389,390] and by the change of colour of indicators adsorbed on them [390]. Aluminosilicates react with solutions of carbonates [391,392] and with the Zerewitinoff reagent and hydrolyse sucrose [391]; they lose their activity when hydrogen ions are removed from their surface by exchange with alkali or alkaline earth metal ions [382] or ammonium ions [387] or when neutralised with organic bases [387,393,394].

The catalytic activity and acidity of aluminosilicates has been ascribed to the complex $(HAlSiO_4)_x$ which is present on the surface of inactive silicon dioxide [29,395] and which can liberate a proton. This complex is produced during the preparation of the catalyst by condensation of the alumina and silica gels produced by hydrolysis [376]. The replacement of silicon atoms (coordination number 4, valency 4) in the silicate lattice by aluminium atoms (coordination number 4, valency 3) produces an excess of electrons around the aluminium atoms, because of the known ability of the aluminium atom to accept an electron pair to complete the *p* orbital [29,376,381]. In an aqueous medium the electron pair is donated by water, and hydroxy-groups become components of the solid phase, as has been shown by isotope exchange of the oxygen of $H_2{}^{18}O$ with aluminosilicates [335]. When aluminosilicate catalysts are activated by heating, the surface loses water, with partial removal of protons [377,396,397]; in this case the activity of the aluminosilicates is apparently due mainly to the formation of an aprotic Lewis acid [391,398]. The formation of a new phase during the preparation of active aluminosilicates is demonstrated by their preparation from the inactive Al_2O_3 and SiO_2, the order of deposition of one oxide on the other not affecting the activity [399]. It has been shown [400-403] that the catalysts of maximum activity contain 30% Al_2O_3 and 70% SiO_2, which corresponds to the compound $Al_2O_3.4SiO_2$. X-Ray diffraction has also shown that the formation of a hydroaluminosilicate phase, similar to montmorillonite, during the preparation of aluminosilicates is a maximum with samples of composition $Al_2O_3.4SiO_2$. [404]

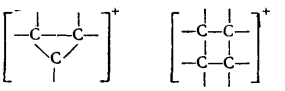
It has been suggested that the proton source in aluminosilicates and certain oxides activated with mineral acids is acid adsorbed on the surface [22,23]; for Al_2O_3 and HCl it has been shown that the acid is not only adsorbed by the oxide, but reacts with it to liberate a proton [207,405]:



Since aluminosilicates are acids and behave like strong mineral acids, their catalytic action has been explained by a mechanism involving the intermediate formation of a carbonium ion [23,29,75,77,267,297,396,406,407], as suggested by Whitmore for the polymerisation of olefins in the presence of acids [408-415]. Recently new forms of carbonium ion have been suggested. In a π-complex the proton occupies a position between the two carbon atoms of the double bond, as opposed to the classical structure of the carbonium ion (or σ-complex) with an open sextet of electrons [271,414-420]. The two forms may undergo interconversion:



In a π-complex the proton may be replaced by a methyl or other alkyl group:



The prevailing opinion, however, is that the reactions of olefinic hydrocarbons in the presence of acid catalysts are better explained by the classical carbonium ion structure [418,421,422], and this finds confirmation in the greatly differing affinities of the proton for the different carbon atoms of the double bond in asymmetric olefins [423-425].

Many investigators [14,218,253,254,284,426-428] have considered a molecular mechanism for the reactions of olefins in the

‡ A similar diagram has previously been published [383], but with certain inaccuracies in the scale when the curves were plotted. We have corrected these and amplified the diagram by including a curve showing the velocity constant for the isomerisation of but-1-ene to isobutene as a function of the SiO_2 content of the catalyst.

presence of aluminosilicates, the basis for this being L'vov's suggestion[429] of the intermediate formation of alkylcyclopropanes in the chemical reactions of olefins and alcohols.

2. Semiconducting Oxides

In their catalytic action semiconducting metal oxides are intermediate between transition metals and non-conducting metal oxides. The catalysis over semiconducting oxides proceeds at temperatures where there is marked lability of oxygen atoms on the surface; this is in accord, in particular, with oxygen exchange between $^{18}O_2$ and MgO, Al_2O_3, Cr_2O_3,[430] and ThO_2.[431] This may be the reason for the temporary deficiency of oxygen on the oxide surface, as a consequence of which its electronic structure alters. At present the catalytic activity of transition metal oxides is ascribed to their semiconductor properties and to the electronic arrangement of the *d* shell of their atoms[4,328,329,369,416,432-434].

Electronic theories of catalysis are based on the band theory of the solid state[435-438], which considers metal oxides as ionic solids[375], the outer free electrons of which belong to the whole crystal and move in the periodic field of the crystal lattice in various energy bands. The presence of free electrons on the surface of metal oxides is caused primarily by ionic defects in the crystal lattice, produced during the preparation of the catalysts or during the reaction by dissolution of the excess of metal or because of the excess of oxygen. In oxides with an excess of metal in the crystal lattice (*e.g.* ZnO, CdO, TiO_2, Al_2O_3, etc. — *p*-type semiconductors) there are either metal ions in the interstices or empty anionic positions with an equivalent number of free electrons. In oxides with an excess of oxygen (*e.g.* NiO, Co_3O_4, Cu_2O, CoO, etc. — *n*-type semiconductors) there are empty cationic positions and an equivalent number of holes. The electronic semiconduction in *n*-type semiconductors is due to electrons moving from donor impurity levels to the conduction band, and in *p*-type semiconductors, to the positive holes produced as a result of the transfer of electrons of the oxide to electron-acceptor impurity levels. The electrical conduction and catalytic activity of oxides can be controlled by the addition of metal cations of known ability to donate or accept electrons[439]. According to other results, the introduction of "foreign" cations into ZnO does not change the electronic structure of its surface, but does change the heterogeneity of the surface[440]. Defects are formed only on the surface of metal oxides, since the rate of diffusion of defects into the lattice at catalysis temperatures has a high temperature coefficient[432]. In oxide semiconductors of a third type (*e.g.* Cr_2O_3) the defects do not arise from impurities in the lattice, since they are stoichiometric in composition, but because of the transfer of electrons from the filled band to the conduction band, when they are excited[4,441] as a result of the reaction.

An important factor in the formation of structural defects is the participation of the carrier. Thus magnetic methods have shown that when deposited on γ-Al_2O_3 NiO has a higher concentration of holes, and hence a higher catalytic activity[442]. Similar results have been obtained for other oxides (Al_2O_3, MoO_2,[443] ZnO, BeO, Fe_2O_3 [444]). All these are the so-called "biographical" defects, which are retained at temperatures near absolute zero. Defects in a catalyst's crystal lattice may also be produced by the action of heat[328], and the equilibrium concentration of thermal and biographical defects in real crystals may be of the same order as the concentration of active centres[445,446]. Finally, defects may arise and disappear because of chemisorption of the reactant molecules, the chemisorbed species being considered as impurities embedded in the surface of the crystal[328].

Irrespective of their method of production, the defects can move along the surface of the crystal lattice, particularly readily as the temperature is raised, can interact among themselves with their disappearance or the formation of new defects, can be absorbed and generated by the crystal lattice, and, finally, can localise free electrons or holes, thus acting as adsorption centres[328,447-450]. When participating in the chemisorption of the reaction components, the free electrons and holes function as free valences[328]. The free valences are not localised in the lattice, but wander about the crystal, continually arising and disappearing. Their equilibrium concentration in the crystal and on the surface depends on a number of factors, primarily on the nature of the catalyst and the reaction conditions; they may be controlled by external action (illumination, introduction of impurities, etc.). The free valences of the catalyst not only participate in the formation of bonds between the surface and the reactants, but also promote dissociation of adsorbed molecules, with the formation of reactive surface species of radical, ionic, or unsaturated valence type, so that the reactions may proceed by a radical[451] or ionic[328] mechanism. The chemisorbed species may change the nature of their bond with the surface, passing from one state into another. The function of the catalyst is basically to generate these reactive species on the surface by means of the free valences[451,452].

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POLYFLUORINATED LINEAR BIFUNCTIONAL COMPOUNDS (CONTAINING LIKE FUNCTIONS) AS POTENTIAL MONOMERS

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INTRODUCTION

An effective method of increasing the stability of polymeric materials is to introduce fluorine atoms into the "framework" of their chains. However, the chemistry of fluorine-containing polymers has developed relatively one-sidedly owing to the poor availability of polyfluorinated bifunctional compounds.

Fluorine-containing polymers have been obtained mainly by the polymerisation of unsaturated fluoro-monomers (mainly fluorine-containing derivatives of ethylene and propene). Nevertheless, during the past two or three years a great deal of experimental information has accumulated on the preparation of perfluorinated and polyfluorinated bifunctional derivatives, such as various perfluorodicarboxylic acids, their esters, nitriles, amides, and amidines, $\alpha H, \alpha H, \omega H, \omega H$-perfluoro-diamines and -glycols, perfluoro-$\alpha\omega$-dienes, perfluoroolefin oxides, and several others.

At the present time a versatile method for the preparation of stable new polymers (by polycondensation) has become available to chemists working in the polymer field. The authors of the present review have endeavoured to survey the methods of preparation and the properties of those polyfluorinated bifunctional compounds, containing two like groups, which may be potential monomers for the preparation of new fluorine-containing polycondensation polymers.

1. FLUORINE-CONTAINING ALKADIENES

The known fluorine-containing alkadienes comprise mainly compounds in which only a proportion of the hydrogen atoms have been replaced by fluorine atoms. Butadienes of various degrees of fluorination have been prepared in many ways and have been relatively well studied. Several perfluoro-$\alpha\omega$-dienes of the type $CF_2:CF[CF_2CF_2]_nCF:CF_2$, where $n = 1, 2, 3$, etc., are also known, as well as some fluorine-containing allenes.

Fluorine-containing alkadienes can polymerise by themselves, or copolymerise with other olefins. The polymerisation of perfluorobutadiene and of fluoroprene and their copolymerisation with other olefins have been studied in some detail. Perfluorobutadiene polymerises only under high pressures, forming a solid polymer. Higher analogues of perfluorodienes condense only on irradiation[1-12].

Fluorine-containing olefins exhibit electron-acceptor properties, and react very easily with nucleophilic reagents, which has enabled fluorine-containing alkadienes to be used to obtain various sulphur-, nitrogen-, and oxygen-containing polymers[13]. Furthermore, fluorine-containing alkadienes present wide opportunities for obtaining other bifunctional compounds, such as acids, esters, amines, diols, etc.

The principal methods of obtaining fluorine-containing alkadienes are examined below.

(*a*) Fluorination of Halogenated Hydrocarbons with Subsequent Dehalogenation or Dehydrohalogenation of the Products

The usual method for obtaining compounds of low molecular weight containing fluorine is the fluorination of halogenated hydrocarbons. Fluorine-containing halogenoalkanes on dehalogenation or dehydrohalogenation are readily converted into olefins in good yields. For example, fluorination of 1,2-dichlorodifluoroethylene gives in one stage 1,2,3,4-tetrachlorohexafluorobutane, from which perfluorobutadiene has been prepared[14] by the action of zinc in alcohol:

$$2CFCl{=}CFCl + F_2 \rightarrow CF_2ClCFClCFClCF_2Cl \xrightarrow[C_2H_5OH]{Zn} CF_2{=}CFCF{=}CF_2.$$

1,2-Dichlorodifluoroethylene on heating forms 1,3,4,4-tetrachlorotetrafluorobut-1-ene, which on chlorination gives hexachlorotetrafluorobutane. Fluorination of the latter with antimony trifluoride, followed by dechlorination of the product, yields perfluorobutadiene[15]:

$$2CFCl{=}CFCl \rightarrow CFCl_2CFClCF{=}CFCl \rightarrow CFCl_2CFClCFClCFCl_2 \rightarrow$$
$$\rightarrow CF_2ClCFClCFClCF_2Cl \rightarrow CF_2{=}CFCF{=}CF_2.$$

Similarly, trichlorofluoroethylene gives 2,3-dichlorotetrafluorobuta-1,3-diene:

$$2CFCl{=}CCl_2 + F_2 \rightarrow CF_2ClCCl_2CCl_2CF_2Cl \rightarrow CF_2{=}CClCCl{=}CF_2.$$

However, by no means all alkadienes containing fluorine can be obtained in this way, since, firstly, the fluorination of hydrocarbons and their halogeno-derivatives usually gives a mixture of products which are difficult to separate, and, secondly, not all halogenoalkanes can be converted into the desired alkadienes. Therefore this method is of very limited application.

Reaction of 3-chloropent-2-ene with hydrogen fluoride and antimony trifluoride gives 3,3-difluoropentane, which on partial chlorination yields 1,5-dichloro-3,3-difluoropentane in one stage, from which 3,3-difluoropenta-1,4-diene can be obtained[16] by the action of alkali:

$$CH_3CH_2CCl{=}CHCH_3 + HF \xrightarrow{SbF_3} CH_3CH_2CF_2CH_2CH_3 \xrightarrow{Cl_2}$$
$$\longrightarrow CH_2ClCH_2CF_2CH_2CH_2Cl \xrightarrow{KOH} CH_2{=}CHCF_2CH{=}CH_2.$$

Further chlorination of 1,5-dichloro-3,3-difluoropentane in the presence of light forms decachloro-3,3-difluoropentane, which on treatment with zinc in alcohol gives a good yield of hexachloro-3,3-difluoropenta-1,4-diene[16]:

$$CH_2ClCH_2CF_2CH_2CH_2Cl \xrightarrow{Cl_2} CCl_3CCl_2CF_2CCl_2CCl_3 \longrightarrow CCl_2{=}CClCF_2CCl{=}CCl_2$$

In order to obtain 1,1-difluoro-3-methylbutadiene, 1-chloro-1,1-difluoro-3-methylbutane was synthesised from 1,1-dichloro-3-methylbut-1-ene and hydrogen fluoride. Chlorination of 1-chloro-1,1-difluoro-3-methylbutane gives two isomers:

$$CF_2ClCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Cl \quad (I) \quad \text{and} \quad CF_2ClCH_2CCl(CH_3)_2. \quad (II)$$

The former gives 4-chloro-1,1-difluoro-3-methylbut-1-ene on treatment with caustic potash, while the latter yields 1,1-difluoro-3-methylbutadiene[17] under the action of tributylamine at 180°:[17]

$$CCl_2{=}CHCH(CH_3)_2 + HF \longrightarrow CF_2ClCH_2CH(CH_3)_2 + HCl,$$

$$CF_2ClCH_2CH(CH_3)_2 + Cl_2 \longrightarrow \begin{cases} CF_2ClCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Cl \xrightarrow{KOH} CF_2{=}CH\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Cl \\ CF_2ClCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}ClCH_3 \xrightarrow{(C_4H_9)_3N} CF_2{=}CH\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 \end{cases}$$

(*b*) Free-Radical Addition of Halogenoalkanes to Olefins with Subsequent Dehalogenation or Dehydrohalogenation of the Products

Reactions involving free-radical addition at a multiple bond have been finding increasing application during recent years in the preparation of fluorine-containing alkadienes. Thus, for example, 1,2-dibromochlorotrifluoroethane when heated in the presence of benzoyl peroxide readily adds on to fluoroethylene to form 1,4-dibromo-2-chloro-1,1,2,4-tetrafluorobutane, which on subsequent treatment with alkali and zinc in alcohol is converted into 1,1,2,4-tetrafluorobutadiene in good yield[18-20]:

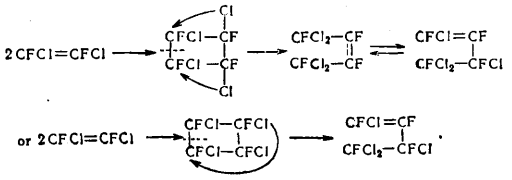
$$CF_2BrCFClBr + CH_2{=}CHF \rightarrow CF_2BrCFClCH_2CHFBr \rightarrow$$
$$\rightarrow CF_2BrCFClCH{=}CHF \rightarrow CF_2{=}CF{-}CH{=}CHF.$$

Thus by using different olefins and halogenoalkanes it is possible to obtain a series of fluorine-containing derivatives of butadiene. Several of them polymerise to form rubber-like resins, insoluble in the usual organic solvents.

Halogenoolefins can be used instead of halogenoalkanes in these additions. An example is the addition of trifluoroiodoethylene to ethylene. The resulting addition product is converted, on treatment with alkali in mineral oil, into 1,1,2-trifluorobutadiene[21]:

$$CF_2{=}CFI + CH_2{=}CH_2 \rightarrow CF_2{=}CFCH_2CH_2I \rightarrow CF_2{=}CFCH{=}CH_2.$$

Another example of the addition of halogenoolefins to unsaturated compounds is the thermal dimerisation of 1,2-dichlorodifluoroethylene into 1,3,4,4-tetrachlorotetrafluorobut-1-ene, which on dechlorination with zinc is converted into 1,4-dichlorotetrafluorobutadiene. Haszeldine[22] regards the dimerisation as a bimolecular reaction taking place according to one of the following mechanisms:



Under the same experimental conditions Ruh *et al.*[23,24] isolated, together with the dimer, a trimer, 1,3,4,5,6,6-hexachlorohexafluorohex-1-ene, from which 1,6-dichlorohexafluorohexa-1,3,5-triene was obtained by the action of zinc in alcohol. Formation of the trimer cannot be explained by the mechanism suggested by Haszeldine for

this reaction, and we regard a radical reaction mechanism as more probable:

$$CFCl{=}CFCl \rightarrow CFCl{=}CF^{\cdot} + Cl^{\cdot},$$
$$CFCl{=}CF^{\cdot} + n\,CFCl{=}CFCl \rightarrow CFCl{=}CF(CFClCFCl)_n^{\cdot},$$
$$CFCl{=}CF(CFClCFCl)_n^{\cdot} + CFCl{=}CFCl \rightarrow CFCl{=}CF(CFClCFCl)_n Cl + CFCl{=}CF^{\cdot},$$

where n = 1 or 2.

$$CFCl{=}CFCFClCFClCFClCFCl_2 \xrightarrow{Zn} CFCl{=}CFCF{=}CFCF{=}CFCl.$$

1,2,3,4,5,6-Hexachlorooctafluorohexane, which reacts with zinc to give perfluorohexa-1,3,5-triene, was obtained from 1,3,4,5,6,6-hexachlorohexafluorohex-1-ene on chlorination followed by fluorination. In this way numerous fluorine-containing derivatives of butadiene and several higher analogues of fluorine-containing alkadienes have been synthesised. Addition of 1,2-dichlorotrifluoroiodoethane to perfluorocyclobutene and subsequent dechlorination of the product with zinc in alcohol result in two isomeric perfluorovinylcyclobutenes[13]:

$$CF_2ClCFClI + \begin{matrix}CF{=}CF\\ |\quad |\\ CF_2{-}CF_2\end{matrix} \rightarrow \begin{matrix}CFClCFClCF - CFI\\ |\qquad\quad |\\ F_2C - CF_2\end{matrix} \longrightarrow$$
$$\longrightarrow CF_2{=}CF{-}\underset{\displaystyle F_2C}{\overset{\displaystyle CF_2}{\diagup\!\diagdown}}C{=}CF; \quad CF_2{=}CFCF{-}\underset{\displaystyle F_2C}{\overset{\displaystyle CF}{\diagup\!\diagdown}}CF.$$

These olefins can be not only polymerised but also migration-copolymerised with nucleophilic bifunctional compounds to form oxygen-, sulphur-, or nitrogen-containing polymers[13].

(c) Telomerisation of Fluorinated Compounds and Subsequent Reactions of the Resulting Telomers

The methods described above permit the synthesis of fluorine-containing alkadienes of low molecular weight only, mainly butadiene derivatives. Telomerisation is of fundamental importance for the synthesis of the higher analogues of fluorine-containing alkadienes, especially perfluorodienes.

Telomers with alternating double bonds are obtained by the telomerisation of acetylenic compounds with fluorocarbons containing another halogen. However, acetylene itself, on interaction with pentafluoroiodoethane in the presence of ultraviolet radiation, gives mainly an addition product and only 0.5% of the telomerisation product, 5,5,6,6,6-pentafluoro-1-iodohexa-1,3-diene[25]:

$$CF_3CF_2I + CH{\equiv}CH \rightarrow CF_3CF_2CH{=}CHI + CF_3CF_2(CH{=}CH)_2I \quad (0.5\%).$$

Fluorine-containing acetylenes, such as 3,3,3-trifluoropropyne, easily undergo telomerisation, irradiation of a mixture of this compound and trifluoroiodomethane yielding 1,1,1,6,6,6-hexafluoro-2-iodo-4-trifluoromethylhexa-2,4-diene[26]:

$$CF_3I + 2\,CH{\equiv}CCF_3 \rightarrow CF_3CH{=}\underset{\displaystyle CF_3}{\underset{|}{C}}{-}CH{=}CICF_3.$$

In a similar manner 2*H*,4*H*-octafluoro-5-iodo-3-pentafluoroethylhepta-2,4-diene, 3*H*,5*H*-decafluoro-2-iodo-4-trifluoromethylocta-2,4-diene, etc. have been obtained.

Since acetylenic compounds undergo telomerisation with difficulty, their use in the preparation of higher telomers is limited.

The telomerisation of chlorotrifluoroethylene with 1,2-dichlorotrifluoroiodoethane yields the telomers $CF_2ClCFCl[CF_2CFCl]_nI$ (n = 1 or 2), which in the presence of mercury or radiation form the dimeric products $[CF_2ClCFCl[CF_2CFCl]_n]_2$. The latter on treatment with zinc in alcohol are converted at 50° into the corresponding chlorofluoro-$\alpha\omega$-dienes, and at 75° into trienes[23,27]:

$$CF_2ClCFClI + n\,CF_2{=}CFCl \rightarrow CF_2ClCFCl(CF_2CFCl)_nI \rightarrow [CF_2ClCFCl(CF_2CFCl)_{n-1}CF_2CFCl]$$
$$\xrightarrow[75^\circ]{50^\circ} \begin{matrix}[CF_2{=}CF(CF_2CFCl)_{n-1}CF_2CFCl]_2\\ [CF_2{=}CF(CF_2CFCl)_{n-1}CF_2CF{=}]_2,\end{matrix}$$

where n = 1, 2.

In a recently developed method for obtaining perfluoro-$\alpha\omega$-dienes, tetrafluoroethylene is telomerised with 1,2-dichlorotrifluoroiodoethane in the presence of benzoyl peroxide with the formation of $\alpha\beta$-dichloroperfluoro-ω-iodoalkanes:

$$CF_2ClCFClI + n\,CF_2{=}CF_2 \longrightarrow CF_2ClCFCl(CF_2CF_2)_nI,$$

where n = 1–4. Dimerisation of the latter with zinc in the presence of acetic anhydride in methylene dichloride yields $\alpha\beta\psi\omega$-tetrachloroperfluoroalkanes, which on dechlorination with zinc in a mixture of glacial acetic acid and anhydride give perfluoro-$\alpha\omega$-dienes[28–31]:

$$2CF_2ClCFCl(CF_2)_nI \rightarrow CF_2ClCFCl(CF_2CF_2)_nCFClCF_2Cl \rightarrow CF_2{=}CF(CF_2CF_2)_nCF{=}CF_2,$$

where n = 2, 3, 4, and 6.

(d) Other Methods

Several fluorine-containing alkadienes have been obtained by the dehydration of fluorine-containing diols[32–34]. However, the diols themselves are not readily available, and owing to their acid properties they split off water with difficulty, so that the alkadienes are obtained in low yields. Better results are obtained by the pyrolysis of diacetates of fluorine-containing diols. Thus, for example, the diacetate of 5,5,5-trifluoropentane-2,4-diol at 470° gives a 75% yield of 5,5,5-trifluoropenta-1,3-diene[32]:

$$CF_3\underset{\displaystyle OCOCH_3}{\underset{|}{C}}H{-}CH_2{-}\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCH_3 \xrightarrow{470^\circ} CF_3CH{=}CHCH{=}CH_2.$$

1,1,1,6,6,6-Hexafluorohexa-2,4-diene and 3,3,4,4-tetrafluorohexa-1,5-diene have been obtained in a similar manner[35].

Pyrolysis of sodium perfluoroadipate yields a mixture of perfluorobutadiene and the sodium salt of the unsaturated acid $CF_2{=}CFCF_2CF_2COONa$, which suggests the following mechanism[36,37]:

$$NaOOC(CF_2)_4COONa \rightarrow {}^-OOC(CF_2)_4COONa \xrightarrow{-CO_2}$$
$$\longrightarrow {}^-CF_2{-}CF_2CF_2CF_2COONa \xrightarrow{-F^-} CF_2{=}CFCF_2CF_2COONa \rightarrow CF_2{=}CFCF{=}CF_2.$$

Although this reaction has been proposed as a general method for obtaining perfluorodienes, it has been accomplished in only one case, and owing to the inaccessibility of perfluorodicarboxylic acids this method has no practical value.

Fluorine-containing alkadienes are readily obtained by the dimerisation of olefins containing both iodine and fluorine. Thus the action of zinc in dioxan on pentafluoro-3-iodopropene and 2-chlorotetrafluoro-3-iodopropene gave

respectively perfluorohexa-1,5-diene and 2,5-dichloroocta-fluorohexa-1,5-diene[38]:

$$2\,CF_2{=}CXCF_2I \rightarrow CF_2{=}CXCF_2CF_2CX{=}CF_2,$$

where X = F or Cl.

It might be expected that 2,2,3,3-tetrafluorocyclobutene could be obtained by the reaction of tetrafluoroethylene with acetylene. But it has been found that at 600° the only products are 1,1,4,4-tetrafluorobutadiene and perfluorocyclobutane[39].

The latter is obviously a product of the dimerisation of tetrafluoroethylene. Formation of 1,1,4,4-tetrafluorobutadiene is probably preceded by that of difluorocarbene ($:CF_2$):

$$CF_2CF_2 \xrightarrow{600^\circ} 2{:}CF_2,$$

$$2CF_2{=}CF_2{+}CH{\equiv}CH \longrightarrow CH_2{=}CH{-}CH{=}CF_2.$$

It is known that substitution takes place when a lithium alkyl or a Grignard reagent reacts with a fluoroolefin. Tetrafluoroethylene reacts with sodium butyl- or phenyl-acetylide to give compounds of the type RC:C.CF:CF.C:CR [40]:

$$RC{\equiv}CNa{+}CF_2{=}CF_2 \longrightarrow RC{\equiv}C{-}CF{=}CF{-}C{\equiv}CR,$$

where R = C_4H_9, C_6H_5.

Heating perfluorobut-2-yne with trifluoromethylsulphur pentafluoride CF_3SF_5 at 525° yields perfluoro-(2,3,4-trimethylhexa-2,4-diene) and perfluoro-(2,3,4,5-tetramethylhexa-2,4-diene) in the proportions 2 : 1. The following mechanism has been suggested for the formation of these hexadienes[41], based on their structure established by nuclear magnetic resonance:

$$2CF_3C{\equiv}C{-}CF_3 \longrightarrow \begin{matrix} CF_3{-}C{=}C{-}CF_3 \\ | \quad | \\ CF_3{-}C{=}C{-}CF_3 \end{matrix},$$

$$\begin{matrix} CF_3{-}C{=}C{-}CF_3 \\ | \quad | \\ CF_3{-}C{=}C{-}CF_3 \end{matrix} + CF_3^{\cdot} + F^{\cdot} \quad \begin{matrix} CF_3C{=}C{-}C{=}CF{-}CF_3 \\ | \qquad | \\ F_3C \quad CF_3 \end{matrix},$$

$$\begin{matrix} CF_3{-}C{=}C{-}CF_3 \\ | \quad | \\ CF_3{-}C{=}C{-}CF_3 \end{matrix} + 2CF_3^{\cdot} \longrightarrow \begin{matrix} CF_3{-}C{=}C{-}C{=}C{-}CF_3. \\ \diagup \quad | \quad | \quad \diagdown \\ CF_3 \quad CF_3 \quad CF_3 \quad CF_3 \end{matrix}$$

2. FLUORINE-CONTAINING ALLENES

The first representative of the fluorinated allenes is perfluoroallene, which has been obtained by the action of alkali on 1,3-dibromo-1,1,3,3-tetrafluoropropane[33,42,43]:

$$CF_2BrCH_2CF_2Br + 2\,KOH \rightarrow CF_2{=}C{=}CF_2 + 2\,KBr.$$

Similarly, elimination of hydrogen bromide from 1,3-dibromo-1,1-difluoropropane gives a good yield of 1,1-difluoroallene[44]:

$$CF_2BrCH_2CH_2Br + 2\,KOH \rightarrow CF_2{=}C{=}CH_2 + 2\,KBr.$$

1,1-Difluoroallene is formed also by the pyrolysis (at 800°–950°) of 2,2,3,3-tetrafluorocyclobutylmethyl acetate, 1,1,2,2-tetrafluoro-3-methylenecyclobutane being obtained as an intermediate product, which suggests the following mechanism for the reaction[45–47]:

$$CH_3COOCH_2\underset{\displaystyle CF_2{-}CF_2}{\overset{\displaystyle |}{CH}}{-}CH_2 \longrightarrow CH_2{=}\underset{\displaystyle CF_2{-}CF_2}{\overset{\displaystyle |}{C}}{-}CH_2 \longrightarrow CF_2{=}C{=}CH_2 + CH_2{=}CF_2.$$

Another representative of the fluorine-containing allenes is 4,4,4-trifluorobuta-1,2-diene, obtained by elimination of hydrogen iodide from 4,4,4-trifluoro-2-iodobut-1-ene, which is formed on addition of trifluoroiodomethane to allene.

The formation of 4,4,4-trifluorobuta-1,2-diene is accompanied by that of 4,4,4-trifluorobut-1-yne[48]:

$$CF_3I + CH_2{=}C{=}CH_2 \rightarrow CF_3CH_2CI{=}CH_2 \rightarrow CF_3CH{=}C{=}CH_2 + CF_3CH_2C{\equiv}CH.$$

Great interest has been shown in the preparation of 1,1,4,4-tetrafluorobuta-1,2,3-triene. Addition of bromine to 1,1,4,4-tetrafluorobutadiene gives 1,4-dibromo-1,1,4,4-tetrafluorobut-2-ene, which is converted by the action of alkali into perfluorobuta-1,2,3-triene:

$$CF_2{=}CH{-}CH{=}CF_2 + Br_2 \rightarrow CF_2BrCH{=}CH{-}CF_2Br \rightarrow CF_2{=}C{=}C{=}CF_2.$$

This product is very unstable, and decomposes violently in air at room temperature[49,50].

3. FLUORINE-CONTAINING DIOLS

Fluorine-containing diols are of great interest as monomers for the synthesis of polyesters[51–53] and polyurethanes[54]. The fluorine-containing polyesters which have been obtained up to the present are heat-resistant rubberlike or glasslike substances. After vulcanisation, the polyester from adipic acid and 2,2,3,3,4,4-hexafluoropentane-1,5-diol, for example, greatly resembles natural rubber in properties and possesses high thermal stability[55]. Several of the known fluorine-containing polyurethanes are successfully applied as coatings. However, the use of both these and others is restricted by the lack of a practicable method for obtaining fluorine-containing diols.

Up to the present there have been no data on the existence of perfluoro-diols, probably owing to the instability of the group CF_2OH, since, at the instant of formation, it splits off hydrogen fluoride to form an acid fluoride. Only $\alpha\omega$-bis(hydroxymethyl)perfluoroalkanes $HOCH_2[CF_2]_nCH_2OH$, where n = 1, 2, 3, 4, and 8, are known.

Fluorine-containing diols are usually obtained by the reduction of esters, anhydrides of dicarboxylic acids, or diketones, and also by the hydrolysis of epoxides. Diols are also formed by the reaction of Grignard reagents with diesters and diketones.

(*a*) Reduction of Fluorine-Containing Diesters, Anhydrides of Dicarboxylic Acids, and Diketones

A practicable method of obtaining fluorine-containing diols, which is widely employed under laboratory conditions, is reduction of esters of fluorine-containing dicarboxylic acids with lithium aluminium hydride or sodium borohydride[56–62]:

$$C_2H_5OOC(CF_2)_nCOOC_2H_5 \rightarrow HOCH_2(CF_2)_nCH_2OH,$$

where n = 2, 3, 4, and 8.

Anhydrides[63] or chlorides[64] of dicarboxylic acids can be used instead of esters. Reaction of difluoromalonyl dichloride with lithium aluminium hydride yields 2,2-difluoropropane-1,3-diol, which is obtained also by the action of the same reducing agent on ethyl $\alpha\alpha$-difluoro-β-hydroxypropionate, obtained by the Prins reaction[65]:

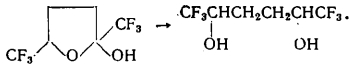
$$CF_2{=}CF_2 + CH_2O + H_2O \xrightarrow{C_2H_5OH} HOCH_2CF_2COOC_2H_5 \xrightarrow{LiAlH_4} HOCH_2CF_2CH_2OH.$$

The reduction of fluorine-containing diketones also results in the formation of diols in good yields. Thus the

action of lithium aluminium hydride on 3,3,4,4-tetrafluorohexane-2,5-dione gives the corresponding diol[35]:

$$CH_3COCF_2CF_2COCH_3 \rightarrow CH_3\underset{OH}{\underset{|}{C}}HCF_2CF_2\underset{OH}{\underset{|}{C}}HCH_3.$$

Reduction of tetrahydro-2,5-bistrifluoromethylfuran-2-ol has given 1,1,1,6,6,6-hexafluorohexane-2,5-diol, which is regarded[35] as a mixture of optical isomers (*dextro*, *laevo*, and *meso* configurations):



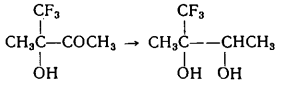
When ethyl perfluorosuccinate, perfluoroglutarate, and perfluoroadipate are reduced with hydrogen in the presence of a catalyst (a mixture of the oxides of copper, chromium, and calcium or barium) in an autoclave at 130°–250°, the corresponding diols are formed in yields of about 50%.[66] Hydrogenation of the diperfluorobutyrate of perfluorooct--4-ene-4,5-diol (see Section 9) results in the formation of 4*H*,5*H*-perfluorooctane-4,5-diol[67]:

$$\underset{F_7C_3\ \ C_3F_7}{C_3F_7COOC{=}COOCC_3F_7} \xrightarrow[Pd/C]{H_2} \underset{OH\ \ OH}{C_3F_7CH{-}CHC_3F_7}.$$

Reduction of trifluoroacetylacetone with hydrogen under pressure in the presence of nickel has given 1,1,1-trifluoropentane-2,4-diol[32]:

$$CF_3COCH_2COCH_3 \rightarrow CF_3\underset{OH}{\underset{|}{C}}HCH_2\underset{OH}{\underset{|}{C}}HCH_3$$

The action of aluminium isopropoxide on 3-hydroxy-3-trifluoromethylbutan-2-one forms 2-trifluoromethylbutane--2,3-diol[23]:



(*b*) Addition of Grignard Reagents to Diesters and Diketones

Secondary and tertiary diols are often prepared by a procedure based on the reaction of carbonyl compounds (esters or ketones) with Grignard reagents. Several fluorine-containing glycols have been obtained by the reaction of ethyl perfluoroglutarate with CH_3MgI, C_2H_5MgI, and C_3H_7MgI. It is interesting that methylmagnesium iodide forms the tertiary diol, 3,3,4,4,5,5-hexafluoro-2,6-dimethylheptane-2,6-diol, in 85% yield, whereas ethylmagnesium and isopropylmagnesium iodides form mainly the corresponding secondary diols, with only a small quantity of the tertiary diols as side-products[33]:

$$CH_3MgI + CF_2(CF_2COOC_2H_5)_2 \longrightarrow CF_2\left(\underset{OH}{\underset{|}{CF_2C}}{-}CH_3\right)_2, \quad (85\%)$$

$$C_2H_5MgI + CF_2(CF_2COOC_2H_5)_2 \longrightarrow \underset{OH}{\underset{|}{CF_2CHC_2H_5}})_2 + CF_2\left(\underset{OH}{\underset{|}{CF_2C}}{-}C_2H_5\right)_2, \quad (23\%)\ (5\%)$$

$$C_3H_7MgI + CF_2(CF_2COOC_2H_5)_2 \longrightarrow CF_2\left(\underset{OH}{\underset{|}{CF_2CH}}\!\!<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}\right)_2. \quad (77\%)$$

An interesting reaction between perfluoroacetone and ethynylenedimagnesium dibromide yields perfluoro-2,5--dimethylhex-3-yne-2,5-diol[68]:

$$2CF_3COCF_3 + BrMgC{\equiv}CMgBr \longrightarrow CF_3{-}\underset{OH}{\underset{|}{\overset{CF_3}{\overset{|}{C}}}}{-}C{\equiv}C{-}\underset{OH}{\underset{|}{\overset{CF_3}{\overset{|}{C}}}}{-}CF_3.$$

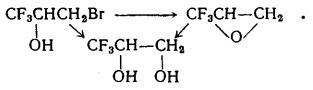
Reaction of ethynylmagnesium bromide with perfluoroacetone gave 4*H*-perfluoro-2-methylbut-3-yn-2-ol, which on oxidation with oxygen in the presence of cuprous chloride gave perfluoro-2,7-dimethylocta-3,5-diyne-2,7-diol[68]:

$$CF_3COCF_3 + CH{\equiv}CMgBr \rightarrow \underset{OH}{\underset{|}{\overset{CF_3}{\overset{|}{C}}}}{-}C{\equiv}CH \rightarrow \underset{OH}{\underset{|}{\overset{CF_3}{\overset{|}{C}}}}{-}C{\equiv}C{-}C{\equiv}C{-}\underset{OH}{\underset{|}{\overset{CF_3}{\overset{|}{C}}}}{-}CF_3.$$

1,1,4,4-Tetrakis(chlorodifluoromethyl)butyne-1,4-diol and 1,1,6,6-tetrakis(chlorodifluoromethyl)hexa-2,4-diyne-1,6--diol[69] have been obtained in a similar manner.

(*c*) Hydrolysis of Fluorine-Containing Epoxides and Other Methods

Owing to the influence of the fluoroalkyl group, fluorine--containing epoxides are more stable to hydrolysis than are the unfluorinated epoxides. However, when they are heated with acids, fluorine-containing diols are readily formed. Thus, for example, 1,2-epoxy-3,3,3-trifluoropropane on boiling with 1% sulphuric acid is converted into 3,3,3-trifluoropropane-1,2-diol, which has also been obtained by heating 1-bromo-3,3,3-trifluoropropan-2-ol with alkali and then with dilute sulphuric acid[70]:



Similarly, 4,4,5,5,6,6,6-heptafluorohexane-2,3-diol, 5,5,6,6,7,7,7-heptafluorooctane-3,4-diol, and other diols containing fluorine[71] have been obtained from the corresponding epoxides. Fluorine-containing diols can be obtained also by the oxidation of fluorine-containing olefins. Thus oxidation of 1,4-dibromo-1,1,4,4-tetrafluorobut-2-ene with potassium permanganate at 5°–10° gives 1,4-dibromo--1,1,4,4-tetrafluorobutane-2,3-diol in good yield[50]:

$$CF_2BrCH{=}CHCF_2Br \rightarrow CF_2BrCH{-}\underset{OH}{\underset{|}{C}}HCF_2Br.$$

4. FLUORINE-CONTAINING DIETHERS

Monoethers containing fluorine have been widely studied, since they are very easily prepared by addition of alcohols to fluorine-containing olefins, but the corresponding diethers have been little studied up to the present. Although, as mentioned above, perfluorinated diols do not exist, perfluorinated diethers have proved to be very stable.

The present review does not cover diethers such as $R_FO[CH_2]_nOR_F$, which can be regarded as derivatives of unfluorinated diols. Some perfluorodiethers have been obtained by electrochemical fluorination of the corresponding unfluorinated diethers. In this way, for example, the

diethyl ether of diethylene glycol has been perfluorinated, the resulting ether being recommended for use as a lubricant[72]:

$$C_2H_5OCH_2CH_2OCH_2CH_2OC_2H_5 \rightarrow C_2F_5OCF_2CF_2OCF_2CF_2OC_2F_5.$$

It is interesting that electrochemical fluorination of dioxan yielded, instead of perfluorodioxan, the perfluorinated dimethyl ether of ethylene glycol[72]:



$$\rightarrow CF_3OCF_2CF_2OCF_3.$$

The chief method of preparing fluorine-containing monoethers is the reaction of fluorinated olefins with alcohols. However, the reaction of fluorine-containing dienes with alcohols has remained almost unstudied. The only example is the reaction of perfluorobutadiene with sodium ethoxide, yielding 1,4-diethoxyperfluorobuta-1,3-diene[73]:

$$CF_2{=}CFCF{=}CF_2 + 2\,C_2H_5ONa \rightarrow C_2H_5OCF{=}CFCF{=}CFOC_2H_5 + 2\,NaF.$$

Diethers are also obtained by alkylating fluorine-containing diols. Thus dimethyl sulphate acts on 1,1,4,4-tetrakis(chlorodifluoromethyl)but-2-yne-1,4-diol to give 1,1,4,4-tetrakis(chlorodifluoromethyl)-1,4-dimethoxybut-2-yne[69]:

$$(CF_2Cl)_2C(OH)-C\equiv C-C(OH)(CF_2Cl)_2 + (CH_3)_2SO_4 \rightarrow (CF_2Cl)_2C(OCH_3)-C\equiv C-C(OCH_3)(CF_2Cl)_2.$$

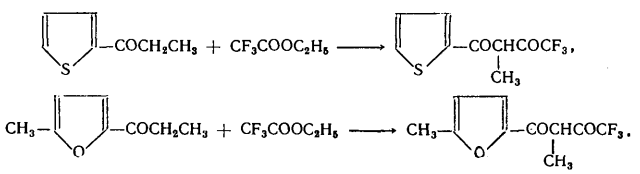
5. FLUORINE-CONTAINING DIKETONES

Fluorine-containing monoketones have been widely studied. They can be synthesised by all the classical methods other than pyrolysis of salts of fluorine-containing carboxylic acids. Perfluorinated diketones and dialdehydes are altogether unknown. Most of the known diketones containing fluorine are β-diketones, the chief method of synthesis being the Claisen reaction.

The action of fluorine-containing esters on ketones or fluorinated ketones of the type R_FCOCH_2R in the presence of sodium ethoxide gives β-diketones in good yield[74-78]:

$$R'_FCOOR + RCH_2COR_F \longrightarrow R'_FCOCH(R)COR_F.$$

Not only aliphatic but also cyclic, aromatic, and heterocyclic ketones undergo the Claisen reaction. Thus ethyl 2-thienyl ketone and ethyl 5-methylfur-2-yl ketone react with ethyl trifluoroacetate to form the corresponding β-diketones[78]:



$$\text{2-thienyl-}COCH_2CH_3 + CF_3COOC_2H_5 \longrightarrow \text{2-thienyl-}COCH(CH_3)COCF_3,$$

$$CH_3\text{-(5-methylfur-2-yl)-}COCH_2CH_3 + CF_3COOC_2H_5 \longrightarrow CH_3\text{-(5-methylfur-2-yl)-}COCH(CH_3)COCF_3.$$

It is noteworthy that propiophenone reacts smoothly with ethyl trifluoroacetate forming the β-diketone, whereas butyrophenone and pentyl phenyl ketone yield only insignificant quantities of the β-diketones, the main products being alkyl trifluoromethyl ketones[78]:

$$C_6H_5COCH_2R + CF_3COOC_2H_5 \longrightarrow CF_3COCH_2R + C_6H_5COOCH_3,$$

where R = C_4H_9 and C_5H_{11}.

The Friedel–Crafts reaction has also been used to obtain β-diketones. Thus reaction of difluoromalonyl chloride with benzene in the presence of aluminium chloride gives a good yield of dibenzoyldifluoromethane[64]:

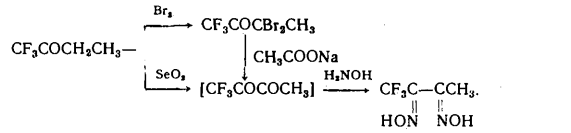
$$CF_2(COCl)_2 + 2C_6H_6 \longrightarrow CF_2(COC_6H_5)_2 + 2HCl.$$

Owing to the influence of the fluoroalkyl group, fluorine-containing β-diketones tend to pass into enolic forms and stable chelate complexes, which can be used to synthesise polymeric chelate complexes.

The only fluorine-containing α-diketone which has been isolated is perfluorooctane-4,5-dione, which is formed on pyrolysis of perfluoro(dipropylvinylene dibutyrate)[67]:

$$C_3F_7COOC(F_7C_3)=C(C_3F_7)OOCC_3F_7 \xrightarrow{600^\circ} C_3F_7COCOC_3F_7.$$

Other α-diketones have been obtained only in the form of dioximes. Thus bromination of 1,1,1-trifluorobutan-2-one gives the 3,3-dibromo-derivative, which on treatment with hydroxylamine in the presence of sodium acetate yields the dioxime of 1,1,1-trifluorobutane-2,3-dione. This last compound has been obtained also by oxidation of 1,1,1-trifluorobutan-2-one with selenium dioxide in aqueous medium, and isolation as the dioxime:



$$CF_3COCH_2CH_3 \xrightarrow{Br_2} CF_3COCBr_2CH_3 \xrightarrow{CH_3COONa} [CF_3COCOCH_3] \xrightarrow{H_2NOH} CF_3C(HON)-C(NOH)CH_3.$$

The dioxime of 3,3,3-trifluoropropane-1,2-dione has been obtained similarly[79].

The only representative of the γ-diketones is 3,3,4,4-tetrafluorohexane-2,5-dione, which has been obtained by treating perfluorosuccinic acid with methylmagnesium bromide:

$$(CF_2COOH)_2 + 2CH_3MgBr \rightarrow CH_3COCF_2CF_2COCH_3 + 2MgBrOH.$$

Under the same conditions perfluoroglutaric acid gives a mixture of

$$CH_2{=}C(CH_3)-(CF_2)_3COCH_3 \text{ and } CH_3CO(CF_2)_3COCH_3,$$

which could not be separated[35].

6. FLUORINE-CONTAINING DICARBOXYLIC ACIDS

The great interest in fluorine-containing dicarboxylic acids is due to the possibility of using them in polycondensations and in the preparation of other fluorine-containing bifunctional compounds.

The polycondensation of fluorine-containing dicarboxylic acids (perfluoroadipic, perfluorosebacic, etc.) or their chlorides with diols, thiols, or diamines has been used to prepare polyesters, polythioesters, polyamides, and polyurethanes[30,31,51,61,62,80-85], but the number of polymeric compounds obtained from fluorine-containing dicarboxylic acids is small owing to the poor availability of these acids.

Perfluorinated succinic, glutaric, and adipic acids have been more thoroughly studied. Perfluorosuberic and perfluorosebacic acids have also been synthesised, as well as several of their higher homologues. Fluorine-containing dicarboxylic acids containing an odd number of carbon atoms have been little studied. Several fluorine-containing unsaturated dicarboxylic acids are also known, such as difluorofumaric, difluoromaleic, etc.

Fluorine-containing dicarboxylic acids have been synthesised by the electrochemical fluorination of dicarboxylic acids, the oxidation of fluorine-containing hydrocarbons, and other methods.

(*a*) Electrochemical Fluorination of Dicarboxylic Acids

Electrochemical fluorination is now applied not only in the laboratory but also on an industrial scale, for example in the production of trifluoroacetic acid. With increasing number of carbon atoms in the initial carboxylic acids, however, the yields of the fluorinated acids drop sharply, which limits the usefulness of this method for the preparation of the higher perfluorodicarboxylic acids. On electrochemical fluorination of succinic anhydride, perfluorosuccinic acid is obtained together with perfluoropropionic acid[58]:

$$(CH_2CO)_2O \rightarrow \underset{(33\%)}{CF_3CF_2COOH} + \underset{(23\%)}{(CF_2COOH)_2}.$$

Fluorination of adipic anhydride yields only a minute quantity of perfluoroadipic acid[58,85].

The electrochemical fluorination of sebacic acid produces a mixture of fluorocarbons, perfluorononanoyl fluoride, and perfluorosebacoyl fluoride[82,86]:

$$HOOC(CH_2)_8COOH \rightarrow FOC(CF_2)_8COF + CF_3(CF_2)_8COF.$$

(*b*) Oxidation of Fluorine-Containing Olefins

The chief method of preparing fluorine-containing dicarboxylic acids is oxidation of fluorine-containing dienes and olefins, among which the more readily available cycloalkenes are most often employed. Oxidation of 3,3-difluoropenta--1,4-diene — see Section 1 (*a*) — with potassium permanganate at 60° gives difluoromalonic acid[16]:

$$CF_2(CH{=}CH_2)_2 \xrightarrow{KMnO_4} CF_2(COOH)_2.$$

When perfluoro-$\alpha\omega$-dienes — see Section 1 (*c*) — are oxidised with potassium permanganate in aqueous acetone medium, the corresponding perfluoro-$\alpha\omega$-dicarboxylic acids are obtained in good yields[30,87]:

$$CF_2{=}CF(CF_2)_n\,CF{=}CF_2 \rightarrow HOOC(CF_2)_nCOOH,$$

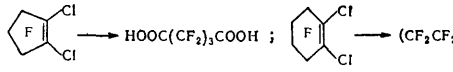
where n = 4, 6, 8, and 12.

A more practicable method for obtaining some fluorine--containing dicarboxylic acids is oxidation of fluorine-containing cycloalkenes. Thus perfluorosuccinic acid has been obtained by the oxidation of perfluoro- or 1,2-dichlorotetrafluoro-cyclobutene[88]:

$$\begin{array}{l} CF_2{-}CX \\ \vert \quad \Vert \\ CF_2{-}CX \end{array} \xrightarrow{KMnO_4} (CF_2COOH)_2,$$

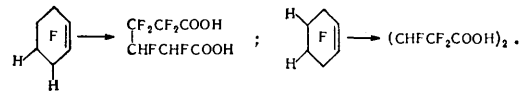
where X = Cl, F.

Similarly, oxidation of 1,2-dichlorohexafluorocyclopentene yields perfluoroglutaric acid[89,91], and 1,2-dichlorooctafluorocyclohexene gives perfluoroadipic acid[90,92-94]:

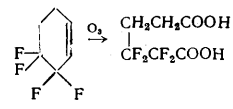


In this way adipic acids having different degrees of fluorination have been obtained.

It is interesting that among the products of the fluorination of benzene 3*H*,4*H*- and 4*H*,5*H*-perfluorocyclohexenes have been isolated, oxidation of the former giving (±)-*erythro*-2*H*,3*H*-perfluoroadipic acids, and of the latter *DL*-3*H*,4*H*-perfluoroadipic acids[95,96]:

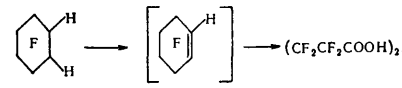


On further oxidation, 2*H*,3*H*-perfluoroadipic acid yields perfluorosuccinic acid, and the 3*H*,4*H* acid gives perfluoromalonic acid. Oxidation goes far more readily and in better yields in acetone or aqueous acetone medium than in water, fluorine-containing olefins being oxidised more readily than are unfluorinated olefins, probably because they are more electrophilic[93]. Ozone can replace potassium permanganate as oxidising agent. Thus ozonolysis of 3,3,4,4-tetrafluorocyclohexene in methylene chloride yields 2,2,3,3-tetrafluoroadipic acid[97]:



3,3,4,4-Tetrafluoroadipic acid has been obtained similarly.

Several fluorine-containing alkanes can also be oxidised by potassium permanganate in neutral medium to form dicarboxylic acids. In this way perfluoroadipic acid has been obtained from 1*H*,2*H*-perfluorocyclohexane. It is obvious that during the reaction hydrogen fluoride is split off from the decafluorocyclohexane forming 1*H*-perfluorocyclohexene, which is then further oxidised:



Similarly, perfluorosuccinic acid has been obtained from 1*H*,2*H*-hexafluorocyclobutane[98].

A new type of oxidation is the reaction with oleum of substituted fluorocarbons possessing $CFCl_2$, CFClH, and CFClBr terminal groups, yielding fluorides of fluorine--containing carboxylic acids. The groups CCl_3 and CF_2Cl are more stable, and therefore when fluorocarbons of the types $CCl_3[CF_2CFCl]_nBr$ and $Cl[CF_2CFCl]_nCl$ were heated with oleum in an autoclave, the main reaction products were monocarboxylic acids and only insignificant quantities of dicarboxylic acids[99-101]:

$$CCl_3(CF_2CFCl)_nBr \rightarrow CCl_3(CF_2CFCl)_{n-1}CF_2COOH + HOOC(CF_2CFCl)_{n-1}CF_2COOH$$

and

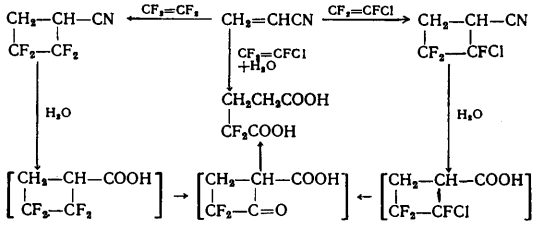
$$Cl(CF_2CFCl)_nCl \rightarrow ClCF_2(CFClCF_2)_{n-1}COOH + HOOC(CFClCF_2)_{n-1}COOH,$$

where n = 2–4. The resulting acids were not isolated in a pure form. As the length of the alkyl chain increases, the reaction requires more forcing conditions.

(*c*) Other Methods

When acrylonitrile reacts with tetrafluoroethylene in the presence of "terpene B" in an autoclave at 150°, 2,2,3,3-tetrafluorocyclobutanecarbonitrile is formed[47],

which on hydrolysis with caustic soda is converted into 2,2-difluoroglutaric acid in 30% yield. This last acid has been synthesised also by the hydrolysis of 2-chloro-2,3,3-trifluorocyclobutanecarbonitrile, obtained from acrylonitrile and chlorotrifluoroethylene in the presence of water and hydroquinone in an autoclave at 150°:[102]



When an attempt is made to obtain perfluoroacrylic acid by the alkaline hydrolysis of perfluoroacrylonitrile, fluoromalonic acid is obtained instead[103]:

$$CF_2=CFCN \xrightarrow{H_2O} CHF(COOH)_2.$$

Several fluorine-containing dicarboxylic acids have been obtained by the hydrolysis of fluorine-containing esters, for whose preparation other, more practicable methods have been found. Thus in the presence of sodium ethoxide, ethyl malonate readily adds on to ethyl 3-(perfluoroalkyl)acrylate to form the ethyl 2-(perfluoroalkyl)-propane-1,1,3-tricarboxylate, which on hydrolysis gives the 2-(perfluoroalkyl)glutaric acid[60]:

$$R_FCH=CHCOOC_2H_5 + CH_2(COOC_2H_5)_2 \rightarrow R_FCHCH_2COOC_2H_5 \rightarrow R_FCH(CH_2COOH)_2,$$
$$\quad\quad\quad

By heating silver perfluoroglutarate with iodine, Hauptschein *et al.* obtained perfluoro-γ-butyrolactone[107], together with hexafluoro-1,3-diiodopropane:

$$AgOOC(CF_2)_3COOAg + I_2 \rightarrow I(CF_2)_3I + CF_2(O)CF_2(CO)CF_2.$$

According to Tiers[108], however, the lactone was actually perfluorosuccinyl fluoride.

8. ESTERS OF FLUORINE-CONTAINING DICARBOXYLIC ACIDS

Esters of fluorine-containing dicarboxylic acids are of great value for identifying the acids, and in several cases also for their preparation. Moreover, it is mostly from them that fluorine-containing diols and diamides are obtained.

Such esters are prepared mainly by esterifying dicarboxylic acids with alcohols, but there exist also many other methods for obtaining them.

(*a*) Esterification of Fluorine-Containing Dicarboxylic Acids

The esterification of fluorine-containing dicarboxylic acids has been accomplished by the classical methods involving reaction of the acids with alcohols in the presence of catalysts such as gaseous hydrogen chloride, concentrated sulphuric acid, toluene-*p*-sulphonic acid, fluorosulphuric acid, etc.[58,61,62,82,88,109]

Diazomethane is often used to obtain the methyl esters of dicarboxylic acids; thus with difluoromalonic acid it gives a good yield of dimethyl difluoromalonate[16,27].

Fluorine-containing dicarboxylic acids can be esterified also with olefins. In the presence of catalytic quantities of concentrated sulphuric acid or toluene-*p*-sulphonic acid, propene adds on to perfluorosuccinic acid to form the diisopropyl ester[110]:

$$(CF_2COOH)_2 + 2\,CH_2{=}CHCH_3 \rightarrow \left(CF_2COOCH\langle{}^{CH_3}_{CH_3}\rangle\right)_2.$$

The diethyl ester has been obtained similarly.

Esters are prepared also by reaction of the acid chlorides or fluorides with alcohols.

(*b*) Addition of Ethyl Malonate to Unsaturated Compounds and to Ketones

Ethyl malonate, which contains active hydrogen atoms, can add on to fluorine-containing unsaturated compounds and ketones to form fluorine-containing derivatives of malonic ester, which on hydrolysis give fluorine-containing mono- or di-carboxylic acids, depending on the structure of the starting materials.

In the presence of sodium ethoxide, ethyl malonate easily adds on to 3,3,4,4,5,5,5-heptafluoro-1-nitropentene forming ethyl 3,3,4,4,5,5,5-heptafluoro-2-nitromethylpentane-1,1-dicarboxylate[111]:

$$C_3F_7CH{=}CHNO_2 + CH_2(COOC_2H_5)_2 \rightarrow C_3F_7CH(CH_2NO_2)CH(COOC_2H_5)_2.$$

Ethyl 2-(perfluoroalkyl)propane-1,1,3-tricarboxylates — see Section 6 (*c*) — have been obtained similarly. In the presence of sodium, malonic ester reacts with tetrafluoroethylene to form ethyl 2,3-difluorobut-2-ene-1,1,4,4-tetracarboxylate[40]:

$$2NaCH(COOC_2H_5)_2 + CF_2{=}CF_2 \longrightarrow (C_2H_5OOC)_2CHCF{=}CFCH(COOC_2H_5)_2.$$

Perfluoroacetone reacts with malonic ester in the presence of pyridine to form ethyl 3,3,3-trifluoro-2-hydroxy-2-trifluoromethylpropane-1,1-dicarboxylate[112]:

$$(CF_3)_2C{=}O + CH_2(COOC_2H_5)_2 \longrightarrow (CF_3)_2C(OH)CH(COOC_2H_5)_2,$$

but in the presence of acetic anhydride and zinc chloride, the corresponding 2-acetoxy ester is formed, and this on low-temperature pyrolysis in the presence of a catalytic quantity of potassium carbonate, eliminates acetic acid to give ethyl perfluoroisopropylidenemalonate[107,113]:

$$(CF_3)_2C{=}O + CH_2(COOC_2H_5)_2 \xrightarrow{(CH_3CO)_2O} (CF_3)_2C(OCOCH_3)CH(COOC_2H_5)_2 \xrightarrow{130^\circ-140^\circ} (CF_3)_2C{=}C(COOC_2H_5)_2.$$

Addition of ammonia to this ester yields ethyl 1-amino-3,3,3-trifluoro-2-trifluoromethylpropane-1,1-dicarboxylate[113]:

$$(CF_3)_2C{=}C(COOC_2H_5)_2 + NH_3 \longrightarrow (CF_3)_2CHC(NH_2)(COOC_2H_5)_2.$$

(*c*) Other Methods

The action of potassium fluoride on ethyl bromomalonate yields, instead of the expected fluoromalonic ester, a small quantity of ethyl difluoromalonate[114]:

$$CHBr(COOC_2H_5)_2 \xrightarrow{KF} CF_2(COOC_2H_5)_2.$$

Ethyl fluoromalonate has been obtained only by the pyrolysis of ethyl 2-fluoro-3-oxosuccinate, which in turn is obtained by the interaction of ethyl oxalate and ethyl fluoroacetate in the presence of sodium ethoxide[114-116]:

$$(COOC_2H_5)_2 + CH_2FCOOC_2H_5 \longrightarrow COCHF(COOC_2H_5)COOC_2H_5 \longrightarrow CHF(COOC_2H_5)_2.$$

Sulphur tetrafluoride acts on ethyl acetonedicarboxylate to give a good yield of ethyl 3,3-difluoroglutarate[117]:

$$CO(CH_2COOC_2H_5)_2 \xrightarrow{SF_4} CF_2(CH_2COOC_2H_5)_2.$$

Esters of fluorine-containing dicarboxylic acids should be obtainable also by the hydrolysis of diethers of the type $ROCF_2XCF_2OR$, but such compounds are not yet known. Ethyl monofluoroethylene 1,2-dicarboxylate has been synthesised by the hydrolysis of 1,4-diethoxytetrafluorobuta-1,3-diene[73] (see Section 4):

$$C_2H_5OCF{=}CFCF{=}CFOC_2H_5 \longrightarrow (C_2H_5OOCCHFCHFCOOC_2H_5) \longrightarrow C_2H_5OOC{-}CH{=}CF{-}COOC_2H_5.$$

When acetyl peroxide decomposes in methyl fluoroacetate, the fluorine-containing radicals recombine to form methyl 2,3-difluorosuccinate[118]:

$$(CH_3COO)_2 \longrightarrow CH_3COO^{\cdot} \longrightarrow CH_3^{\cdot} + CO_2,$$

$$CH_3^{\cdot} + CH_2FCOOCH_3 \longrightarrow CH_4 + {}^{\cdot}CHFCOOCH_3,$$

$$2\,{}^{\cdot}CHFCOOCH_3 \longrightarrow (CHFCOOCH_3)_2.$$

9. ESTERS OF FLUORINE-CONTAINING DIOLS

Fluorine-containing diols react with monocarboxylic acids or their chlorides to form esters of the diols.

It is interesting that, when acted upon by tetracarbonylnickel in benzonitrile, chlorides of perfluorocarboxylic acids form esters of the type $R_FCOOCR_F=CR_FOCOR_F$.[67]

$$R_FCOCl \xrightarrow[C_6H_5CN]{Ni(CO)_4} [R_F\dot{C}O] \rightarrow [R_FCOCOR_F] \xrightarrow{R_F\dot{C}O} R_F-C(=O)-O-C(R_F)=C(R_F)-O-C(=O)-R_F,$$

where $R_F = C_3F_7$, $H[CF_2]_4$.

10. FLUORINE-CONTAINING DIAMIDES AND IMIDES

The diamides are important derivatives of fluorine-containing dicarboxylic acids. Most of them are obtained by interaction of the chlorides or the esters with ammonia or with amines in ether or in aqueous medium. Interaction of the anhydrides of fluorine-containing dicarboxylic acids with ammonia yields only monoamides[105,119].

A specific method for obtaining fluorine-containing amides is the addition of ammonia and amines to fluoroolefins with subsequent hydrolysis of the addition products. Thus hydrolysis of the addition product from ethylamine and perfluorobutadiene results in formation of *NN'*-diethylfluoroethylene-1,2-dicarboxyamide, together with the corresponding monoamide[73]:

$$CF_2=CFCF=CF_2 \xrightarrow{C_2H_5NH_2} \begin{cases} (CF_2=CFCF=CFNHC_2H_5) \rightarrow CF_2=CFCHFCONHC_2H_5, \\ (C_2H_5NHCF=CFCF=CFNHC_2H_5) \rightarrow \\ \rightarrow C_2H_5NHCOCF=CHCONHC_2H_5. \end{cases}$$

Fluorine-containing imides have been obtained by heating fluorine-containing diamides with concentrated sulphuric acid; perfluorosuccinimide, perfluoroglutarimide, etc. have been obtained in this way[73,120].

Heating of the monoanilide of difluoromaleic acid affords *N*-phenyldifluoromaleimide[105]:

$$HOOC-CF=CFCONHC_6H_5 \longrightarrow \begin{matrix} CF-C(=O) \\ \| \quad \quad N-C_6H_5 \\ CF-C(=O) \end{matrix}.$$

N-*p*-Chlorophenyldifluoromaleimide has been obtained similarly.

With diazomethane difluoromaleimide gives the *N*-methylimide[120]:

$$\begin{matrix} CF-C(=O) \\ \| \quad \quad NH \\ CF-C(=O) \end{matrix} + CH_2N_2 \longrightarrow \begin{matrix} CF-C(=O) \\ \| \quad \quad NCH_3 \\ CF-C(=O) \end{matrix}.$$

11. FLUORINE-CONTAINING DINITRILES AND DIAMIDINES

Fluorine-containing dinitriles have been little studied. Perfluoroglutaronitrile and perfluoroadiponitrile have been obtained from the corresponding diamides by removing water with phosphorus pentoxide[90,121]:

$$H_2NOC(CF_2)_nCONH_2 \xrightarrow{P_2O_5} NC(CF_2)_nCN,$$

where $n = 3, 4$.

Perfluoroacrylonitrile when heated dimerises to form a dinitrile[103]:

$$2CF_2=CFCN \longrightarrow \begin{matrix} CF_2-CF-CN \\ | \quad \quad | \\ CF_2-CF-CN \end{matrix}.$$

Reaction of the sodium derivative of diphenylacetonitrile with tetrafluoroethylene gives 1,1,4,4-tetraphenyldifluorobut-2-ene-1,4-dicarbonitrile[40]:

$$2(C_6H_5)_2CNaCN + CF_2=CF_2 \longrightarrow (C_6H_5)_2CCF=CFC(C_6H_5)_2.$$
$$\quad\quad\quad

13. FLUORINE-CONTAINING DINITRO-COMPOUNDS

Fluorine-containing dinitro-compounds have not been extensively studied. Most of the known ones have been obtained by the addition of nitrogen dioxide to fluorine--containing olefins.

Hass[124], Coffman[65], and Haszeldine[125] reported that reaction of nitrogen dioxide with tetrafluoroethylene and chlorotrifluoroethylene yields tetrafluoro-1,2-dinitroethane and chlorotrifluoro-1,2-dinitroethane respectively. Probably lack of care in the experiment or of precision in the reaction conditions prevented these workers from noticing several other most interesting products which are also formed, and from studying these reactions.

In a study of the nitration of perfluoroolefins with nitrogen dioxide, Knunyants and his coworkers established[126] that the process is more complicated, that it depends to a considerable extent on the characteristics of the fluoroolefin involved, and that it results in the formation of interesting substances. Thus in the reaction of tetrafluoroethylene with nitrogen dioxide in non-polar solvents, formation of small quantities of telomers of tetrafluoroethylene is accompanied by that of a mixture of tetrafluoro--1,2-dinitroethane and tetrafluoro-2-nitroethyl nitrite in the proportions 1 : 1.

$$CF_2=CF_2 \xrightarrow{N_2O_4} \begin{cases} O_2N-CF_2CF_2-ONO \\ O_2N-CF_2CF_2NO_2 \\ O_2N(CF_2CF_2)_nNO_2 \end{cases}.$$

When tetrafluoroethylene is nitrated in polar solvents, the yield of the dinitro-compound is lower. In the absence of solvents, perfluoropropene and perfluoroisobutene react with nitrogen dioxide under more severe conditions.

It is interesting that, when perfluoropropene is nitrated under these conditions, almost the sole reaction product is hexafluoro-2-nitropropyl nitrite, with only an insignificant quantity of hexafluoro-1,2-dinitropropane. In the case of perfluoroisobutene, pentafluoro-1,2-dinitro-2-trifluoromethylpropane and pentafluoro-2-nitro-2-trifluoromethylpropyl nitrite are formed in equal proportions.

From the experimental results, fluoroolefins can be arranged in the following sequence according to their reactivity towards nitrogen dioxide:

$$CF_2=CF_2 > CF_3CF=CF_2 > \begin{matrix} CF=CF \\ | \quad | \\ CF_2-CF_2 \end{matrix} < \begin{matrix} CF_3 \\ \diagdown \\ CF_3 \end{matrix}\!\!>C=CF_2.$$

The conditions under which nitration of fluoroolefins is accomplished, the nature of the products, and several other facts indicate that this reaction proceeds by a free radical mechanism:

$$CF_2=CF_2 + {}^{\bullet}NO_2 \longrightarrow O_2NCF_2\dot{C}F_2 \begin{cases} \xrightarrow{\dot{O}NO} O_2NCF_2CF_2NO_2 \\ \xrightarrow{ONO^{\bullet}} O_2NCF_2CF_2ONO \end{cases}.$$

Tetrafluoroethylene reacts with nitric oxide to form tetrafluoro-1,2-dinitroethane, but the main reaction product is tetrafluoro-1-nitro-2-nitrosoethane[127]. It is interesting that this last product reacts smoothly with tetrafluoroethylene to give an oxazetidine or a polymer thereof:

$$O_2NCF_2CF_2NO + CF_2=CF_2 \longrightarrow O_2NCF_2CF_2N \begin{matrix} - O \\ | \\ CF_2-CF_2 \end{matrix} \longrightarrow \left(\begin{matrix} - N-O-CF_2-CF_2- \\ | \\ CF_2-CF_2NO_2 \end{matrix} \right)_x.$$

The reaction is carried out at 0°–20°, and results in a 60–65% yield of polymer. The polymers obtained are viscous oils or elastomers, depending on their molecular weight, and possess high frost-resistance.

Dinitro-compounds are obtained also by the addition of nitromethane to fluorine-containing nitroolefins. Thus in the presence of sodium methoxide nitromethane adds on to 3,3,4,4,5,5,5-heptafluoro-1-nitropentene to form 1,1,1,2,2,3,3-heptafluoro-5-nitro-4-nitromethylpentane in good yield[111]:

$$C_3F_7CH=CHNO_2 + CH_3NO_2 \longrightarrow C_3F_7CH(CH_2NO_2)_2.$$

14. FLUORINATED BIFUNCTIONAL COMPOUNDS CONTAINING HETEROATOMS

Fluorinated bifunctional compounds containing heteroatoms have been little studied. A few fluorine-containing thia-, oxa-, and aza-compounds and fluoroalkadienes containing heteroatoms have been synthesised. The first group includes aza-, oxa-, and thia-dicarboxylic acids and their derivatives, and the second group compounds of the type $(CF_2{:}CF)_nM$ and their derivatives, where M = Hg, P, As, Sb, Si, and Sn. These compounds have not yet found any application.

(*a*) Fluorine-Containing Thia-, Oxa-, and Aza-Compounds

Most of the thia- and aza-compounds have been obtained by the addition of mercapto- or amino-esters to fluorine--containing unsaturated esters, which enables long-chain fluorine-containing bifunctional compounds to be prepared. In the presence of a quaternary base, mercaptoacetic ester adds on to ethyl 3-(perfluoropropyl)acrylate, forming ethyl 3-perfluoropropyl-4-thiaadipate, which is converted into the acid on hydrolysis with formic acid[60,128,129]:

$$C_3F_7CH=CHCOOC_2H_5 + HSCH_2COOC_2H_5 \rightarrow \begin{matrix} C_3F_7CHCH_2COOC_2H_5 \\ | \\ SCH_2COOC_2H_5 \end{matrix} \longrightarrow \begin{matrix} C_3F_7CHCH_2COOH \\ | \\ S-CH_2COOH \end{matrix}.$$

This ester has been obtained also by the reaction of bromoacetic ester with ethyl 4,4,5,5,6,6,6-heptafluoro-3--sodiothiohexanoate, itself obtained by the action of sodium hydride on the corresponding mercapto-ester[128]:

$$C_3F_7CHCH_2COOC_2H_5 + NaH \longrightarrow \begin{matrix} C_3F_7CHCH_2COOC_2H_5 \\ | \\ SNa \end{matrix} \xrightarrow{BrCH_2COOC_2H_5} \begin{matrix} C_3F_7CHCH_2COOC_2H_5 \\ | \\ SCH_2COOC_2H_5 \end{matrix}.$$

Aza-compounds have been obtained similarly. However, oxa-compounds cannot be prepared by these methods.

Reaction of ethyl 3-(perfluoropropyl)acrylate with hydrogen sulphide in the presence of a quaternary base in pyridine forms ethyl 3,5-bis(perfluoropropyl)-4-thiapimelate, which has been converted into the acid, the acid chloride, and the corresponding diol[60]:

$$2C_3F_7CH=CHCOOC_2H_5 + H_2S \longrightarrow \begin{matrix} S(CHCH_2COOC_2H_5)_2 \\ | \\ C_3F_7 \end{matrix} \longrightarrow \begin{matrix} S(CHCH_2COOH)_2 \\ | \\ C_3F_7 \end{matrix} \longrightarrow \begin{matrix} S(CHCH_2COCl)_2 \\ | \\ C_3F_7 \end{matrix} \longrightarrow \begin{matrix} S(CHCH_2CH_2OH)_2 \\ | \\ C_3F_7 \end{matrix}.$$

Oxa-compounds have been prepared by the addition of fluorine-containing diols to unsaturated compounds. Thus addition of 2,2,3,3,4,4-hexafluoropentanediol to acrylonitrile yields 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecane--1,11-dicarbonitrile, which is converted into the ethyl

TABLE. Fluorine-containing bifunctional compounds.

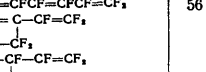
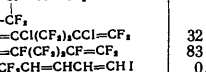
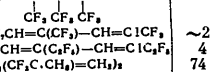
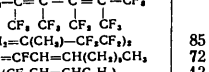
Compound	Yield, %	B.p., °C/mm	M.p., °C	n_D^{20}	d_4^{20}	References
1	2	3	4	5	6	7
Alkadienes						
$CF_2=C=CF_2$		—38				42, 43, 135, 136
$CF_2=C=CH_2$	56	—27				44—47, 137
$CF_2=CClCCl=CFCl$		104/740				135
$CF_2=C=C=CF_2$		—5				49, 50
$CF_2=CFCCl=CFCl$		72				135
$CF_2=CClCCl=CF_2$		69		1.3832		135, 138
$CFCl=CFCF=CFCl$	78	79		1.403		22, 135, 139
$CF_2=CFCF=CFCl$		35			1.471 (25)	140
$CF_2=CFCCl=CF_2$		37				135, 139, 141
$CF_2=CF-CF=CF_2$	3—98	7.4	—132	1.378	1.553 (—20)	14, 15, 18, 21, 22, 27, 36, 37, 135, 138, 139, 142—145
$CF_2CF=C=CF_2$	~1	6				146
$CF_2=CFCH=CFCl$	64	53		1.3804	1.431 (24)	18
$CF_2=CFCH=CF_2$	80	15.5				18, 21
$CF_2=CH-C\equiv CH$	85	0±2°				147
$CF_2=CFCF=CH_2$	54	—12				13, 148
$CF_2=CHCH=CF_2$	80	5				39, 141, 149
$CF_2=CFCH=CHF$	80	16.5		1.3427	1.342 (0)	18, 21
$CF_2=CClCH=CH_2$						141
$CF_2CH=C=CH_2$	44	16				48
$CF_2=CFCH=CH_2$	65—88	8.0				18, 19, 21
$CF_2=CHCF=CH_2$	42	16.9				19
$CFCl=CHCH=CH_2$		53.4		1.4267	1.066 (25)	150
$CH_2=CFCCl=CH_2$						151
$CF_2=CHCH=CH_2$	50	3.5—5		1.338	1.0 (2)	20, 141, 150, 152
$CH_2=CFCF=CH_2$		5—8	—92	1.373	1.001 (0)	9, 153
$CH_2=CHCF=CH_2$		12.0		1.400	0.843 (4)	154—156
$CF_2(CCl=CCl_2)_2$	91	101/13	—40.8	1.5171	1.748	16
$CF_2=CFC(CF_3)=CF_2$		37		1.3250	1.289	18, 135, 157
$CF_2=C(CF_2Cl)-CCl=CHCl$	54	43/38		1.4125(25)		69
$CF_2=C(CF_3)-CH=CF_2$	78	32.8		1.3087	1.494 (0)	157
$CF_2=CF-CH=CHCF_3$		50.5		1.3322	1.389 (22)	18
$CF_2=CHCF_2CH=CF_2$		45		1.3583	1.3935	158
$CF_2=C(CF_3)-CH=CH_2$	78	32		1.3372	1.310 (0)	157
$CF_2=CFCH=CHCH_3$	60	44		1.3689	0.9974 (+24)	159
$CF_2CH=CHCH=CH_2$	75	45		1.3751	1.027	32
$CF_2=CFCH_2CH=CH_2$	65	38/870		1.3435	1.0324 (27)	159
$CF_2=C(CH_3)-CF=CH_2$	60	50		1.3631	1.095 (25)	19, 39
$CH_2=C(CF_3)-CH=CH_2$	20	41		1.3485	1.064	32, 34, 160, 161
$CF_2(CH=CH_2)_2$	83	47	—135	1.3552	0.9368	16
$CF_2=CHC(CH_3)=CH_2$	61	35		1.3705	0.946 (25)	17, 20, 39, 150
$CF_2=C(CH_3)-CH=CH_2$	23	39		1.3760	0.9582 (25)	20, 39, 150 152
$CH_2=C(CH_3)-CF=CH_2$		47		1.397	0.847 (25)	155, 156
$CFCl=CFCF=CFCF=CFCl$	46	132		1.4324	1.6116 (25)	23, 24
$CF_2=CFCF=CFCF=CF_2$	56	65/748			1.537 (25)	23
						13
						13
$CF_2=CCl(CF_2)_2CCl=CF_2$	32	113.9	—34.1	1.3613	1.6789	38, 136
$CF_2=CF(CF_3)_2CF=CF_2$	83	59.6	—70.0	1.296	1.609	31, 38
$CF_2CF_2CH=CHCH=CHI$	0.5	104/46				25
$CF_2CH=CHCH=CHCF_2$	66	85.5		1.3403	1.286 (25)	35
$CF_2=CFCH=C(CH_3)-CF_2$		71		1.3531	1.350 (22)	18
$CF_2CH=CHC(CF_3)=CH_2$	58	74		1.3780	1.052	32
$CH_2=C(C_2F_5)-CH=CH_2$		54		1.3328(24)		161
$CH_2=CH(CF_2)_2CH=CH_2$	67	75.5		1.3415	1.135	35
$CF_2=CFCH=C(CH_3)_2$	42	52		1.3606	0.8538 (24)	159
$CF_3-CH=C(CF_3)-CH=CICF_3$	9	60/77				26
$CH_2=C(C_2F_7)-CH=CH_2$		68		1.3260		161
$CF_2CH=C(CH_3)-CH=CICH_3$		54/7		1.3260		26
$(CF_2=CFCF_2CF_2-)_2$	72.5	106		1.3020	1.695	28—31
$(CF_2=CFCF_2CF=)_2$	78	99				27
$(CF_2=CFCF_2CFCl-)_2$	51	58/20				27
$(CF_3)_2C=CClCCl=C(CF_3)_2$		123		1.3462	1.6838	162
		92		1.2886	1.6998 (25)	41
$C_6F_7CH=C(CF_3)-CH=CICF_3$	~2	83/56				26
$CF_3CH=C(C_2F_5)-CH=CIC_2F_5$	4	86/100				26
$CF_2(CF_2CH=CH_2)_2$	74	140		1.3682	1.110	33
$CH_2=CF(CH_2)_2CF=CH_2$		87/4		1.4036	0.9978	163
$CF_2=CF(CF_2)_2CF=CF_2$	67.8	148		1.3100	1.796	30, 31
		111.5		1.2994	1.7359 (25)	41
$(CH_2=C(CH_3)-CF_2CF_2)_2$	85	31/4		1.3620	1.228	33
$CF_2=CFCH=CH(CH_3)_2CH_3$	72	25/35		1.3810	0.838 (24)	159
$CF_2(CF_2CH=CHC_2H_5)_2$	12	86/19		1.3884	1.214	33
$(CF_2=CFCF_2CFClCF_2CF=)_2$		115/20				27
$(CF_2=CFCF_2CFClCF_2CFCl-)_2$	56	150/0.1				27
$CF_2=CF(CF_2)_2CF=CF_2$	60	181		1.3115	1.826	28—31
$(-CF_2CF_2CH=CHC_2H_5)_2$	10	92/14		1.3800	1.250	33
$(=CFC\equiv CC_4H_9)_2$	30	91/1		1.4842(25)		40
$CF_2=CF(CF_2)_{12}CF=CF_2$	72.9	147/33	73			30, 31
$(=CFC\equiv CC_6H_5)_2$	9		82			40
Diols						
$CF_2CHOHCH_2OH$	30	69.5/10	25.3	1.3617	1.505	70
$HOCH_2CF_2CH_2OH$	93		52.5			56, 64
$CF_2BrCHOHCHOHCF_2Br$		80/1	74.5			50
$HOCH_2(CF_2)_2CH_2OH$	90		85			56, 58, 63, 66
$CF_2CHOHCHOHCH_3$		77/23	66.5			164
$CF_2CHOHCH_2CH_2OH$	83	104/20				165
$HOCH_2(CF_2)_3CH_2OH$	93		77.5			56, 63, 66
$CH_3C(CF_3)OHCHOHCH_3$		58/5.5		1.3866	1.3282 (25)	34

TABLE (contd.)

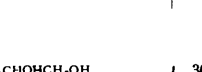
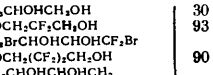
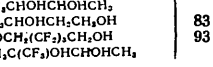
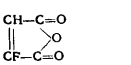
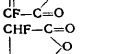
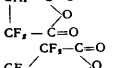
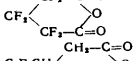
1	2	3	4	5	6	7
$CF_2CHOHCH_2CHOHCH_2$	85	78/3		1.3798	1.294	32
$HOCH_2(CF_2)_4CH_2OH$	88		68			56, 57, 66, 166
$C_3F_7CHOHCH_2CH_2OH$			90			167
$C_3F_7CHOHCF_2OHCH_2$						71
$HOCH_2(C_4HF_7)CH_2OH$		139/15	20—30			59
$CF_2CHOHCH_2CH_2CHOHCF_2$	75		75-120**			35
$CH_2CHOHCF_2CF_2CHOHCH_2$	64	201		1.3865	1.359 (25)	35
$C_3F_7CHOHCHOHC_2H_5$			88			71
$C_3F_7CHOHC(CH_3)_2OH$						71
$[\equiv C-C(CF_2Cl)_2OH]_2$	71		51			69
$[\equiv C-C(CF_3)_2OH]_2$	57.3		59			68
	50		71			67
HO—C(CF3)2C≡CC(CH3)2OH	63		77			68
$C_6F_7CH(CH_2CH_2OH)_2$	62	82/0.1		1.3752		60
$CF_2(CF_2CHOHC_2H_5)_2$	23		94			33
$CF_2[CF_2C(CH_3)_2OH]_2$	82		78			33
$[C\equiv C-C(CF_2Cl)_2OH]_2$	79		79			69
$[C\equiv C-C(CF_3)_2OH]_2$	83.3		70***			68
$HOCH_2(CF_2)_4CH_2OH$	85		136			166
$[CF_2CF_2C(CH_3)_2OH]_2$	98		81			33
$CF_2(CF_2CHOHC_2H_5)_2$	77		80			33
$CF_2[CF_2C(C_2H_5)_2OH]_2$	5		68			33
Diethers						
$CF_2OCF_2CF_2OCF_2$		13				72
$C_2F_5O(CF_2CF_2O)_2C_2F_5$		96.6/737		1.250	1.617 (30)	72
$(CF_2=CFOC_2H_5)_2$	41.8	83—5/17		1.3871	1.1883	73
$[=CFOCH(CH_3)_2]_2$		58—65/40				168
$[\equiv CC(CF_2Cl)_2OCH_3]_2$	46	67/0.2		1.4061(25)		69
$(CH_3)_2COCF=CFOC(CH_3)_2$						168
Diketones						
$CF_2COCH_2COCF_2$	72	63				74, 75
$CF_2COCH_2COCH_3$	62—80	107		1.3892		74—77
$C_2F_5COCH_2COCH_3$	84.5	111/631		1.3729		76
$CH_3COCF_2CF_2COCH_3$	45	128—130				35
$CF_2COCH_2COC_2H_5$	84	124/755		1.3951	1.22	77
$CF_2COCH(CH_3)COCH_3$	4.9	123/755		1.356	1.22	77
$C_3F_7COCH_2COCH_3$	78.5	56/38		1.3646		76
$CF_2COCH(CH_3)COC_2H_5$	66	148/735		1.3921	1.22	77, 78
$C_3F_7COCOC_2F_7$		95				67
$C_4F_9COCH_2COCH_3$	80	68/33		1.3589		76
$CF_2COCH_2COCH_2CH(CH_3)_2$	87	88/64		1.4103	1.13	77
$CF_2COCH(C_2H_5)COC_2H_7$	34	113/98				78
$CF_2COCH_2COC_6H_{13}$	55	65/6		1.4196	1.09(23)	77
Dicarboxylic acids						
$CF_2(COOH)_2$	63		117			16, 27, 169
$CHF(COOH)_2$			135			103, 114
HOOCCF=CFCOOH (*trans-*)	34		268—270			105, 106
HOOCCF=CFCOOH (*cis-*)			219—220			105, 106
$HOOCCF_2COCOOH$	81		116—118			170
$(CFClCOOH)_2$	62	100—105/0.1				22
$HOOCCF_2CFClCOOH$	85		55			105, 106
$(CF_2COOH)_2$	96	150/15	115—116			38,88,98,104,119
HOOCCH=CFCOOH (*trans-*)	77		236—237			105
HOOCCH=CFCOOH (*cis-*)	78		132—133			105
$HOOCCHFCF_2COOH$	83		111—112			105, 106
$HOOCCH_2CF_2COOH$	79		154—155			105, 170
$(CHFCOOH)_2$						104
$HOOCCF_2CH(OH)COOH$	57		139—140			170
$CFCl(CF_2COOH)_2$		130—145/0.1				99
$CF_2(CF_2COOH)_2$	90	134/3	78—88			89—91, 93
$HOOCCF_2CH_2COCOOH$						170
$HOOCCH_2CH_2CF_2COOH$	30		103			102
$(CFClCF_2COOH)_2$	51					27, 90
$(CF_2CF_2COOH)_2$	86		134			30, 31, 57, 90, 92—94, 171
$HOOCCF_2CHFCF_2CF_2COOH$	54		128			59, 95, 172, 173
$HOOCCHF(CF_2)_2COOH$			116			172—174
						170
$HOOCCHFCHFCF_2CF_2COOH$			126			93, 95, 96
$(CHFCF_2COOH)_2$			163			95, 174
$HOOCCH_2CH_2CF_2CF_2COOH$						97
$(CF_2CH_2COOH)_2$			247			97
$HOOC(CF_2CFCl)_2CF_2COOH$		145—165/0.2				99
$HOOCCF_2C(CF_3)FCF_2CF_2COOH$			60			109, 175
$CF_2C_4H_7(COOH)_2$						176
$HOOC(CF_2CFCl)_2COOH$	75	140—160/1				100
$HOOC(CF_2)_4COOH$	95		143			30, 31
$C_3F_7CH(CH_2COOH)_2$	94		121			60
$HOOC(CF_2CFCl)_3CF_2COOH$			105			99
$HOOC(CF_2CFCl)_4COOH$		155/0.6				100
$HOOC(CF_2)_6COOH$	92	160				30, 31, 80, 82, 87
$HOOC(CF_2CFCl)_4CF_2COOH$						99
$HOOC(CF_2CFCl)_5COOH$		140/0.08				100
$C_7F_{15}CH(CH_2COOH)_2$	53		125			60
$HOOC(CF_2)_{14}COOH$	71.8		191			30, 31
Anhydrides of dicarboxylic acids						
	89	128	20	1.4179 (25)		105, 106, 177
	81	78		1.3661 (25)		105
	62	54		1.3240	1.6209	63, 64, 119

TABLE (contd.)

1	2	3	4	5	6	7
	76	162		1.4452 (25)		105, 178
		122				105
	76.5	72		1.3190	1.6541(25)	83
	86	93/0.2	48.5			60

Chlorides and fluorides of dicarboxylic acids

$CF_2(COCl)_2$		66.8				64
$(CF_2COCl)_2$		86				64
$(CF_2COF)_2$	44—56	18	—59			107, 108
$(CF_2CF_2COCl)_2$	78.3	131		1.3488	1.679	30, 31
$(CF_2CF_2COF)_2$						85
$(C_4HF_7)(COCl)_2$		138				59
$C_5F_7CH(CH_2COCl)_2$	88	65/1.6		1.3926		60
$ClOC(CF_2)_4COCl$	80	101/23	29	1.3336	1.771 (37)	30, 31
$C_7F_{14}CH(CH_2COCl)_2$	73	80/0.7		1.3699		60

Esters of dicarboxylic acids

$CF_2(COOCH_3)_2$	81	60/12	—35	1.3721	1.3059	16, 27, 114
$CH_3OOCCF_2CFClCOOCH_3$	61	192		1.3908 (25)		105
$(CF_2COOCH_3)_2$		173		1.3555 (25)		120
$(CHFCOOCH_3)_2$	53	68/0.7				118
$CF_2(COOCH_2CF_3)_2$	57	157		1.326	1.525	64
$CF_2(CF_2COOCH_3)_2$	80	100/34	—31	1.3518	1.4856	89
$CH_3OOCCF_2CH_2COCOOCH_3$		89/3		1.4064 (25)		170
$CH_3OOCCF_2CH_2CH_2COOCH$	70	65/12				102
$(CFClCF_2COOCH_3)_2$		155/2				27
$(=CFCOOC_2H_5)_2$ (*cis-*)		55/1.1		1.4121 (25)		105
$(=CFCOOC_2H_5)_2$ (*trans-*)		72/1.1		1.4273 (25)		105
$C_2H_5OOCCF_2COCOOC_2H_5$	38	63/1		1.3972 (25)		170
$C_2H_5OOCCF_2CFClCOOC_2H_5$		219		1.3945 (25)		105
$(CF_2COOC_2H_5)_2$	60	89/15		1.3690	1.2640	58,88,107,110,119
$(CF_2COSC_2H_5)_2$		108/8				107
$C_2H_5OOC—CH=CFCOOC_2H_5$	83.6	74/1.5		1.4330	1.1456	73
$C_2H_5OOC—COCHFCOOC_2H_5$	67	95/1.5		1.42	1.261	114—116
$C_2H_5OOC—CHFCF_2COOC_2H_5$		75/2				105
$C_2H_5OOC—CH_2CF_2COOC_2H_5$	81	205/749		1.3912 (25)		105, 170
$C_2H_5OOCCH(OH)CF_2COOC_2H_5$	74	69/0.5		1.4078 (25)		170
$CF_2(CF_2COOC_2H_5)_2$	81—95	76/3—5		1.3585	1.3444	90, 120, 121
$CH_3OCCO—CHCF_2COOCH_3$ (COOCH$_3$)						170
$CF_2(CF_2COSC_2H_5)_2$	90	122/8		1.4351	1.3858(25)	83
$CF_2(CH_2COOC_2H_5)_2$	29	63/2		1.4038 (25)		117
$C_2H_5OOCCF_2CH_2CH_2COOC_2H_5$		127/28				102
$(CF_2)_2C=C(COOC_2H_5)_2$	87.6	59/6		1.3720	1.3025	113
$(CF_2CF_2COOC_2H_5)_2$	71	70/2—3		1.3541	1.4026	90,94,166,179,18
$(CF_2)_2C(OH)—CH(COOC_2H_5)_2$	78.5	58/1		1.3700	1,3730	112
$(CF_2)_2CHC(NH_2)(COOC_2H_5)_2$	53	60/1		1.3840	1.4534	113
$C_2H_5OOCCF_2C(OH)COOC_2H_5$ (CH$_2$COOH)	92		113			170
$[CF_2COOCH(CH_3)_2]_2$	88	83/5		1.3728		110
$(CF_2CH_2COOC_2H_5)_2$				1.3920 (25)		106
$CF_2CFCF_2COOC_2H_5$ (CF$_2$CF$_2$COOC$_2$H$_5$)		112/14		1.361 (12)		109
$CF_2CCl=C(CF_2)CH(COOC_2H_5)_2$		80/1		1.4018	1.3659 (29)	181
$(CF_2CF_2COOCH_2CH=CH_2)_2$		150—160/30				179
$(CF_2)_2C—OCOCH_3$ (CH(COOC$_2$H$_5$)$_2$)	41.7	112/10		1.3842	1.3608	68
$C_4F_7CHCH(COOC_2H_5)_2$ (CH$_2$NO$_2$)	49	145/9		1.3904		111
$[CF_2CF_2COOCH(CH_3)_2]_2$		232/745				179
$C_4F_7CH(CH_2COOC_2H_5)_2$	92	79/1.5		1.3738	1.320	60
$C_2H_5OOCCH_2CHCF_2COOC_2H_5$ (COOC$_2$H$_5$)	25	125/1		1.4215 (25)		170
$CF_2(CH_3)_2C(COOC_2H_5)_2$ (NHCHO)	59		87			182
$(CF_2COSC_2H_5)_2$		85—105/ <0.01		1.4719	(25)	183
$(CF_2)_2(COOCH_2C_2F_7)_2$	59	129/30		1.3142	1.7090 (24)	184
$C_2H_5OOC(CF_2)_4COOC_2H_5$		156/27		1.341	1.592 (25)	82, 166
$[CF_2CF_2COO(CH_2)_2CH_2]_2$	86	126/8.5		1.3725	1.2711 (25)	180
$[CF_2CF_2COOCH_2CH(CH_3)_2]_2$	57	118/8		1.3697	1.2671 (25)	180
$[CF_2CF_2COOCH(CH_3)C_2H_5]_2$	87	111/5		1.3680	1.2643 (25)	180
$[CF_2CF_2COOC(CH_3)_3]_2$		100—110/8				180
$C_4F_7CHCH(COOC_2H_5)_2$ (CH$_2$COOC$_2$H$_5$)	90	104/0.7		1.3900	1.306	60
$[=CFCH(COOC_2H_5)_2]_2$	48.5	150/1		1.4452		40
$CF_2(CF_2COOC_4H_{13})_2$	74	158/5		1.3938	1.1447 (25)	180
$(CF_2CF_2COOC_4H_{13})_2$	58	155/3.5		1.3888	1.2038 (25)	180
$(CF_2COSC_{10}H_7)_2$			130			184

Esters from fluorine-containing diols

$CF_3COOCHCH_2CHOOCCF_3$ (CF$_3$ CH$_3$)	75	158		1.3350		32
$CH_3COOCHCH_2CHOOC—CH_3$ (CF$_3$ CH$_3$)	88	188		1.3809		32

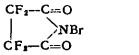
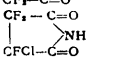
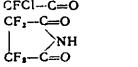
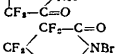
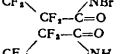
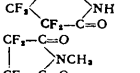
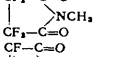
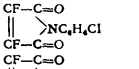
TABLE (contd.)

1	2	3	4	5	6	7
$[CH_2COOCH(CF_3)CH_2]_2$	100	133/75		1.3630	1.310 (26)	35
$[CH_2COOCH(CH_3)CF_2]_2$	87	205		1.3870	1.246 (25)	35
$(C_2F_5COOCH_2CF_2)_2CF_2$	62	131/30		1.3140	1.7085 (23)	184
$(C_4F_9COOCH_2CF_2CF_2)_2$	72	85/1.5		1.360	1.734 (25)	184
$(C_3H_7COOCH_2CF_2CF_2)_2$	77	112/1		1.3793	1.3181 (25)	185
$C_3F_7COOC=COOCC_3F_7$ (F_7C_3 C_3F_7)	5	89/19				67
$(NO_2C_6H_4COOCH_2)_2CF_2$			107			64
$(CH_2C_6H_4SO_2CH_2CF_2)_2CF_2$	79		92			123
$[H(CF_2)_4C=$ $H(CF_2)_4COO]_2$	19	167/20		1.3255		64
$(NO_2C_6H_4COOCH_2CF_2CF_2)_2$			105			57
$(C_6H_5COOCH_2)_2(C_6HF_7)$	66		74			59
$[\equiv C—C(CF_2Cl)_2SO_2C_6H_4CH_3]_2$	75		189			69
$[(CF_2)_4COOCH_2(CF_2)_4H]_2$	quant.		58			31
$[(CF_2)_4COOCH_2(CF_2)_6H]_2$	quant.		110			31

Diamides of dicarboxylic acids

$CF_2(CONH_2)_2$			206			16, 27, 169
$CHF(CONH_2)_2$			198			128
$H_2NCOCF=CFCONH_2$ (*trans-*)	84		>280			105
$H_2NCOCHFCF_2CONH_2$	78		195			105
$H_2NCOCF_2CFClCONH_2$	83		250			105
$(CF_2CONH_2)_2$			261			79, 119, 169
$(CHFCONH_2)_2$ (CF$_2$—CONH / CF$_2$ / CF$_2$—CONH)						133
$H_2NCO(CF_2)_4CONH_2$	96		208			90, 121
$(CF_2CF_2CONH_2)_2$			237			90, 94, 121
$H_2NCOCF_2CF_2CHFCF_2CONH_2$			205			59, 172
$H_2NCOCHF(CF_2)_2CONH_2$			180			172
$(CHFCF_2CONH_2)_2$			206			96
$CF_2CFCF_2CONH_2$ (CF$_2$CF$_2$CONH$_2$)	70		168			109
$CF_2(CF_2CONHCH_2)_2$	87.5		144			123
$(CF_2CONHCH_2CH_2OH)_2$			142			119
$C_3H_7NHCOCH=CFCONHC_3H_7$			55			73
$CF_2(CF_2CONHC_6H_5)_2$	91.3		120			123
$H_2NCO(CF_2)_4CONH_2$			239			30, 31, 82, 123
$CF_2[CF_2CONHCH(CH_3)_2]_2$	62		139			123
$(CF_2CONHC_6H_5)_2$			130			119
$CF_2(CF_2CONHCH_2C_3F_7)_2$	45		135			123
$CF_2(CF_2CONHC_6H_5)_2$	88		117			123
$CF_2[CF_2CONHC(CH_3)_3]_2$	66		120			123
$(CF_2CONHC_6H_5)_2$ [CF$_2$CON(CH$_2$)$_2$]$_2$			227			64
$(CF_2CF_2CONHC_6H_5)_2$	quant.		196			119
$(C_4HF_7)(CONHC_6H_5)_2$			164			30, 31
$(C_6HF_7)(CONHC_6H_{11})_2$			196			59
$[(CF_2)_4CONHC_6H_5]_2$	quant.		199			59
$(CF_2CONHC_{18}H_{37})_2$			105			30, 31

Imides of dicarboxylic acids

	87					120
	39	48/2		1.4333(25)		105
	80	178	66			120
						120
	89	159	27			120
			97			120
	90		74			105
	46		88			105

Dinitriles and diamidines of dicarboxylic acids

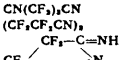
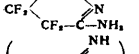
$CN(CF_2)_4CN$		38/745				90, 121
$(CF_2CF_2CN)_2$	64	63		1.2770	1.4303	90, 121
						122
			125			122
$(C_6H_4)_2CCF=CFC(C_6H_4)_2$ (CN CN)	46	166				40

TABLE (contd.)

1	2	3	4	5	6	7
Diamines						
$CF_3(CF_2CH_2NH_2)_2$						90, 121
$(CF_3CF_2CH_2NH_2)_2$	40	65/5—6	44			90, 121
$CF_3(CF_2CH_2NHCH_3)_2$	43.8	55/10.5		1.3771(26.5)		123
$CF_3(CF_2CH_2NHC_2H_5)_2$	44	46/0.05		1.3864 (27)		123
$CF_3[CF_2CH_2NHCH(CH_3)_2]_2$	41.4	70/0.55		1.3917 (25)		123
$CF_3(CF_2CH_2NHCH_2C_3F_7)_2$	52.5	72/0.04		1.3278 (28)		123
$CF_3(CF_2CH_2NHC_4H_9)_2$	39.8	70/0.5		1.4038 (25)		123
$CF_3[CF_2CH_2NHC(CH_3)_3]_2$	39.2	67/0.37		1.4020 (26)		123
Dinitro-compounds						
$NO_2CFClCFClNO_2$	47	55/35	12—18	1.4116(25)	1.646	124
$NO_2CF_2CCl_2NO_2$	47	81/103				125
$NO_2CF_2CFClNO_2$	51	98		1.3748	1.674 (25)	124, 125
$NO_2CF_2CF_2NO_2$	53	59	—41.5	1.3249	1.622	65, 124—126
$CF_3CF(NO_2)CF_2NO_2$		76		1.3141	1.6313	126
$(CF_3)_2C(NO_2)CF_2NO_2$		92		1.3212	1.660	126
$C_3F_7CH(CH_2NO_2)_2$	68		62			111
Thia-, oxa-, and aza-compounds						
$C_3F_7CHCH_2COOH$ | SCH_2COOH	82		72.5			128, 129
$C_3F_7CHCH_2COOH$ | $NHCH_2COOH$	89		156			128, 129
$CF_3(CF_2CH_2OCH_2COCl)_2$	93	110/0.1	49—52			129, 130
$CF_3(CF_2CH_2OCH_2COOH)_2$	76		82			129, 130
$CF_3(CF_2CH_2OCH_2CONH_2)_2$			147			129, 130
$CF_3(CF_2CH_2OCH_2CH_2CN)_2$	28	180/0.08		1.4040	1.381	130
$S[CH(C_2F_7)CH_2COCl]_2$	85	86/0.7		1.3892		60
$S[CH(C_2F_7)CH_2COOH]_2$	78		156			60
$S[CH(C_2F_7)CH_2CH_2OH]_2$	86	109/0.2	47			60
$C_3F_7CHCH_2COOC_2H_5$ | $SCH_2COOC_2H_5$	85	85/0.4		1.4028	1.363	128, 129
$S[CH(CF_3)CH_2COOC_2H_5]_2$	57	114/3	3	1.3737		60
$C_3F_7CHCH_2COOC_2H_5$ | $NHCH_2COOC_2H_5$	75	80/0.11		1.3831	1.326	129
$CF_3(CF_2CH_2OCH_2CH_2COOCH_3)_2$	22	125/0.06		1.4028	1.348	129, 130
$CF_3(CF_2CH_2OCH_2COOC_2H_5)_2$	77	134/0.1		1.4010	1.345	129, 130
$C_3F_7CHCH_2COOC_2H_5$ | $CH_3NCH_2COOC_2H_5$	58	95/1.9		1.3860	1.298	128, 129
$CF_3(CF_2CH_2OCH_2CH_2COOC_2H_5)_2$	70	131/0.07		1.4041	1.287	129, 130
$S(CHCH_2COOC_2H_5)_2$ | C_3F_7	74	100/0.6		1.3763	1.475	60
Fluoroalkadienes containing heteroatoms						
$(CF_2{=}CF)_2Hg$		65/17				131
$(CF_2{=}CF)_2PCl$	60	94		1.4095	1.550 (28)	132, 186
$(CF_2{=}CF)_2PF$	50	63				132, 186
$(CF_3C{\equiv}C)_2Hg$			42			134
$(CF_2{=}CF)_3P$	35.4	99		1.3909	1.6150 (23.5)	132, 186
$(CF_2{=}CF)_3As$	40	110/746		1.3838	1.8400 (18)	133, 186
$(CF_2{=}CF)_3Sb$	41	75/74		1.4190	2.06 (24)	133, 186
$(CH_3)_2Sn(CF{=}CF_2)_2$	65	58/38				187
$CF_2{=}CFCH{=}CHSi(CH_3)_3$	78	36/40		1.4151	1.4159 (24)	188
$(CF_2{=}CF)_4Si$	42	119		1.3621	1.6182	189
$(CF_2{=}CF)_2PN(C_2H_5)_2$	37.5	60/25		1.4098	1.291 (25)	132, 186
$[CF_2CH{=}CHSi(CH_3)_3]_2$	23.6	60/60		1.4348	0.9009 (22)	188

* Where the specific gravity or refractive index is not given for 20°, the corresponding temperature is indicated in parentheses.

** Mixture of *D*, *L*, and *meso*-forms.

*** Hydrate.

ester on hydrolysis with alcoholic hydrogen chloride; this ester has been obtained also by the direct addition of 2,2,3,3,4,4-hexafluoropentane-1,5-diol to ethyl acrylate[129,130]:

$$CF_2(CF_2CH_2OH)_2 \xrightarrow{CH_2{=}CHCN} CF_2(CF_2CH_2OCH_2CH_2CN)_2 \xrightarrow{HCl-C_2H_5OH} CF_2(CF_2CH_2OCH_2CH_2COOC_2H_5)_2$$

The C—O—C bond in compounds of this type is comparatively unstable, and on hydrolysis with alkali or mineral acids it undergoes cleavage with the formation of a diol. However, on cautious hydrolysis of the above ester with formic acid, a good yield of the corresponding acid is obtained, and this has been converted into the chloride and the diamide[129,130].

(*b*) Fluoroalkadienes Containing Heteroatoms

These compounds are obtained by the action of fluorine-containing Grignard reagents on the chlorides of certain elements. Trifluorovinylmagnesium iodide reacts with mercuric chloride at -10° to form bis(trifluorovinyl)mercury[131]:

$$2CF_2{=}CFMgI + HgCl_2 \longrightarrow Hg(CF{=}CF_2)_2 + MgCl_2 + MgI_2.$$

The compounds $Si(CF{:}CF_2)_4$ and $M(CF{:}CF_2)_3$, where M = P, As, Sb, have been prepared in a similar manner[132,133].

Reaction of trifluorovinylmagnesium iodide with diethylphosphoramidous dichloride forms *NN*-diethylbis(trifluorovinyl)phosphinous amide, which on treatment with hydrogen chloride followed by fluorination with antimony trifluoride is converted into bis(trifluorovinyl)phosphinous fluoride[132]:

$$CF_2{=}CFMgI + Cl_2PN(C_2H_5)_2 \longrightarrow (CF_2{=}CF)_2PN(C_2H_5)_2 \xrightarrow{HCl} (CF_2{=}CF)_2PCl \xrightarrow{SbF_3} (CF_2{=}CF)_2PF.$$

Trifluorovinylmagnesium iodide reacts with dimethyltin dichloride to give dimethylbis(trifluorovinyl)tin[12]:

$$(CH_3)_2SnCl_2 + 2CF_2{=}CFMgI \longrightarrow (CH_3)_2Sn(CF{=}CF_2)_2.$$

Bis(trifluoroprop-1-ynyl)mercury has also been described[134]:

$$CF_3C{\equiv}CH \longrightarrow (CF_3C{\equiv}C)_2Hg.$$

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CHROMATOGRAPHY OF PROTEINS ON CELLULOSE ION EXCHANGERS

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INTRODUCTION

Chromatography of proteins on cellulose ion exchangers was first successfully used in 1956 by Peterson and Sober [1-3] and by Ellis and Simpson [4], and in the following years it became the most widely used procedure in preparative protein chemistry, particularly in the later purification stages. Cellulose ion exchangers have several properties that make them suitable for the chromatography of proteins, the most outstanding being high separating power; many crystalline proteins, and also protein preparations, that appear homogeneous under electrophoresis and ultracentrifuging have been found to be heterogeneous when they are chromatographed on cellulose ion-exchange columns [5-10]. Proetins suffer very little damage on these columns and the yield often reaches 100%. The chemical stability of the columns, their low adsorptive capacity for low-molecular-weight compounds, and their low resistance to liquid flow are also of great importance.

Experimental work on the chromatography of proteins on cellulose ion exchangers has been summarised in several reviews [11-14]. However, no attempt has yet been made to examine the experimental results in a methodical manner with the object of elucidating the mechanism of adsorption and separation. The development of this promising method is greatly hindered by the absence of information of this kind, and the necessity of selecting experimental conditions empirically means that full use cannot be made of all the possibilities of the technique.

In the present paper we do not aim at covering all the literature on the subject, but we have collected and summarised the main results that throw some light on the mechanism of adsorption and separation and which can be used for the setting up and planning of experiments. Not all the theories in the paper have a reliable experimental basis; some are partly hypotheses. However, their discussion is justified by the almost complete absence of special studies on the chromatography of proteins, and we hope it will promote the development of investigations of this kind.

I. CELLULOSE ION EXCHANGERS

1. The Synthesis of Cellulose Ion Exchangers

The fibre in natural cellulose is partly oriented, having a semicrystalline structure, but when cellulose is treated with a concentrated alkali solution, as in mercerisation, the alcoholate (alkali cellulose) is formed:

$$[C_6H_7O_2(OH)_3]_n + n\,NaOH \longrightarrow [C_6H_7O_2(OH)_2ONa]_n + n\,H_2O\,.$$

When the solution is diluted with water, free cellulose is re-formed, but the orientation of the fibres is completely destroyed. This is accompanied by an increase in hydrophilic properties and reactivity. The general method of preparing cellulose ethers, the class of compounds to which the cellulose ion exchangers at present in use belong, consists in the reaction of an alkyl halide with alkali cellulose in the presence of an excess of alkali:

$$[C_6H_7O_2(OH)_2ONa]_n + m\,n\,R\,CH_2Cl + 2n\,NaOH \rightarrow [C_6H_7O_2(O\,CH_2\,R)_m]_n + 3n\,NaCl\,.$$

Here m = 1, 2, or 3, and n depends on the degree of polymerisation of the cellulose, being generally 6000–10 000. If R contains ionising groups, the cellulose ether formed will be an ion exchanger. The number of ether bonds m per polymer unit is determined by the concentration of the alkyl halide in the reaction mixture. The more ionising groups are present, the greater is the adsorptive capacity of the exchanger, but the presence of too many of these groups leads to gelatinisation, or even to dissolution of the cellulose. In the exchangers generally used, the number of ionising groups does not, as a rule, exceed 1–2 mg-equiv. per gramme of adsorbent, *i.e.* about one ionising group per 4–8 glucose residues.

Phosphocellulose is an ester of phosphoric acid and cellulose. Esters of cellulose with organic acids have also been synthesised and used as ion exchangers [15-17]. Diethylaminoethyl cellulose was first synthesised by Hartmann [18] in 1930. More recently, aminoethylcellulose [19], *p*-aminobenzylcellulose [20], triethylaminoethylcellulose [21], ecteola-cellulose, and cation exchangers [21], including carboxymethylcellulose [22], have been prepared. The ion-exchange properties of cellulose exchangers were first pointed out by McIntire and Schenk [17], and the first attempt to employ them for purifying proteins was made by Hoffpauir and Guthrie [23]. Syntheses of the most widely used cellulose ion exchangers are described by Peterson and Sober [2] and by Ellis and Simpson [4], and also in "Biochemical Preparations" [24]. The use of these exchangers in paper form appears to be very promising [25,26]. Recently, diethylaminoethyl Sephadex [27-31] has been synthesised and used in the fractionation of proteins and other compounds; this differs from cellulose ion exchangers in the structure of the insoluble ion, being based on the polysaccharide dextran, in which the chains are cross linked. The adsorbent therefore has a three-dimensional mesh structure.

Attempts have been made to prepare enzyme-specific adsorbents in which the ionising group is an analogue of the substrate of the enzyme to be separated [32]; simple unmodified cellulose acts as a specific adsorbent for enzymes that hydrolyse cellulose [33]. For enzymes that act on ionising substrates, these attempts can hardly be regarded as soundly based, because the non-specific electrostatic interaction between the protein and the exchanger will predominate over the interaction between the exchanger and the active centre of the enzyme.

2. General Properties of Cellulose Ion Exchangers

All cellulose ion exchangers are weak acids or bases. The number of ionising groups and the ionisation constants can be determined by titrating a suspension in a 1 M solution of NaCl with a glass electrode; Fig. 1 shows typical titration curves. The number of ionising groups may also be found from nitrogen, phosphorus, or sulphur determinations.

The presence of like charges on molecules of the ion exchanger leads to mutual repulsion between sections of the chain; this renders the ionising groups more readily accessible even to large exchanging ions.

The rate of exchange on synthetic resins is determined by the time required for ions to diffuse into the adsorbent granules, this being the slowest process. This factor is of particular importance in the adsorption of high-molecular-weight compounds such as proteins[32]; for this reason, in protein chromatography on synthetic resins extremely slow flow rates must be used (~ 2 ml h^{-1} per cm^2 of cross-section). In cellulose ion exchangers, the matrix is not a three-dimensional mesh, as in synthetic ion-exchange resins, but consists of "one-dimensional" fibres, separated from one another in the column by a layer of hydrate or capillary water through which protein molecules pass freely. The internal diffusion factor is therefore eliminated and very high flow rates (up to 50 ml h^{-1} per cm^2 of cross-section) may be used without impairing the results.

Because of the hydrophilic properties of cellulose in aqueous suspensions, these ion exchangers do not form sharp liquid–solid boundaries, unlike mineral adsorbents, or liquid–oil boundaries, and unlike synthetic ion-exchange resins. The adsorbent is, as it were, covered by an envelope of water of hydration. This has two important consequences: first, the sorption of proteins on surfaces is excluded, and second, surface denaturation is eliminated. As has been pointed out, the yield of proteins in cellulose ion-exchange chromatography can reach 100%; when thyrotropine is chromatographed on Amberlite, ~ 50% is lost, but on a column of carboxymethylcellulose the same degree of purification is achieved with 100% yield[35].

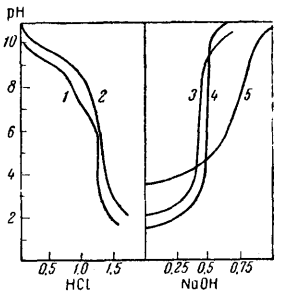


Fig. 1. Titration curves of cellulose ion exchangers:
1) diethylaminoethylcellulose; 2) triethylaminoethylcellulose; 3) sulphomethylcellulose; 4) sulphoethylcellulose; 5) carboxymethylcellulose.

The pK values of cellulose cation exchangers range from 2 to 2.5, and those of anion exchangers from 7 to 9.5. The exchangers are thus weak acids or bases. Their salts should therefore be strongly hydrolysed, especially those with weak acids or bases, for example, amino-acids. This means that low-molecular-weight compounds of this type move along the column at the same rate as the solvent, or at a rate differing only slightly from that of the solvent[36,37]. Proteins are also weak acids or bases, but they are strongly adsorbed, because the multiplicity of charge on the protein ion allows multiple bonds to be formed between the protein and the exchanger.

An increase in the content of ionising groups increases the adsorptive capacity and separating power of the cellulose ion exchanger[3], but the tendency to gelatinisation with increasing capacity leads to increased resistance to liquid flow, which hinders chromatography or make it impossible. Completely soluble polysaccharides with a high content of ionising groups (1–3 per glucose residue) may be used for the fractional precipitation of proteins[38,39].

Particle size has no appreciable effect on adsorptive properties. The adsorbents generally used have a particle size of 200–400 mesh. If the particles are in the form of long fibres (over 1 mm long), uniform packing of the column is impeded, as ion exchangers of this size form lumps; moreover, after the column has been packed and the external pressure removed, the volume of the packed exchanger may increase considerably because of the mechanical elasticity of the fibres. The type of cellulose from which the sorbent has been prepared has some effect on the properties[2].

3. Cellulose Anion Exchangers

Diethylaminoethylcellulose, or DEAE-cellulose, is prepared by the reaction of 2-chlorotriethylamine hydrochloride with cellulose in concentrated alkali solution. In aqueous suspension it forms a hydrate, which dissociates to give a hydroxide ion, the ion which undergoes exchange:

$$\text{Cell.}C_2H_4N(C_2H_5)_2 + H_2O \rightleftharpoons \text{Cell.}C_2H_4\overset{+}{N}H(C_2H_5) + OH^-.$$

DEAE-cellulose is a weakly alkaline anion exchanger (pK' = 9.5) and the most versatile cellulose ion exchanger. It is widely used for the fractionation of proteins; it can also be used for the separation of nucleic acids[40], nucleotides[41–43], viruses[44], peptides[45–48], polysaccharides[49], and other compounds[50,51].

Triethylaminoethylcellulose, or TEAE-cellulose, is obtained by the reaction of DEAE-cellulose with ethyl bromide[21]. The ionising group appears to have the structure of a quaternary ammonium base with hydroxide as the exchangeable ion. It differs little from DEAE-cellulose in properties and range of application[52–54].

Aminoethylcellulose, or AE-cellulose (Cell. .$C_2H_4NH_2$), is a somewhat less alkaline exchanger than DEAE-cellulose (pK' = 9.3).[55,56]

Ecteola-cellulose, or ecteola, is a product of the reaction of epichlorohydrin and triethanolamine with cellulose in concentrated alkali solution. The structure of the ionising group is unknown. It is a less alkaline anion exchanger than DEAE-cellulose (pK' = 7.6). Ecteola is most suitable for fractionating nucleic acids[57–60] and

nucleoproteins[61-63], and it is also used for isolating nucleotides[64,65], heparin and hyaluronic acids[66,67], and viruses[68-70]. It is curious that the chromatographic behaviour of bacteriophage on ecteola columns is determined by the protein and not by the nucleic acid component[71]. Ecteola has been successfully used for purifying the alkaline phosphatase from pig's kidney, but this enzyme is probably not a protein[72].

Paraminobenzylcellulose, or PAB-cellulose (Cell.$CH_2C_6H_4NH_2$), is a still less alkaline anion exchanger than ecteola. It is mainly used in the preparation of protein ion exchangers for the isolation of antibodies and the fractionation of nucleic acids[73-75].

Guanidoethylcellulose, or GE-cellulose (Cell.$OC_2H_4NHC{=}NHNH_2$), is prepared by the guanidation of aminoethylcellulose. The ionising groups are titrated at pH 8.5–10.[56]

4. Cellulose Cation Exchangers

Carboxylmethylcellulose, or CM-cellulose (Cell.CH_2COOH), is obtained by the reaction of cellulose with monochroroacetic acid in concentrated alkali solution. It is a weak cation exchanger ($pK' = 3.6$), and is used for separating alkaline, neutral and weakly acid proteins[76-82], and also peptides[83-85] and viruses[86].

Phosphocellulose, or P-cellulose, is an ester of phosphoric acid and cellulose [Cell.$PO(OH)_2$]. It is prepared by the reaction of cellulose with phosphorus oxychloride in concentrated alkali solution and is more strongly acid than CM-cellulose. In each phosphoric acid residue two hydroxy-groups are capable of dissociating ($pK_1' = 3$; $pK_2' = 7$). It is used in the chromatography of proteins and some other compounds[54,88].

Sulphoethylcellulose, or SE-cellulose (Cell.$C_2H_4SO_2OH$) and sulphomethylcellulose (SM-cellulose, Cell.CH_2SO_2OH) are still more acid cation exchangers than phosphocellulose[21]; they are used for fractionating proteins[89-92].

II. NATURE OF THE INTERACTION OF PROTEINS WITH CELLULOSE ION EXCHANGERS

1. Adsorption by an Ionic Mechanism

The adsorption of proteins on cellulose ion exchangers is mainly due to electrostatic forces. This hypothesis is supported by the following facts: (1) the overwhelming majority of proetins that are adsorbed on these exchangers are not adsorbed by untreated cellulose containing no ionising groups; (2) the adsorptive capacity of the exchanger increases with the number of ionising groups; (3) adsorption is rapid, equilibrium being reached in a few minutes[93]; and (4) when proteins are eluted from cellulose cation exchangers by a solution of increasing pH, the components appear in the order of decreasing electrophoretic mobility; when they are eluted from anion exchangers by an eluent of decreasing pH, the fractions appear in the eluate in the order of increasing electrophoretic mobility[3,94,95].

Mitz and Schlueter[96] observed a stoichiometric relationship in the interaction of proteins with cellulose ion exchangers: 1 g of DEAE-cellulose containing 0.8 mg-equiv. per gramme of ionising groups binds 0.8 g of pepsin (equivalent weight 1000); if half the carboxy-groups of pepsin are uncharged, the same amount of adsorbent binds twice as much pepsin; if the number of active adsorbent groups is doubled, the amount of pepsin bound is also doubled.

The adsorption of proteins on cellulose ion exchangers may therefore be represented by the following ion-exchange equations:

$$\text{Cell-a}^+\text{A}^- + \text{P}^- \rightleftharpoons \text{Cell-a}^+\text{P}^- + \text{A}^-, \quad (1)$$

$$\text{Cell-c}^-\text{C}^+ + \text{P}^+ \rightleftharpoons \text{Cell-c}^-\text{P}^+ + \text{C}^+, \quad (2)$$

where Cell-a^+ and Cell-c^- are the insoluble ions of the cellulose anion and cation exchangers respectively, A^- and C^+ are their exchangeable ions, and P^- and P^+ are the anionic and cationic forms of the protein.

In the ion exchange of proteins specific features of the protein molecule must be considered, the main ones being (1) amphoteric character, (2) the multiplicity of charge on the protein ion, and (3) the large dimensions of the protein molecule and the distribution of active ionising groups over its whole surface.

In the adsorption of dipolar ions, in addition to electrostatic attraction that occurs in the adsorption of ions with like charges, electrostatic repulsion also occurs. However, Samsonov and Kuznetsova[97] have shown that the adsorption of dipolar ions on H-exchangers proceeds as follows:

$$\text{RSO}_3^-\text{H}^+ + \text{NH}_3^+\text{R}_1\text{COO}^- \rightleftharpoons \text{RSO}_3^-\text{NH}_3^+\text{R}_1\text{COOH}, \quad (3)$$

that is, the exchangeable hydrogen ion passes to a negatively charged group of the dipolar ion, and the ion is converted to a cation and adsorbed without electrostatic repulsion. This interpretation leads to the conclusion that dipolar ions of the amino-acid type should be adsorbed to a much smaller extent by ion exchangers in the salt form, since the salt is always dissociated, and in this case electrostatic attraction and repulsion will compete. This conclusion has been confirmed experimentally by Samsonov and Kuznetsova. Proteins are also adsorbed better by cellulose from a salt-free medium[93,98], which enables Eqn. (3) to be applied. The further apart the oppositely charged groups, the weaker is the repulsion effect. Thus diglycylglycine and glycylglycine are adsorbed much better than glycine by SBS-2 resin and DEAE-cellulose[36,97]. Although the ionising groups of the polypeptide chain of the protein molecule are generally separated from one another by several amino-acid residues, they may approach when the polypeptide chain curls, as in the formation of secondary, etc. structures.

The following equations represent the adsorption of proteins on cellulose ion exchangers in the hydrogen and hydroxide forms, the special features of the ion exchange of bipolar ions being taken into account:

$$\text{Cell-a}^+\text{OH}^- + {}^-\text{OOCPNH}_3^+ \rightleftharpoons \text{Cell-a}^{+-}\text{OOCPNH}_2 + \text{H}_2\text{O}, \quad (4)$$

$$\text{Cell-c}^-\text{H}^+ + {}^+\text{H}_3\text{NPCOO}^- \rightleftharpoons \text{Cell-c}^-\text{H}_3^+\text{NPCOOH}, \quad (5)$$

where $^-OOCPNH_3^+$ is the dipolar protein ion. However, these equations cannot be regarded as an accurate description of the process; on the one hand, the number of positively and negatively charged groups on the protein ion may not be the same and, on the other, the spatial arrangement of the charged groups that give rise to repulsion may be such that they remain dissociated.

Another peculiarity of the exchange of dipolar ions is that the same ion may be adsorbed by both cation and anion exchangers; in some separation methods proteins are adsorbed successively by anion and cation exchangers [94,95,98,99]. This property is reflected in Eqns. (4) and (5), in which the protein residues may be identical.

The multiplicity of charge on the protein ion coupled with the large dimensions of the protein molecule lead to another peculiarity in the adsorption of proteins: in adsorption the reacting unit is not the whole molecule but only a limited section of its surface. Since the ionising groups are not distributed uniformly over the molecule, it is clear that under the same conditions, the same protein ion can be held by the same adsorbent with a force that varies according to the orientation of the molecule on the adsorbent surface. This may be one reason why chromatographic zones become diffuse in the elution of proteins from cellulose ion-exchange columns.

Naturally, the properties of the protein molecule as a whole also affect the adsorption properties, the magnitude of the total charge on the molecule being of primary importance. As has been mentioned, when a protein mixture is chromatographed the components are often eluted in the order of increasing (on cellulose cation-exchange columns) or decreasing (on anion-exchange columns) electrophoretic mobility, the pH of the eluent being somewhat lower than the isoelectric point of the protein in elution from anion-exchange columns, and somewhat higher in elution from cation-exchange columns. Thus the protein may remain in the adsorbed state even when the total charge is of the same sign as that of the insoluble cellulose-exchanger ion. On the other hand, if the total charge on the protein molecule is opposite to that of the insoluble cellulose-exchanger ion, this does not mean that the protein will be adsorbed. Thus thetin homocystein methyltransferase, with an isoelectric point of 6.4, is not adsorbed on DEAE-cellulose at pH 6.8. [100] Therefore, although the magnitude of the total charge affects the adsorption properties of proteins, it does not determine them completely.

The presence of a dipole in the protein molecule may also affect the adsorption properties; the adsorption will, of course, increase with the dipole moment. Since cellulose ion exchangers are either weak acids or weak bases, it would seem that their saltlike compounds with proteins, which are also weak acids and bases, should be strongly hydrolysed, that is, adsorption of proteins on cellulose ion exchangers in an aqueous medium should be negligible. The stability of the compounds formed by proteins with cellulose ion exchangers in aqueous suspensions can be explained by the multiplicity of charge on the protein molecule, which makes possible the formation of a large number of salt bonds with the exchanger. Amino-acids and small peptides, which have the same ionising groups as proteins, are either not adsorbed or they form only a weak bond with the ion exchanger. Thus, only the most alkaline amino-acids, histidine, lysine, and arginine, are adsorbed on CM-cellulose, and only aspartic and glutamic acids on DEAE-cellulose [37]. Glycylglycine and diglycylglycine are adsorbed on DEAE-cellulose, but they are very easily eluted, glycylglycine by water and diglycylglycine by a solution of CO_2 at 1 atm. [36] The effect is also observed in the converse experiment; soluble ionising derivatives of polysaccharides form complexes with proteins, but similar derivatives of oligosaccharides (with four carbohydrate residues) are not complexed [101-103]. The effect of the number of charged groups is clearly shown in the chromatography of adenylic acid polymers on cellulose ion exchangers: polymers from the dimer to the hexamer are eluted in the order of increasing chain length, that is, in the order of increasing number of charged groups in the molecule [104]. Statistically, the strength of the multiple bond is explained in the following way: the exchange of one multicharged ion for several singly-charged ions requires the simultaneous approach of these several ions to the bond, which is unlikely; on the other hand, the formation of one salt linkage between a protein and a cellulose ion exchanger promotes the formation of subsequent bonds by binding the protein to the exchanger.

All that has been said above about the relative electrostatic interaction between the protein and the cellulose ion exchanger may be summarised in the following equations. If X is the sum of all the ionising groups of the protein molecule that form charges on it opposite in sign to those on the insoluble exchanger ion, x and x' are ionising groups of the same type as X that do not participate in bond formation with the exchanger for steric reasons (x) or because they are not dissociated under the given conditions (x'), the number of salt linkages will be

$$Z = X - x - x'. \quad (6)$$

We shall term Z, the number of salt bonds formed between the exchanger and the protein molecule, the effective valency of the protein molecule. The main properties of the effective valency are its dependence on pH and on the orientation of the protein molecule on the adsorbent surface.

The total charge E of the protein molecule is

$$E = (X - x') + (Y - y'), \quad (7)$$

where Y is the sum of all the ionising groups of the protein molecule that on ionising acquire charges opposite in sign to the charges of the X groups; y' represents ionised type Y groups. Denoting the dipole moment by D, we can represent the adsorptivity m as a function of the effective valency, the total charge, and the dipole moment:

$$m = f(Z, E, D). \quad (8)$$

We introduce N, the electrostatic charge which would produce the same attractive force between the protein and the exchanger as the combined action of the factors Z, E, and D. We shall henceforth call N the effective charge on the protein molecule:

$$m = f(N); \quad (9)$$

this effective charge may be positive, negative, or zero.

We note further that in accordance with Eqns. (4) and (5) the total charge on the protein ion in the exchanger–ion complex differs from the total charge on the ion in solution. Denoting the charge on the adsorbed ion by E_a, we may write

$$E_a = (X - x') + (Y - y' - y''), \quad (10)$$

where y'' represents type Y groups that are no longer ionised after being adsorbed.

Clearly, the following relationship is always valid:

$$E_a > E. \quad (11)$$

and therefore

$$N_a > N, \qquad (12)$$

where N_a is the effective charge on the adsorbed protein.

In chromatography inequality (11) is reflected in the fact that proteins are eluted from anion-exchange columns at a pH below the isoelectric point, and from cation-exchange columns at a pH above the isoelectric point. However, this does not always hold good, because the effective charge, which determines the adsorption, contains the additional factors Z and D.

It follows from inequality (12) that when $N = 0$ the protein may be adsorbed on both cation and anion exchangers, N_a being positive with the former and negative with the latter. When N is positive the protein is adsorbed only on cation exchangers, and when N is negative only on anion exchangers, N_a having the same sign but a larger absolute value. Under all these conditions the most probable state of the system is that in which the protein is adsorbed on the cellulose ion exchanger, since at the moment of adsorption the interaction between the protein and the exchanger is increased; also for desorption to occur, forces greater than those that led to adsorption must be overcome.

The values of Z, E, and D may change independently from protein to protein; Z and D may depend on the dimensions and shape of the protein molecule (increasing as the dimensions increase or as the shape becomes less spherical), but E does not depend on these properties. These factors have a corresponding effect on the adsorptivity. Thus, cytochrome c, with a molecular weight of 97 000 is more strongly adsorbed on DEAE-cellulose than the rhodospirillum haem protein (RHP), with a molecular weight of 36 000, although both compounds have identical isoelectric points[105]. γ-Globulin (sedimentation constant 6.6 S) is not distinguishable electrophoretically from γ-macroglobulin (sedimentation constant 18 S) but the latter is more strongly adsorbed on DEAE-cellulose[106,107].

The following example is an excellent illustration of how adsorption is affected by the effective valency and the total charge. Nicotinamide-adeninedinucleotide, which has two phosphate residues per molecule, is less strongly adsorbed on DEAE-cellulose than nicotinamide-adeninedinucleotide phosphate, which has three phosphate residues. On the other hand, the oxidised forms of these nucleotides, which have a positively charged quaternary nitrogen in the pyridine ring, are adsorbed less strongly than the reduced forms, which have no positively charged groups in the molecule[108]. In the example given the effects of electrostatic charges on adsorption are all the more convincing because the molecules of the four compounds differ only slightly in structure and dimensions.

2. Other Adsorption Mechanisms

At present the behaviour and interaction of macromolecules in solutions and suspensions is being intensively studied, and problems of the chromatography of proteins on cellulose ion exchangers are a part of this general problem. In the early research work "anomalies" in the thermodynamics of polymer solutions were encountered[109]. The following results are of particular interest here. Several authors noted a positive or very small negative entropy change in the association of protein molecules with one another [110-112] or with carbohydrate polyions[101]. It was difficult to explain the entropy increase by the liberation of water of hydration, because the free energy decreased with association. An analogy can be drawn between these results and the adsorption of proteins on cellulose ion exchangers; in both cases electrostatic interaction occurs between two hydrophilic macroions. This analogy is further justified because in both cases the bond between the ions is extremely sensitive to pH changes; for example, when the pH changes from 8 to 4.4 the constant for the association of soya-bean trypsin inhibitor with trypsin changes by a factor of 100 000;[113] on the other hand, the adsorption properties of proteins on cellulose ion exchangers change so sharply with pH that several workers have referred to the process as adsorption on the "all-or-none" principle.

Proteins are not adsorbed on cellulose containing no ionising groups, but they are precipitated on columns of such cellulose at a lower concentration of ammonium sulphate that that required for precipitation from solution[114,115]. There is therefore some interaction between the protein and the cellulose, and this may increase the strength of the adsorption of proteins on cellulose ion exchangers. This interaction may be due to van der Waals' forces or to the formation of hydrogen bonds. In adsorption on carboxyl ion exchangers, in addition to the usual hydrogen bonds, bonds may also be formed between the protein carboxyls and the cellulose ion exchanger, all the more so because adsorptivity on these exchangers is greater in an acid medium, when dissociation of the carboxyls is largely suppressed. Bonds of this type are formed in protein–protein interaction[116]. The carboxyl–carboxyl hydrogen bond is extremely sensitive to pH changes; even a small change in pH leads to mass destruction of bonds of this type, or to an "ionisation explosion". This could be explained by a sharp change in the adsorption properties of proteins on cellulose ion exchangers as the pH changes. However, the adsorption properties are just as sensitive to pH changes on cellulose ion exchangers containing no carboxyls.

It is thus clear that a rigorous theory of protein chromatography on cellulose ion exchangers is very complex. At present there are no special studies of this kind and we are again compelled to turn to results on the wider problem of polyelectrolyte interaction. General questions of protein interaction (poly-equilibrium theory) have been discussed by Klotz[117].

Harris and Rice proposed a theory for the interaction of flexible polyelectrolytes with charges of the same sign which makes the best allowance for all possible polymer-structure and charge effects on interaction[118,119]. Cellulose ion exchangers are polyelectrolytes of exactly this type. This theory was later extended to polyampholytes[120].

Overbeek and Voorn[121] developed a theory for the interaction that accompanies phase separation. Notwithstanding several simplifying assumptions made by the authors, all the equations proposed are extremely complicated; since the simplifications exclude such factors as hydration, hydrogen bonding, and steric hindrance, these equations cannot be applied to real systems.

The adsorption of proteins on cellulose ion exchangers is characterised by the variety of effective forces and by the complexity of the mechanism. Nevertheless, the predominance of electrostatic forces is clear; the experimental results in the first section show this conclusively. It is therefore advantageous and useful to apply the laws of ion exchange to the interpretation of experimental results

for protein adsorption and chromatography on cellulose ion-exchange columns, even if only qualitative data can be obtained.

III. THE EFFECT OF NEUTRAL SALT AND HYDROGEN ION CONCENTRATION ON THE ADSORPTION OF PROTEINS BY CELLULOSE ION EXCHANGERS

1. Adsorption in a Salt-Free Medium

Proteins are most strongly adsorbed on cellulose ion exchangers from a salt-free medium, or from dilute buffer solutions. It is extremely important to note that the adsorptivity does not depend on the protein concentration; all the protein in solution is adsorbed until the adsorptive capacity is reached[93,96]. A method of concentrating protein solutions may be based on this property. On the other hand, we have here confirmation that the laws of ion exchange apply to the adsorption of proteins on cellulose ion exchangers. The exchange of ions with different charges is represented by Nikol'skii's equation[122]:

$$\frac{m_1^{\frac{1}{z_1}}}{m_2^{\frac{1}{z_2}}} = K\frac{c_1^{\frac{1}{z_1}}}{c_2^{\frac{1}{z_2}}}, \qquad (13)$$

where m_1 and m_2 are the amounts of adsorbed ions with charges z_1 and z_2 respectively and c_1 and c_2 are their concentrations in solution. It can be shown that dilution of the solution always leads to increased adsorption of a multicharged ion. If $c_1/c_2 = P$ (P is a constant), Eqn. (13) takes the form:

$$\frac{m_1^{\frac{1}{z_1}}}{m_2^{\frac{1}{z_2}}} = KP^{\frac{1}{z_1}}c_2^{\frac{1}{z_1}-\frac{1}{z_2}} = A. \qquad (14)$$

If $z_1 > z_2$, then $\lim A_{c_2 \to 0} = \infty$, which can only be satisfied by $m_2 = 0$ and $m_1 = m$ (m is the exchange capacity)[123].

Inequality (12) gives another explanation of the preferred adsorption of proteins from dilute solutions of salts (see p. 481).

2. Effect of Neutral Salts

If

$$c_1 + c_2 = c_0 \qquad (15)$$

and

$$m_1 + m_2 = m, \qquad (16)$$

the dependence of m_1 on c_1 is unambiguously expressed by the equation[123]

$$\frac{m_1^{\frac{1}{z_1}}}{(m-m_1)^{\frac{1}{z_2}}} = K\frac{c_1^{\frac{1}{z_1}}}{(c_0-c_1)^{\frac{1}{z_2}}}. \qquad (17)$$

where m is the adsorptive capacity and c_0 is the concentration of the displacer ion introduced into the system. Parameters of the displaced ion are indicated by the subscript (1) and those of the displacer ion by the subscript (2).

Since the curve of the dependence of m_1 on c_1 has no point of inflection, the curvature of the adsorption isotherm $m_1 = f(c_1)$ will always be either entirely positive (curve convex towards the concentration axis) or entirely negative. Convex isotherms may change to concave with a change in the parameters c_0, m, z_1, and z_2. When m, z_1, and z_2 are constant, this change occurs at a certain critical concentration, $c_0 = c_{cr}$, at which the isotherm is linear. The plot of m_1 as a function of c_0 must therefore be S-shaped, the critical concentration corresponding to a point of inflection on this curve. The plots of the adsorptivity of ribonuclease[124] and other proteins[93] on cellulose ion exchangers at different concentrations of sodium chloride are S-shaped (Fig. 2). This is further confirmation that the laws of ion exchange are applicable to the adsorption of proteins on cellulose ion exchangers.

Since c_{cr} for given values of m, z_1, and z_2 is related to the exchange constant by the expression[125]

$$c_{cr} = mK^{\frac{z_1 z_2}{z_1 - z_2}}, \qquad (18)$$

it is evident that the exchange constant can be determined from the dependence of m_1 on c_0. We have found no experimental confirmation of this in the literature.

Theoretically, the change in adsorptivity from zero to the maximum, which is the adsorptive capacity of the cellulose exchanger, occurs over an infinitely wide range of concentrations of the neutral salt. However, the rate of this change drops sharply as extremal values of the adsorptivity are reached and is large over a certain narrow concentration range. We shall apply the term transition range to the concentration range of neutral salt (or pH values) in which the adsorptivity changes from a value differing little from zero to a value close to the adsorptive capacity. It can easily be shown that this transition range decreases as the effective valency of the displaced ion increases. In fact, from Eqn. (14) we note that if $z_1 \gg z_2$, when c_2 decreases the value of m_1 more rapidly approaches a limit equal to the exchange capacity m. Because of the small width of the transition range in the adsorption of proteins on cellulose ion exchangers, some workers have spoken of the "all-or--none" principle applying to the adsorption[11,126]. The isotherms for adsorption from neutral salt solutions of varying concentration directly disprove this principle: while all

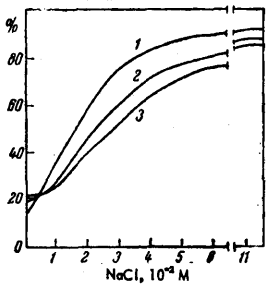


Fig. 2. Dependence of the adsorptivity of ribonuclease on CM-cellulose on pH and salt concentration: 1) pH 8.8; 2) pH 7.5; 3) pH 7.1. Unadsorbed ribonuclease is plotted along the ordinate.

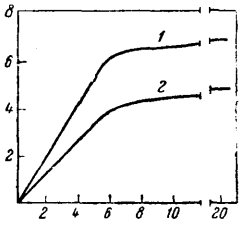


Fig. 3. Adsorption isotherms of asparaginase on DEAE-cellulose: 1) salt-free medium; 2) 0.08 M solution of NaCl. The quantity of asparaginase in the initial solution is plotted along the abscissa and the adsorbed asparaginase is plotted along the ordinate (arbitrary units).

the protein in solution is adsorbed in the absence of salts, irrespective of its concentration, the amount of protein adsorbed from salt solutions depends on its concentration, that is, an equilibrium is established (Fig. 3). In a salt-free medium the equilibrium is displaced towards the adsorbed protein, but when salts are added it is displaced more and more towards the dissolved protein[93]. Statistically, this is explained in the following way: when the concentration of the displacing ion is increased the number of complex collisions required for the displacement of a multicharged protein ion increases.

It should also be noted that in the presence of salts not only the rising but also the horizontal branch of the isotherm is lowered, that is, the adsorptive capacity of the cellulose ion exchanger decreases. This may be one of the causes of diffuse zones when proteins are eluted from these columns.

Salts may affect adsorptivity by another mechanism: salt ions may become bound to the protein, changing its electrostatic charge and therefore the adsorptivity. Changes in the activity of the ions and in the states of ionisation of the exchanger and the protein, due to changes in the ionic strength of the solution, may also be of some importance.

3. Effect of pH

The mechanism of the effect of pH of the medium is essentially different, since a change in pH leads to a change in ionisation of the exchanger and the protein. Since adsorptivity is greater on cellulose cation exchangers in an acid medium and on anion exchangers in an alkaline medium, that is, under conditions such that the ion exchanger is least dissociated and the ionising groups of the protein taking part in adsorption are most dissociated, it is evident that the state of ionisation of the protein, and not that of the exchanger, is important. A change in pH leads to a change in the effective valency, total charge, and dipole moment of the protein molecule, that is, affects all three quantities which determine the effective charge. If the pH changes in such a way as to reduce the effective valency, at a definite pH value ions of the buffer mixture and the protein will begin to exchange as ions that differ little or not at all in the number of charges. It is evident that the protein can then be displaced from the ion exchanger at a low eluent concentration; this has been observed in many studies on the chromatography of proteins on cellulose ion-exchange columns. Here there is also an equilibrium distribution of the protein between the adsorbent and the solution[93]. As the pH changes further, the effective charge may acquire the same sign as the charge on the ion exchanger, which completely excludes the possibility of adsorption.

In this case the very narrow pH range within which adsorptivity changes from zero to the maximum is also noticeable. This narrow range appears to be due to the simultaneous change of all the components of the effective charge, an entirely different reason from that which leads to a narrow pH range in elution by solutions of neutral salts.

IV. MECHANISM OF PROTEIN SEPARATION ON CELLULOSE ION-EXCHANGE COLUMNS

The main process in all chromatographic methods consists in the successive redistribution of the material to be separated between two substances moving relative to each other — between an adsorbent and a solvent, or between two solvents, two phases, etc. If proteins were adsorbed on cellulose ion exchangers according to the "all-or-none" principle, the adsorptivity of the protein should be either zero or equal to the adsorptive capacity of the exchanger, and the rate of movement of the protein along the column should be either zero or equal to the rate of movement of the solvent itself. This means that the protein is not redistributed between the exchanger and the solvent, and there is no true chromatographic process. This view does not explain the extremely high effectiveness of cellulose ion exchangers in fractionating proteins, and especially the tremendous advantages of the column technique over separation under static conditions. Moreover, some experimental results confirm that protein zones can move at rates intermediate between zero and the flow rate of the solvent. Thus, Boman and Kaletta found that when snake venom is chromatographed on DEAE-cellulose columns, an increase in pH or a reduction in eluent concentration leads to lengthening of the chromatogram and to a better separation of components[127]. The "all-or-none" principle excludes the use of elution analysis, but metmyoglobin and carboxymyoglobin can be separated on a DEAE-cellulose column by elution analysis[128].

The equilibrium character of the adsorption of proteins on cellulose ion exchangers over a certain pH range, or range of neutral salt concentration, shows that successive adsorption and desorption occur: the main separation mechanism is a true chromatographic process. It is therefore essential for the separation of proteins that the process be carried out under equilibrium conditions and that the transition ranges should not coincide. In elution with salt solutions the position of the transition range is determined by the effective charge on the protein, and in elution with solutions of varying pH by the pK values of the ionising groups of the protein that form the effective charge. Since the nature of these groups is practically the same in all proteins, selectivity will be low in elution with solutions of varying pH. For this reason, this elution procedure has been less widely used than elution with solutions of neutral salts.

Displacement of protein by protein is another possible separation mechanism, especially in the initial stage of the

chromatography immediately after the protein mixture has been deposited on the column [129-131]. However, great importance can hardly be attached to this mechanism, since at the column outlet protein zones are very often separated from one another by large protein-free zones, and therefore any interaction between the proteins is excluded here.

V. ELUTION OF PROTEINS FROM CELLULOSE ION--EXCHANGE COLUMNS

1. General Principles. Stepwise Elution

There are three main eluting procedures: elution, frontal, and displacement methods. The elution procedure is rarely used in the chromatography of proteins; the separation of myoglobins by Brown [128] on DEAE-cellulose columns is an example. The single-stage elution method is a combination of elution and displacement procedures [131,132]. The frontal method is unsuitable for preparative purposes, but it has been used in the analysis of mixtures of compounds, including protein mixtures [131].

Displacement is the method mainly used in the chromatography of proteins. Displacement is effected either by changing the salt concentration or by changing the pH within limits close to physiological values. The variation of pH with salt concentration can be either stepwise or smooth; if it is smooth, the procedure is termed gradient elution. As has been mentioned, the main condition for the separation of proteins on a column is that the transition ranges of the different proteins in the mixture should not coincide. Let us consider a model experiment.

The protein A is adsorbed on the upper part of a column; curve a represents the dependence of m_1 on c_0 and a' is the transition range (Fig. 4). When the column is washed with eluent of concentration c_1, the zone boundaries do not change. If the concentration is increased to c_2, the protein zone becomes diffuse (because the capacity of the exchanger is reduced) and begins to move along the column at a rate less than the flow rate of the eluent (because of equilibrium distribution of the protein between the adsorbent and the liquid phase). In this movement further spreading occurs, of the front boundary because the concentration of the eluent is below the critical value [125], and of the back boundary because the adsorption isotherms of proteins on cellulose exchangers in the presence of salts are curves convex away from the concentration axis. Fig. 5a shows the shape of the elution

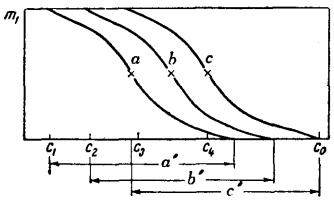


Fig. 4. Transition ranges of proteins. The concentration of the displacer ion is plotted along the abscissa and the quantity of adsorbed protein along the ordinate. Points of inflection on the curves corresponding to critical concentrations are indicated by crosses.

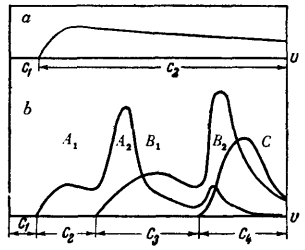


Fig. 5. Elution of a mixture of proteins (explanation in text).

graph or chromatogram. A very large volume of solution of concentration c_2 is required to elute all the protein.

If at the instant when a volume v_1 of eluent of concentration c_2 has passed through the column the concentration is raised to c_3, the remains of the protein form a new zone on the column before the front of the new eluent, and a second peak A_2 of the same protein A is obtained on the chromatogram (Fig. 5b). Since $c_3 > c_{cr}$, the front of the new zone becomes sharper. As before, the back boundary of the new zone spreads.

Let us now consider the elution of a mixture of proteins A, B, and C, for which the dependence of m_1 on c_0 is represented by curves a, b, and c, and the transition ranges are a', b', and c' (Fig. 4). When the column is washed with solution of concentration c_2, only protein A (peak A, Fig. 5b) is eluted; when the concentration is increased to c_3 the remains of protein A (peak A_2) and part of protein B (peak B_1) are eluted. At an eluent concentration c_4 the remains of protein B (peak B_2) are eluted with protein C. Thus, in this model only protein A (peak A_1) is obtained pure.

Fig. 5b shows the results of the chromatographic separation of three thyroglobulin fractions on a column of DEAE--cellulose [133]. With complex mixtures and a lower eluent concentration "step height", the same compound may form not two but several peaks [134,135]. This makes clear the disadvantages of elution in which the conditions are changed in steps. An uncritical approach to this method may have given rise to some unfounded conclusions [136].

Theoretically, even the most complex mixtures of compounds having different transition ranges should be separable by stepwise elution on sufficiently high columns. However, the necessity of using an eluent concentration lower than c_{cr}, with consequent extensive spreading of zones, often means that the method cannot be applied in practice. Nevertheless, stepwise elution often gives good results in the chromatography of simple mixtures of proteins, for example, in final purification stages [137-139]. It is evident that a significant difference in transition ranges is the main requirement for the successful application of the method. Thus, if protein B is excluded from the model system examined above, the remaining proteins A and C can be separated by the stepwise method without significant spreading; protein A is eluted with a solution of concentration c_3 ($c_3 > c^a_{cr}$) and the protein C zone remains unchanged, since its transition range lies at concentrations higher than c_3. Protein C may then be eluted as a compact zone with eluents of concentration $> c_4$ ($c_4 = c^c_{cr}$).

2. Gradient Elution

Gradient elution may be regarded as the automatic selection of the salt or hydrogen-ion concentration at which proteins can be separated chromatographically. This method is particularly suitable when the transition ranges of the proteins to be separated are not known beforehand; and, what is more important, there is an active mechanism compressing the zone boundaries, since the back boundary of the zone moves under conditions of lower capacity.

Elution with a capacity gradient was first used by Harteck and Suhr [140]. Alm, Tiselius, and coworkers [141-143] and others [144,145] set up a capacity gradient by varying the concentrations of the eluent components. Sober and Peterson [146] were the first to use gradient elution in the separation of proteins. Zhukhovitskii and Turkel'taub have developed the theory of this method [147,148].

Physically, the phenomenon of zone compression has the following consequences. Material that accidentally remains behind the zone is under conditions of weaker adsorption (in the chromatography of proteins it is the region where the pH is unfavourable or the salt concentration is high); as a result it begins to move more rapidly. When it overtakes the zone, the material is in a region of strong adsorption and its movement is retarded. At a certain point the whole zone is under conditions of zero adsorptivity (upper limit of transition range), and it begins to move along the column at the same speed as the solvent; the material of the zone is then in the liquid phase. The mechanism of chromatographic separation and active zone compression operates only until the zone reaches its maximum rate of movement.

The chromatographic separation of proteins with gradient elution can be clearly divided into three stages.

1. The adsorption stage. This is sometimes accompanied by separation of components due to protein–protein displacement. In this stage both dilution and concentration of the protein can occur, depending on the concentration of the protein solution and the capacity of the adsorbent.

2. The separation stage. The protein zones move along the column with increasing speed, the limit being the flow rate of the solvent itself. The components are separated by a true chromatographic process. The zones tend to spread because they move for some time at an eluent concentration below the critical, because the effective charge on a given protein is not constant, and because adsorbent capacity decreases. The presence of a capacity gradient moving at a rate faster than that of the zone tends to counteract spreading.

3. The passive transfer stage. The rate of movement of the zones is equal to the flow rate of the solvent and no further separation occurs. Hydrodynamic effects cause the zones to spread.

It follows that for the best separation the relationship between the column height and the capacity gradient should be such that the rate of movement of the zone is a maximum when it leaves the column. The concentration or pH of the solution at which elution then occurs is a characteristic of the given protein (elution concentration c_e or elution pH, pH_e) that can be used for identification. It is evident that c_e or pH_e is the upper limit of the transition range and is close to the minimum salt or hydrogen ion concentration at which the protein is no longer completely adsorbed by the cellulose ion exchanger. For example, Huisman found that when haemoglobins are chromatographed on a CM-cellulose column with different pH gradients, other conditions being the same, they emerge from the column in different volumes of eluate but at the same pH. [94] It is obvious that the exchange capacity of the adsorbent affects the value of c_e. Thus, an increase in the capacity of DEAE-cellulose leads to an increase in the concentration of NaCl at which pepsin and pepsinogen are eluted [149].

If we assume that the adsorption isotherm asymptotically approaches a limit, theoretically an infinitely long column would be required to achieve the maximum rate. However, as experiment shows, a column height of even a few centimetres is sufficient to obtain most of the material in the form of compact zone moving at the same rate as the eluent [150,151]. This is due to the very narrow transition range of proteins.

VI. TECHNIQUE OF PROTEIN CHROMATOGRAPHY ON CELLULOSE ION EXCHANGERS

1. Technique of Gradient Elution

The following is the commonest method of setting up a concentration gradient in a column. Vessel A (Fig. 6*a*), the mixer, contains a solution of concentration c_1; it is equipped with a stirrer and a bottom outlet connected to the column. Vessel B, the supply vessel, contains solution of concentration c_2; solution flowing out of A is replaced by solution from B. The concentration of solution issuing from the apparatus changes from c_1 to c_2 according to the equation [152]

$$c = c_2 + (c_1 - c_2)\, e^{-\frac{v}{q}}, \qquad (19)$$

where c is the concentration when the volume v has run out, q the volume of the mixer, and e the base of natural logarithms. The concentration gradient is represented graphically by a curve asymptotically approaching c_2.

Another elution procedure, which gives a linear variation of concentration, operates in the following way [153]. Two communicating vessels, a mixer A and a supply vessel B, contain solutions of concentration c_1 and c_2 respectively (Fig. 6*b*). The loss of solution from the mixer is made up by solution from the supply vessel, but the volume of solution in the mixer decreases. The variation in concentration of the solution issuing from the mixer is given by the equation [154]

$$c = c_2 - (c_2 - c_1)\left(1 - \frac{v}{V}\right)^{S_2/S_1}, \qquad (20)$$

where S_2 is the cross-sectional area of the supply vessel and S_1 that of the mixer, and V is the total volume of solution in both vessels. When $S_1 = S_2$, the equation is linear:

$$c = c_1 + \frac{v}{V}(c_2 - c_1). \qquad (21)$$

Other methods of setting up a gradient [155-158] include arrangements in which the gradient concentration can be changed at will during the experiment [159,160]. Kočent constructed nomograms for determining the eluent concentration at any time during the experiment with different arrangements for setting up a gradient [161].

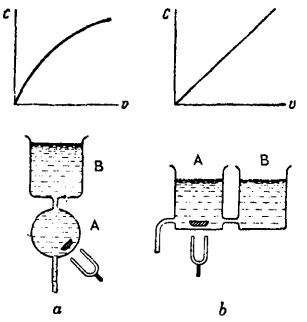


Fig. 6. Diagram of apparatus for setting up (*a*) exponential and (*b*) linear concentration gradients.

Formulae (19)–(21) reflect the variation of the concentration of the solution issuing from the mixer. However, the separation of compounds depends on the actual concentration gradient along the height of the column, and this depends not only on the design of the apparatus for producing the gradient but also on the cross-sectional area of the column and on the packing density. Eqns. (19)–(21) do not therefore represent the complete characteristics of separation conditions in gradient elution. The use of a linear concentration gradient has the advantage that it enables a simple formula to be used for the variation of eluent concentration along the column height, that is, in the region where the actual chromatographic process occurs[162,163]. If h is the height of the column, c the concentration of eluent issuing from the column, and c' the concentration at the upper surface of the column, the gradient G, the variation of concentration per unit height of column, will be given by

$$G = \frac{c' - c}{h} . \qquad (22)$$

From Eqn. (21) it follows that

$$c' = c_1 + \frac{v + v_m}{V}(c_2 - c_1), \qquad (23)$$

where v_m is the volume of mobile liquid in the pores of the column of height h. On substituting the values of c and c' from Eqns. (21) and (23) in Eqn. (22), we obtain

$$G = \frac{v_m}{h} \times \frac{c_2 - c_1}{V} . \qquad (24)$$

Denoting the factor v_m/h, which represents the volume of liquid in the pores of a column 1 cm high, by α, we obtain

$$G = \alpha \frac{c_2 - c_1}{V} . \qquad (25)$$

Thus, for identical separation conditions, values of the gradient G in all experiments must be the same. For example, in two experiments A and B the following conditions must be observed:

$$\alpha_A \frac{c_{2A} - c_{1A}}{V_A} = \alpha_B \frac{c_{2B} - c_{1B}}{V_B} . \qquad (26)$$

The initial concentration in the mixer c_1 is so chosen that the rate of movement of the protein zone is zero at the beginning of the chromatographic process. If in experiments A and B the initial concentrations are the same, Eqn. (26) may be rewritten thus:

$$\alpha_A \frac{c_{2A} - c_1}{V_A} = \alpha_B \frac{c_{2B} - c_1}{V_B} . \qquad (27)$$

In this case it can be shown that in experiments A and B the concentrations of eluent issuing from the column become the same at the point where the following condition obtains:

$$\frac{v_A}{\alpha_A} = \frac{v_B}{\alpha_B} = K_e . \qquad (28)$$

Since the position of the transition range on the concentration scale and the elution concentrations (p. 485) do not depend on the dimensions of the column, values of K_e, the elution constant, will be the same for a given protein on columns of different dimensions under the conditions of Eqn. (27); both the eluent concentration and the elution constant can be used for the identification of proteins.

2. Other Problems in Chromatographic Technique

Choice of adsorbent. The anion exchanger DEAE-cellulose and the cation exchanger CM-cellulose are most frequently used for the chromatography of proteins, and of the two, DEAE-cellulose is much more widely used, probably because the overwhelming majority of proteins are anions at the pH values used in chromatography. This should also determine the choice of adsorbent (anion or cation exchangers) when work is begun on the separation of a protein with unknown properties.

Because of the limited amount of published information on the use of other cellulose ion exchangers, it is not possible to draw any conclusions about their advantages. We merely point out that maltase and saccharase from intestinal juice are separated somewhat better on TEAE-cellulose than on DEAE-cellulose[131]. However, chromatography of thyrotropins gave identical results with these two adsorbents[164]. Identical results were also obtained in the chromatography of phosphoproteins on TEAE-cellulose and ecteola-cellulose[134].

Preparation of columns. In the chromatography of proteins cellulose ion exchangers should be packed uniformly and fairly tightly. The dimensions and shape of the column are determined by the composition and amount of the mixture to be separated and by the elution procedure. In gradient elution the separation may be improved by increasing the height of the column[165] or by reducing the magnitude of the gradient while the height of the column is kept constant[124]. If the conditions of Eqn. (27) are observed, only the productivity of the column, measured by the amount of the mixture separated, depends on the diameter; the productivity, and to a certain limit, the separating power of the column depend on its height. Satisfactory separations of proteins have been reported even on very short columns (~3 cm)[166,167].

Preliminary treatment of cellulose ion-exchange columns. Cellulose ion exchangers adsorb most strongly in a salt-free medium, but when proteins are eluted from unbuffered columns with salt solutions, the pH changes sharply and this may lead to denaturation of the proteins; on cation-exchange columns,

when the medium becomes acid, it may lead to the precipitation of large amounts of protein. To prevent this, the column must be washed before the experiment with a dilute buffer solution (0.001–0.05 M) to equalise the pH of the outflow with that of the initial solution ("column equilibration"). The concentration and pH of the initial buffer are selected so as to make the mobility of the protein zones in the adsorption stage zero; this gives the narrowest zones. In the chromatography of oxidisable proteins antioxidants (mercaptoethanol or cysteine) are added to the buffer solution. However, it must be borne in mind that this can lead to the formation of several zones from a single protein [100,168].

Quantity and concentration of protein chromatographed. The quantity of protein transferred to the column is best expressed in mg per cm^2 of column cross-section; other conditions being equal, the widths of the zones on columns of different diameter will then be the same. Generally 50–150 mg of protein is used per cm^2 of column cross-section. With larger quantities the resulting zones are too broad and the separation stage must then be improved by lengthening the column or by reducing the gradient. Thus, on a 0.9 × 10 cm column of CM-cellulose, 40 mg of ribonuclease can be separated completely, but if 200 mg is used the fractions overlap; with a reduced gradient separation is again achieved [124].

The concentration of protein in the initial mixture is not significant if the adsorption stage is carried out under conditions such that proteins are completely adsorbed.

Repeated chromatography. In the chromatography of proteins on cellulose ion exchangers, sometimes a single protein will form several zones. The formation of multiple zones in stepwise elution has been mentioned above (p. 484). There is evidence that proteins can change reversibly during chromatography and the modifications formed may differ in their mobility on a column [4]. Antioxidants may also react with proteins and change their adsorption properties [100,169]. On the other hand, it is known that some proteins with the same biological activity may differ in physicochemical properties, including adsorptivity on cellulose ion exchangers. In all such cases, repeated chromatography of the separate fractions under the same conditions may give information on the homogeneity or the cause of heterogeneity of a preparation. Final conclusions can only be reached by examining the fractions by different methods.

VII. SOME RESULTS AND POSSIBILITIES

1. Chromatography of Proteins on Cellulose Ion Exchangers as a Criterion of Homogeneity

As already mentioned, many protein preparations that appear to be homogeneous in electrophoresis or ultracentrifuging have been separated into fractions by chromatography on cellulose ion exchangers. Thus, a crystalline preparation of myoglobin was separated by chromatography on CM-cellulose and DEAE-cellulose into three components differing in amino-acid composition, whereas it was homogeneous when ultracentrifuged [6]. A trypsin inhibitor preparation from Lima bean, homogeneous when ultracentrifuged, was separated into four components by electrophoresis and into six by chromatography on DEAE-cellulose; the six components had about the same amino-acid composition but they differed in structure [8]. Trypsin inhibitor from ox blood loses 20–30% of its activity on storage, and electrophoresis and ultracentrifuging indicate that the stored preparation is still homogeneous, but the active and inactive fractions can be separated by gradient elution on a DEAE-cellulose column [9]. Many similar results have been reported [7,10,106,133]. Chromatography on cellulose ion-exchange columns can therefore provide one of the most effective criteria of homogeneity for protein preparations as well as being a good method of identification. This may be explained in the following way. In electrophoresis the principle factor governing the separation of proteins is the total charge, and in ultracentrifuging it is the density of the protein molecule; the mobility of proteins on cellulose ion-exchange columns, however, is governed by several factors, including the total charge, the number of charged groups on the protein molecule and their distribution on its surface, as well as properties such as the dimensions and shape of the molecule, prosthetic groups, etc.

2. Families of Proteins [170]

The problem of families of enzymes, that is the existence in the same organism, or even in the same organ, of more than one protein with the same enzymic activity (isoenzymes [171]), has been discussed for a long time; recently, however, it has attracted particular interest because of new experimental results obtained mainly by cellulose ion-exchange chromatography, but also by electrophoresis on gels [172–178]. Sometimes the number of isoenzymes can be quite large. Thus, Taborsky separated seven isoribonucleases, differing in sedimentation constant and isoionic point, by chromatography on a CM-cellulose column [124]. Press and coworkers found 15 isocathepsins D in ox spleen by chromatography on DEAE- and CM-cellulose columns [179]. Since differences between fractions within a family are often found by other methods [5,180,181], it can be assumed that we are really dealing here with enzyme families. However, another question remains to be answered: do these families arise from modifications in the protein during the separation process, or do they exist in the organism? Obviously, both possibilities have to be considered. It is well known that partial hydrolysis, which sometimes removes over 50% of amino-acid residues, does not lead to a loss of enzymic activity, but much smaller changes are sufficient to alter the physicochemical properties, and therefore the chromatographic mobility. Changes of this kind may be produced in the protein in the separation process by the action of endogenic proteases, or in other ways. The possibility of adsorptivity on cellulose ion exchangers being altered by changes limited to the secondary, tertiary, or quaternary structure must also be considered [182,183]. The reversible interconversion of family components appears to be a phenomenon of this kind [184–187]. The spontaneous synchronous changes in enzymes [188,189] that accompany changes in adsorption properties [190] are an interesting example of reversible changes.

There is evidence that enzyme families exist in the organism. Thus, lactate dehydrogenase, obtained by the same method from different organs was found to be homogeneous in some and heterogeneous in others [191]; crystalline preparations of this enzyme obtained from different organs of the same animal showed greater differences in tryptic hydrolysis than preparations obtained from the same organ of different species [192]. The components of esterase

and of lactate, malate, isocitrate and glycerophosphate dehydrogenases are also not identical in different organs and in different animals [193,194].

3. The Use of Cellulose Ion-Exchange Chromatography of Proteins in Clinical Analysis

Investigation of specific changes in enzymic activity in various pathological conditions is being increasingly used in clinical analysis [195]. Because of the high separating power of cellulose ion-exchange columns and the extreme simplicity of the method, this form of chromatography can be used to detect pathological changes in proteins under clinical conditions. Thus, the chromatograms of serum from patients suffering from leukaemia, cancer, and myeloma differ in many cases from chromatograms of normal serum [196-198]. Using adsorption on DEAE-cellulose, Hess and Walter detected quantitative differences in the serum isolactate dehydrogenases of people suffering from hepatitis, myocardial infarction and haemolytic anaemia [199]. These authors suggest that analysis of serum isolactate dehydrogenases could be used for differential diagnosis [200]. In macroglobulinaemia macroglobulins can be easily separated by chromatography on DEAE-cellulose: CM-cellulose and DEAE-cellulose have been used to separate several pathological haemoglobins [12,94,95,201]. The possibility of separating antibodies [202-204] enables cellulose ion exchangers to be used for studying immunity phenomena [205,206]. Thus cellulose ion-exchange chromatography may prove to be a very useful method in clinical analysis.

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ORGANIC DERIVATIVES OF LAMINAR SILICATES

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1. INTRODUCTION

Organic derivatives of silicates are an extremely interesting group of compounds. Rather more than 20 years ago Berger first reported[1] the preparation of methoxylated montmorillonite; this was the first of a series of intensive investigations of organic derivatives of laminar silicates, and attracted the attention of investigators studying the surface structure of various clays.

An accurate knowledge of the surface structure of clays is necessary for understanding many of their properties, such as their acidity, adsorption and exchange capacity, thixotropy, and so on, which are due to the presence of a negative charge on their particles.

Disperse crystals of clays are known to possess structural irregularities and defects, because of the inclusion of foreign atoms and groups in the lattice, the presence of difficultly removable impurities and of holes, etc. These deviations from the ideal structure in the smallest clay microcrystallites are often used in theories of the negative charge on their surface. The best known hypothesis is that of Marshall and Van der Meulen[2,3], which ascribes the negative charge to the replacement of multiply charged cations in the crystal lattice by less highly charged cations: for instance, Si^{4+} is replaced by Al^{3+} in a tetrahedral layer such as is typical of vermiculite, or Al^{3+} is replaced by Mg^{2+} or Fe^{2+} in an octahedral layer, which often occurs in montmorillonite. The theory of isomorphous substitution, while explaining the existence of wide differences in the chemical composition of similar clays, has its weak points. Calculations show[4] that if their acidity is considered to arise solely as a result of isomorphism, clays should be strong acids in the H-form, but their acidity is known to be constant between pH 3 and pH 5–5.6.

Edelman and Favejee[5] explained the negative charge on clay particles in terms of the acidity due to the presence of acidic Si–OH groups on the surface. Although several years ago the existence of Si–OH groups in laminar silicates was considered to be improbable, more recent studies[6-9], especially of infrared absorption spectra of certain hydrosilicates[10-13], demonstrate their presence in various silicate formations.

Definite proof of their presence is not easy, however. One possibility is the production of organic derivatives of the hydrosilicates by replacing the hydroxy-groups attached to silicon by organic radicals.

The organic derivatives are not merely of interest for investigating the surface structure of laminar silicates, since they have their own practical significance for the sterilisation and stabilisation of soils, the deactivation of poisons, the preparation of hydrophobic silicate materials, and so on. Organic derivatives of laminar silicates will undoubtedly also find practical application as fillers for various types of rubber and as selective adsorbents.

The experience gained in more than a century's study of the chemistry of organosilicon compounds has been applied

to the production and investigation of the organic derivatives of laminar silicates. Three methods are at present known for their production: the replacement by organic radicals of the active surface OH or OM groups attached to silicon, the addition of organic radicals to broken Si–O–Si or Si–O–Al bonds in silicates, and the production of synthetic silicates containing organic radicals.

2. PRODUCTION OF ORGANIC DERIVATIVES OF LAMINAR SILICATES BY REPLACEMENT OF OH OR OM GROUPS ATTACHED TO SILICON

The Si–OH groups on the surface of clays are chemically similar in behaviour to the Si–OH groups in silanols. The acidic hydroxy-groups attached to silicon in H-montmorillonite were first replaced by methoxy-groups by the action of diazomethane in ether solution[1]:

$$\equiv Si-OH + CH_2N_2 \longrightarrow \equiv Si-OCH_3 + N_2 .$$

Analysis of the product for methoxy-groups[14] has shown that not all the hydroxy-groups of the clay can be methylated. Further study of this reaction[15–17] led to the disuse of ether as the solvent and concentration on the drying of the samples, since hydrolysis of diazomethane produces methanol:

$$CH_2N_2 \xrightarrow{H_2O} CH_3OH + N_2,$$

and the presence of methanol and ether interferes in the determination of methoxy-groups.

In hydrogen montmorillonite dried at 300° only 10% of the exchangeable hydrogen ions react with diazomethane. The prolonged action of gaseous diazomethane replaces a further 10% of the H^+ ions.

The hydroxy-groups of silica gel could be partially replaced by methoxy-groups by the action of diazomethane[1,18,19].

Most work on the production of organic derivatives of silicates has been carried out with montmorillonite, and, to a lesser extent, with kaolinite, pyrophyllite, halloysite, attapulgite, amorphous aluminosilicate, and certain other minerals. Montmorillonite has attracted most attention because of its high content of surface-active hydroxy-groups. A fairly large number of three-layer plates, made up of two outer silicon–oxygen tetrahedral layers and an intermediate aluminium–oxygen octahedral lattice, are known to be held in the montmorillonite crystal by relatively weak van der Waals' forces; montmorillonite thus has a planar laminar lattice, able to swell, and with an extended available internal surface. It has been studied in the acid (hydrogen montmorillonite) and alkaline (potassium and sodium montmorillonite) forms.

Bart and Gusman[20,21] investigated the reaction of sodium and potassium montmorillonite with methyl, ethyl, and allyl iodide, and concluded that etherification and not alkali exchange, occurs:

$$\equiv Si-O^-M^+ + RI \longrightarrow \equiv Si-OR + MI,$$

where R = CH_3, C_2H_5, or $CH_2{=}CHCH_2$ and M = K or Na. Deuel[22] later repeated these experiments, and also obtained methoxylated and ethoxylated montmorillonite.

The reaction between sodium montmorillonite and di-(β-chloroethyl) sulphide (Yperite, mustard gas)[22,23] proceeds analogously; Yperite has a bifunctional molecule and can form the mono- or di-ether:

$$2 \equiv Si-ONa + ClCH_2CH_2SCH_2CH_2Cl \rightarrow \equiv Si-O-CH_2CH_2SCH_2CH_2-O-Si\equiv + 2NaCl.$$

The reaction proceeds readily in aqueous medium at room temperature, with substitution of more than 80% of the acid groups. Alkoxy-derivatives of this type are fairly stable to the action of water, but dilute alkali produces rapid hydrolysis, with the formation of the original sodium montmorillonite.

Alkoxylated clays are more stable to hydrolysis the larger the organic radical present. Montmorillonite hydroxypropyl ether, obtained by the action of propylene oxide on an aqueous suspension of hydrogen montmorillonite[23]:

$$\equiv Si-OH + CH_2-CH-CH_3 \longrightarrow \equiv Si-OCH\begin{matrix}CH_3\\CH_2OH\end{matrix}$$

(O)

or $\equiv Si-OCH_2CH-CH_3$ (OH),

is also relatively stable to the action of water. The ether was produced at room temperature, in a maximum yield of 89%.

The practical value of these reactions of clays with Yperite and propylene oxide is evident. The former shows that clays can deactivate poisons, and the reaction with propylene oxide can be used for the sterilisation of clay soils and humus.

The reaction of clays with alkylchlorosilanes[4]:

$$\equiv Si-OH + ClSi(CH_3)_3 \longrightarrow \equiv Si-O-Si(CH_3)_3 + HCl ,$$

is also of practical interest, but unfortunately the resulting hydrophobic materials were not sufficiently well characterised.

The Si–OH groups of silanols and laminar silicates behave very similarly in acylation reactions. Acetic anhydride and acetyl chloride have been investigated as acylating agents, and have been used for the preparation of acyloxysilanes from silanols[24–26]. Heating hydrogen montmorillonite with acetyl chloride or acetic anhydride replaces the OH groups by acetoxy-groups[27,28]:

$$\equiv Si-OH + (CH_3CO)_2O \longrightarrow \equiv Si-OCOCH_3 + CH_3COOH,$$
$$\equiv Si-OH + CH_3COCl \longrightarrow \equiv Si-OCOCH_3 + HCl .$$

Acetic anhydride acetylates montmorillonite to a considerably greater extent than does acetyl chloride; the explanation given for this by Spencer and Gieseking[28] is that the reaction temperature is higher with acetic anhydride, the reaction being carried out at boiling point.

Benzoyl chloride evidently reacts with hydrogen montmorillonite in the same way as acetyl chloride, but Slabaugh, who carried out this reaction[29], did not consider the possibility of hydrolysis of the acyloxy-derivatives of the montmorillonite, and treated the reaction products with 80% ethanol.

Acetylated montmorillonite is a hydrophobic powder which adsorbs organic liquids to a greater extent than does hydrogen montmorillonite[28]. Hydrolysis of the acyloxy-derivative gives a product having the hydrophilic properties of the original hydrogen montmorillonite:

$$\equiv Si-OCOR \xrightarrow{H_2O} \equiv Si-OH + RCOOH,$$

where R = CH_3 or C_6H_5.

The most systematic studies of the organic derivatives of laminar silicates and their preparation were conducted by Deuel and his coworkers[23,30-34], who used Wyoming bentonite, which is almost pure montmorillonite.

Thionyl chloride replaces the hydroxy-groups of sodium or hydrogen montmorillonite attached to silicon by chlorine:

$$\equiv SiOH\,(M) + SOCl_2 \longrightarrow \equiv Si{-}Cl + SO_2 + H\,(M)\,Cl\,.$$

Preliminary studies have shown that gibbsite $Al_2O_3.H_2O$ does not react with thionyl chloride[30], *i.e.* OH groups attached to aluminium in clays are not replaced by chlorine under these conditions.

The production of reactive Si–Cl bonds in laminar silicates offered wide possibilities for the preparation of varied types of organic derivatives. Chemically the Si–Cl bond in the chloro-derivatives of laminar silicates is very like the Si–Cl bond in chlorosilanes. Montmorillonite chloride, like chlorosilanes, is readily hydrolysed by water[23]. Alcohols (methanol, ethanol, propanol, butanol, phenol, D-glucose) gives the alkoxy-derivatives of the alkoxy-type, more than 80% of the acidic groups of the montmorillonite being replaced[23,30]:

$$\equiv Si{-}Cl + HOR \longrightarrow \equiv Si{-}OR + HCl.$$

The reaction of montmorillonite chloride with ethylenediamine gives the amino-derivative[23]:

$$\equiv Si{-}Cl + H_2NCH_2CH_2NH_2 \longrightarrow \equiv Si{-}NHCH_2CH_2NH_2 + HCl\,,$$

and the second amino-group may also react, to give the diamino-derivative of montmorillonite:

$$\equiv Si{-}NHCH_2CH_2NH{-}Si\equiv\,.$$

Of particular interest is the reaction of montmorillonite chloride with organomagnesium and organolithium compounds, producing derivatives containing the Si–C bond, which is stable towards hydrolysing agents. Ethylmagnesium chloride and phenylmagnesium bromide or phenyllithium have given ethyl- and phenyl-montmorillonite respectively by reaction with montmorillonite chloride[28,30]:

$$\equiv Si{-}Cl + RMgX \longrightarrow \equiv Si{-}R + ClMgX,$$

where R = C_2H_5 or C_6H_5 and X = Cl or Br.

The reaction between methylmagnesium halides and hydrogen montmorillonite can be used for the determination of active hydrogen by the Tserevitinov (Zerewitinoff) method[30].

Phenylmontmorillonite has also been obtained by the Friedel–Crafts reaction between montmorillonite chloride and benzene in the presence of aluminium chloride[30,33]:

$$\equiv Si{-}Cl + C_6H_6 \xrightarrow{AlCl_3} \equiv Si{-}C_6H_5 + HCl.$$

A high degree of substitution is produced in this reaction, because of two processes simultaneously taking place, the reaction at the Si–Cl bond, and the splitting of Si–O–Si bonds by the aluminium chloride.

3. PRODUCTION OF ORGANIC DERIVATIVES OF LAMINAR SILICATES BY ADDITION OF ORGANIC RADICALS TO BROKEN Si–O–Si and Si–O–Al BONDS

There are few studies on organic derivatives of laminar silicates prepared in this way. As mentioned above, there is rupture of Si–O–Si bonds in the reaction between montmorillonite chloride and benzene in the presence of aluminium chloride. Deuel and Huber[30] represent this process as follows:

$$\equiv Si\diagdown\!\!\diagup O + AlCl_3 \longrightarrow \left[\equiv Si\diagdown\!\!\diagup O \rightarrow AlCl_3\right] \longrightarrow \equiv Si^{(+)} \quad \equiv Si{-}O{-}AlCl_3^{(-)}\,.$$

Voronkov *et al.*[35] also indicated the possible formation of the intermediate complex

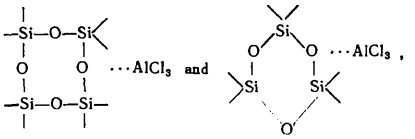
$$\left[\equiv Si\diagdown\!\!\diagup O \rightarrow AlCl_3\right]$$

in their study of the decomposition of hexaalkyldisiloxanes by aluminium halides to produce halogenosilanes:

$$\left[R_3Si\diagdown\!\!\diagup O \rightarrow AlX_3\right] \longrightarrow R_3SiX + [R_3Si{-}O{-}AlX_2]\,,$$

$$[R_3Si{-}O{-}AlX_2] \longrightarrow R_3SiX + O{=}AlX\,.$$

It has recently been shown that aluminium chloride can coordinate an oxygen atom in cyclic poly(dialkylsiloxanes)[36]; the resulting complexes



give chlorine-containing aluminoxypolysiloxanes when the ring is subsequently opened:

$$Cl{-}\left[\begin{matrix}|\\Si{-}O\\|\end{matrix}\right]_n{-}AlCl_2,$$

where n = 3 or 4.

The use of methods such as infrared spectroscopy[36] and differential thermal analysis for studying the final products of the acylation of amorphous aluminosilicate by acetyl chloride and acetic anhydride has shown that, as well as the normal replacement of hydroxy-groups on the surface of the aluminosilicate by acyloxy-groups, there is rupture of Si–O–Al bonds[37,38]. The final reaction products obtained with acetic acid are different from those obtained with acetyl chloride:

$$\equiv Si\diagdown\!\!\diagup O + CH_3COOH \begin{cases} \nearrow \equiv Si{-}OH + {=}AlOOCCH_3 \\ \searrow \equiv Si{-}OOCCH_3 + {=}Al\,(OH) \end{cases}$$

$$\equiv Si\diagdown\!\!\diagup O + CH_3COCl \longrightarrow \equiv Si{-}OOCCH_3 + {=}AlCl\,.$$

Controlled hydrolysis of the acylation products with water also confirms the suggested mechanism involving rupture of an Si–O–Al bond[37].

It has been suggested that thionyl chloride reacts with laminar silicates in the same way as aluminium chloride, by breaking siloxane and aluminosiloxane bonds[39].

The production of organic derivatives by tribochemical methods is also doubtless a reaction of this type.

Weyl[40] has suggested that the mechanical rupture of Si–O–Si bonds leads to the formation on the surface of active electrically charged areas which react readily with water:

$$\equiv Si{-}O{-}Si\equiv \xrightarrow{\text{comminution}} \equiv Si{-}O^{(-)(+)}Si\equiv \xrightarrow{H_2O} 2{\equiv}Si{-}OH\,.$$

This newly formed surface can also react with other compounds used as milling media. A patent specification[41] has described the comminution of silica gel and quartz in

the presence of alkenes, and specifically styrene, to produce a stable Si–C bond. These processes have been studied in more detail only with silica[42,43]. By pulverising silica in an atmosphere of helium, it was shown that the active areas produced by rupture of Si–O–Si bonds have a lifetime of up to 260 h.

Styrene produces a compound $\equiv O_3Si-CH_2CHC_6H_5$,[43] which can react with more styrene to produce a polymeric product:

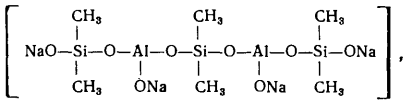
$$\equiv O_3Si\,(CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}})_n CH_2CHC_6H_5 \cdot$$

Many other organic reagents have since been used. Silica has been milled in the presence of methanol, butanol, benzene, ether, and 2-methyl-5-vinylpyridine. The comminution is accompanied by a considerable rise in temperature, reaching 1000° in places within a short time. Benson and Castle[43] have suggested that a thermo-ionic process takes place during the milling.

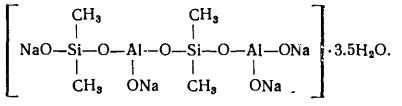
The mechanical method for the production of derivatives with stable non-hydrolysable bonds will undoubtedly find wide application both for the preparation of organic derivatives of silicates and for the production of technically valuable materials based on them.

4. PRODUCTION OF SYNTHETIC SILICATES CONTAINING ORGANIC RADICALS

Kreshkov and coworkers[44-48] have reported the formation of organoaluminosilicates from alkylalkoxysilanes and aqueous alkaline aluminate solutions[44]. The products obtained depend on the molar ratio of Al to Si in the initial mixture. With Al : Si = 1 : 1 the product is:

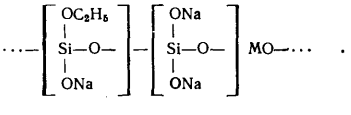


and with Al : Si = 2 : 1 it is:



X-Ray structural and crystalloscopic analysis of the products showed them to be organohydroalumino- and organoalumino-silicates of similar structure to alkali metal hydroalumino- and alumino-silicates such as kaolinite, albite, and anorthoclase.

Organic derivatives with an Si–O–C bond are formed in reactions of tetraalkoxysilanes with certain metal hydroxides, particularly with calcium and aluminium hydroxides. Microscopic investigation of these derivatives has shown them to be definitely similar to the calcium and aluminium hydrosilicates pyrophyllite and okenite[45,46]. Later Kreshkov *et al.*[44] reported that tetraethoxysilane reacts with aqueous alkaline stannate and plumbate solutions to produce compounds of the general formula



Alkylalkoxysilanes react with potassium, magnesium, zinc, calcium, and other acetates in alcoholic solution to form the corresponding organosilicates[47,48]. The properties of these products varied greatly with the number and nature of the alkyl radicals in the initial alkylalkoxysilane; dialkyldialkoxysilanes generally gave resinous film-forming compounds with physical properties like those of organosilicon polymers.

The production of artificial silicates by Kreshkov's method is of great interest, since an accurate determination of the structure of the resulting compounds would be a direct proof of the possible existence of a covalent bond in the mineral–organic radical system.

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The main difficulty met with in the chemistry of organic derivatives of silicates is the pronounced tendency of laminar silicates towards adsorption and exchange reactions. Many non-ionic organic molecules are dipoles. When in contact with liquids, solutions, or suspensions containing polar substances, clays, which are also polar, attract the oppositely charged centres of the surrounding polar particles. Stable association with molecules which are not dipoles is also met with, for example by the formation of a hydrogen bond between aliphatic chains and oxygen on the surface of the clay particles. Studies in desorption[49] have shown that the desorption processes are very complex and depend on the nature of the minerals and the adsorbed materials. In most cases complete desorption is attained only with great difficulty, and sometimes residual adsorbed organic compounds cannot be completely removed even at 200°–300°. At lower temperatures adsorbed products may remain in spaces within the mineral for 2–10 months.

Furthermore, clays retain water molecules very readily on the surface and between the layers, and it is very difficult to remove this water and obtain the mineral completely dry. This very considerably complicates the investigation of organic derivatives of silicates, since the presence of water cannot be tolerated in the production of hydrolysable derivatives such as alkoxy-, acyloxy-, and halogeno-compounds.

It is also known that uncompensated charges in clays are generally neutralised by adsorbed cations which lie mainly on the basal cleavage surface; these adsorbed cations can be replaced by organic cations such as substituted ammonium ions. The views of those investigators who reject the possibility of formation of organic derivatives of clays are based on such adsorption and ion-exchange processes[50,51], but some do accept that Si–OH groups can exist on the surface of clays[51].

It must also be borne in mind that Greenland, Russell, Brown, and coworkers[50,51] generally worked with readily hydrolysable organic derivatives of the laminar silicates (the halogeno-, acyloxy-, and alkoxy-derivatives), and some hydrolysis products may have been adsorbed if the starting mineral and the reaction apparatus were insufficiently dry or if insufficient precautions had been taken to avoid all contact of the reactants and reaction products with atmospheric moisture. However, a complete analogy in the behaviour of products adsorbed on the initial and the modified clays could clearly not be expected under desorption conditions. This is confirmed by Soviet studies of the adsorption properties of modified silica gels[18,19,52-55].

The existence of organic derivatives of laminar silicates and particularly of derivatives containing the Si–C bond (which is stable to hydrolysis) has been decisively demonstrated by differential thermal analysis[38,56,62], infrared spectroscopy[32,38,63], and X-ray structure analysis[28].

The Institute of Silicate Chemistry of the Academy of Sciences of the USSR has recently undertaken studies on the production of organic derivatives of Chinese kaolin, which according to its chemical composition is almost pure kaolinite[59,61]. This mineral was chosen mainly because kaolinite does not undergo ion exchange with organic ions[57]. Because of its low cation-exchange capacity the amount of organic cations adsorbed by it is very low. Organic molecules cannot penetrate between the elementary layers of kaolinite, and adsorption takes place only at the boundaries and on the outer surface of the mineral[58]. This considerably reduces the difficulties of distinguishing between the effects of adsorption and exchange reactions on the one hand, and reactions leading to the formation of an organic derivative on the other.

The kaolin was ultrasonically comminuted in organic compounds such as biphenyl and diphenylmethane and in poly(alkylsiloxane) liquids. In all cases organic derivatives of the kaolin were produced, which were hydrophobic powders containing 0.1–0.3% of carbon by weight. The organic residues, which were evidently covalently bound to the mineral particles as alkyl-, alkoxy-, and siloxy-groups, could not be removed by repeated extraction with organic solvents.

The differential thermal analysis curves obtained with the organic kaolin derivatives exhibited exothermic peaks, because of the combustion of the organic components, at temperatures of the order of 450°–650° (depending on the nature of the organic groups)[56]. The initial kaolin does not give an exothermic effect in this temperature range[60].

The rupture of Si–O–Si bonds when laminar silicates are comminuted is confirmed by our investigation of chrysotile asbestos: ultrasonic pulverisation of Bazhenov chrysotile asbestos in an aqueous medium leads to an increase in the number of hydroxy-groups attached to silicon[61]. The active hydrogen of the Si–OH groups was determined by the Terent'ev micromodification of the Tserevitinov (Zerewitinoff) method[64], which gives sufficient reproducibility[61].

The organic derivatives of mineral polymers can be expected to find wide practical application in the near future, because of their valuable physicochemical properties such as water-repellency and selective adsorption.

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CHEMICAL CHARACTERISTICS, STRUCTURE, AND PROPERTIES OF LIQUID CRYSTAL

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1. INTRODUCTION

Some organic compounds, heated below their melting point, can form a structure whose properties are intermediate between those of true solid crystals and those of true liquids [1,2]. Liquid crystals combine properties of liquids (fluidity, drop formation, etc.) with properties of solid crystalline materials (anisotropy, electrical, optical, and other properties).

Heating is not the only method of preparing liquid crystals: dissolution of solid crystals of certain substances in specific solvents can also give rise to liquid crystals.

The nature of liquid crystals has been the object of many investigations. The problem has been reviewed by Vul'f [3], Lehmann [4], Friedel [5], Mauguin [6], Vorländer [7], Tsvetkov [8], Weygand [9], Brown and Shaw [10], and Chistyakov [11]. The most comprehensive survey, by Brown and Shaw, cites 475 original papers. The properties of liquid crystals have been discussed at symposia in Germany [12], held in 1931, and in England [13,14], held in 1933 and in 1958.

The last few years have witnessed a renewal of interest in liquid crystals, due above all to their practical importance [15]. Liquid crystals play an important part in the metabolism of living organisms [16-19], and their study is of interest in medicine and biology. Because many wetting agents and detergents, dyes, and polymers can form liquid crystals, their study is of great importance to chemical technology. Shubnikov has pointed out [15] that the remarkable properties of liquid crystals (very large specific rotation of the plane of polarisation, strong pleochroism, electrical and magnetic properties) can be utilised by preparing these materials in a glassy form.

Lehmann [4] distinguished two types of liquid crystals, of widely different viscosities, which he called, respectively, liquid crystals ["Flüssige Kristalle" (Ed. of Translation)] (viscosity of the order of 10^{-2} P) and flowing crystals ["Fliessende Kristalle" (Ed. of Translation)] (viscosity approximately 10 times higher).

Friedel [5] showed that the most essential characteristic of liquid crystals is not their viscosity, but their internal structure, which is intermediate between the three-dimensional lattice of solid crystals and the structureless, amorphous liquid state. Friedel introduced the concept of a mesomorphic state, and distinguished two types of mesomorphs, the nematic and the smectic, corresponding respectively to Lehmann's liquid and flowing crystals.

States of matter can be classified as follows from the point of view of their internal structure:

1. Amorphous state. This is characterised by a completely disordered distribution of molecular position and motions. Molecular rotation is possible about three mutually perpendicular axes.

2. Nematic state. The centres of gravity of the chain-like molecules of which the liquid crystal is composed are randomly distributed, but the chains themselves are oriented along a strictly defined direction. The centres of gravity of the molecules can move in all three dimensions, and molecular rotation is possible about the long axis (Fig. 1*a*).

Compounds which form nematic liquid crystals include *p*-azoxyanisole (t_1 = 116°, t_2 = 133°) and anisaldazine (t_1 = 160°, t_2 = 180°). Throughout the present article, t_1 is used for the melting point of the solid crystal to the liquid-crystalline state and t_2 for the melting point of the liquid crystal to the isotropic liquid state.

3. Smectic state. The centres of gravity (and the chain ends) of the molecules are located on equidistant planes. The centres of gravity can move in two directions (on their plane); molecular rotation is possible about one axis (Fig. 1*b*).

Smectic liquid crystals are formed, for example, by ammonium oleate (at room temperature) and by ethyl *p*-azoxybenzoate (t_1 = 114°, t_2 = 120°).

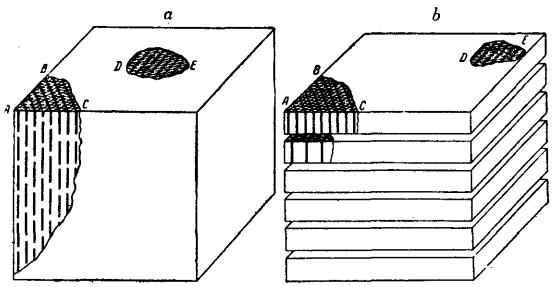


Fig. 1. *a*) schematic arrangement of molecules in the nematic state; *b*) schematic arrangement of molecules in the smectic state.

4. Crystalline state. The positions of the molecules are fixed in a three-dimensional crystal lattice. Molecular rotation can be: (a) permitted about one or more axes, or (b) absent.

The distinguishing feature of liquid crystals, therefore, is their internal structure, which can be described by considerations of symmetry. According to Shubnikov[20,21], smectic liquid crystals show space semicontinuum microsymmetry of the first kind, arising from parallel translation of a given plane A (two-dimensional continuum) along the translation axis C (perpendicular to the plane A). The symmetry symbol in this case is given as $C:A$.

Nematic liquid crystals have space semicontinuum microsymmetry of the second kind, associated with infinitely small displacements of the ornament B [*sic*. (Ed. of Translation)]. The symmetry symbol is now $C^1:B$, where C^1 is the axis of infinitely small translations and B is the ornament symbol [*sic*. (Ed. of Translation)].

Thus the symmetry of nematic liquid crystals is described by continuous, linear symmetry groups, whilst the symmetry of smectic liquid crystals corresponds to planar continuous symmetry groups.

Alexander and Herrmann[22] classify the states of matter, from the point of view of their symmetry, as shown in Table 1. In the nematic state, molecules are arranged in filamentary formations described by one-dimensional space groups, whilst in the smectic state we find ordered layers with true planar space groups.

An article by Neronova and Belov[23] gives a comprehensive discussion of black–white and classical symmetry groups, including those needed to describe liquid crystals.

Hermann[24] approached the symmetry problem from a different angle. He discusses the symmetry groups of amorphous phases and liquid crystals in terms of statistical translation groups, and introduces the concepts of statistical translations (S), direct translations (D), pseudo--translations (P), and reciprocal translations (R).

In amorphous substances the translation group is statistical in three dimensions (SSS), whilst solid crystals are given the symbol $(RD),(RD),(RD)$ because in these materials direct and reciprocal translations are possible in all three dimensions. Between these extremes we find 18 possible translation types for the liquid-crystalline state. Hermann's twenty translation types are arranged in Table 2 so

TABLE 1. Symmetry of the states of aggregation.

Substance	Dimensions of symmetry group	Number of groups
Amorphous	0	—
Nematic	1	∞
Smectic	2	80
Crystalline	3	230

TABLE 2. Possible translation types and corresponding X-ray diffraction patterns.

Brown and Shaw's number	Hermann's number	Translation type	Number of statistical translations	Sets of planes	X-Ray diffraction patterns
1	1	SSS	3	—	no sharp rings
2	3-*a*	SSP_2	2	—	ditto
3	3-*b*	SSP_1	2	—	»
4	3-*c*	SSP_0	2	—	»
5	3	SSD	2		»
6	2	SSR	2	1	one set of sharp rings
7	4-*a*	$SS(SP_1)$	2	1	ditto
8	4-*b*	$SSRP_0$	2	1	»
9	4	$SS(RD)$	2	1	»
10	5-*a*	SP_1R	1	1	»
11	5-*b*	SP_0R	1	1	»
12	5	SDR	1	1	»
13	7-*b*	P_1P_0R	—	1	»
14	7-*c*	P_0P_0R	—	1	»
15	7-*a*	P_0DR	—	1	»
16	7	DDR	—	1	»
17	6	DRR	—	2	at least two sets of sharp rings
18	8-*a*	$DR(RP_0)$	—	2	ditto
19	8	$DR(RD)$	—	2	»
20	9	$(RD)(RD)(RD)$	—	many	many sharp rings

that each succeeding triplet represents a higher order than the preceding; also included is the X-ray diffraction pattern proposed by Hermann for each type. This arrangement does not appear in the original article by Hermann, and is due to Brown and Shaw[10]. The translation types (SSD), $(SSS)C_{00}$, and (P_1P_0R) correspond to the classical types of nematic, smectic, and cholesteric liquid crystals respectively.

Vainshtein has recently pointed out[164] that the symmetry perturbations which occur in real liquid crystals must be taken into consideration. If we take a cross-section normal to the long axes of the molecules we reveal a lattice with two translation axes, t' and t''. This lattice is ordered in a sufficiently small region surrounding any given point, but it does not possess long-range order.

The perturbation of the lattice is described by a distribution function $f(t't'')$, which shows a definite periodicity within any small region surrounding the origin but becomes damped and approaches a constant value at larger distances from the origin. Under these conditions, a group of finite translations $t't''$ becomes a group of continuous displacements $\tau'\tau''$. The symmetry symbol of nematic liquid crystals is $\tau f(t't'')$, that for smectic liquid crystals is $tf(t't'')$.

Five types of $t't''$ lattice are possible for liquid crystals. Relatively large volumes (several mm^3) of liquid crystals have the appearance of a turbid liquid. This is because the specimen consists of a multitude of small regions within which the molecules have their optic axes

parallel. These regions (or "swarms") are birefringent, electrically polarisable, and diamagnetically anisotropic. Each swarm contains 10^4–10^5 molecules[25,26].

There are also other theories of the liquid-crystalline state in which the medium is treated as highly continuous and the concept of swarms is abandoned. The orientation of the molecules in the liquid crystal is considered to vary gradually from point to point along some well-defined directions. These theories include the nematic threaded texture ["structure à fils" (Ed. of Translation)] and the smectic focal-conic texture of related ellipses and hyperbolas[27-29].

More detailed discussions of the various theories of the liquid-crystalline state can be found in a number of review articles[25-33].

2. CHEMICAL CHARACTERISTICS OF MOLECULES

Up to the time of writing, approximately 3000 compounds all of them organic, have been found to exist in the liquid-crystal state. There have been some reports of inorganic liquid crystals, but they have been few and usually not very convincing. Thus, liquid crystals of silver iodide and other monohalides of silver and thallium have been described[2], but it is now generally believed that these materials are highly plastic aggregates of ordinary crystals rather than true liquid crystals.

Perhaps the most interesting claim to have observed liquid crystals in an inorganic system (in this case, metallic bismuth) is that of Donat and Stierstand[34]. These workers placed a single crystal of bismuth in a mould which was specially shaped so as to minimise the relative displacement of adjacent volume elements produced by the volume change on melting. The crystal was melted and on cooling a single crystal of the same orientation as the original charge was obtained provided the melt had not been superheated by more than 10° above the melting point. The authors suggested, therefore, that bismuth can exist in the liquid crystal state.

There is, of course, no fundamental reason why inorganic substances should not form liquid crystals. The new inorganic polymers would seem to open definite possibilities in this direction.

The most important studies of the chemical properties associated with the liquid-crystalline state are due to Vorländer[7] and to Weygand and Gabler[9,35]. According to Vorländer[7], the ability to form liquid crystals depends first and foremost on the shape of the molecule.

There can be no doubt that substances capable of forming liquid crystals must have elongated, relatively straight molecules. Molecular branching and side-chains tend to inhibit the formation of liquid crystals. However, rod-shaped molecules do not invariably form liquid crystals.

Formation of liquid crystals cannot yet be reliably predicted from a knowledge of the chemical formula of the material.

Both aliphatic and aromatic compounds can form the liquid-crystal state, but the vast majority of known liquid crystals belong to the aromatic series. This is due obviously to the relative lack of rigidity of long aliphatic chains and their consequent inability to retain a linear configuration in the liquid state.

Vorländer[7] pointed out that all aliphatic mesomorphic compounds are salts. Salts have a much greater tendency to orientation owing to the equivalence of the oxygen atoms of the carboxyl groups, which affects the rigidity of the chain.

Some aliphatic mesomorphs which are not salts are known already, but they are very few. Those most studied are aliphatic monocarboxylic acids; there is some information about alcohols and esters[36,37].

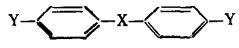
Typical aliphatic compounds that can exist in a liquid-crystalline state are 2,4-nonadienoic acid ($t_1 = 23°$, $t_2 = 49°$), 2,4-undecadienoic acid ($t_1 = 32°$, $t_2 = 58°$), and the sodium salts of monocarboxylic acids listed in Table 14.

Vold and coworkers[38] showed that sodium palmitate and stearate pass through several liquid-crystalline modifications when the crystals are heated to the liquid; this phenomenon has been studied by other workers[39-41].

The present writers have described a thermographic method[42-45] which identifies unambiguously the nature and the number of liquid-crystalline modifications.

Additional information on the properties of aliphatic compounds with a liquid-crystalline modification is given in Brown and Shaw's review[10].

Aromatic molecules, according to Bernal and Crowfoot[46], must possess the following structure in order to show mesomorphism: (1) the molecule must be geometrically anisotropic and either rod-shaped, flat, or lath-shaped; (2) there must not be more than one group in the molecule with a high dipole moment. Brown and Shaw[10] interpret Bernal and Crowfoot's requirements in terms of the following basic structure for aromatic compounds with a liquid-crystalline modification:



Tables 3 and 4 list a series of compounds of this type, divided into symmetrical and unsymmetrical molecular structures (after Brown and Shaw).

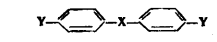
It is pointed out that aromatic substances which exist in a liquid-crystalline modification and contain a single aromatic ring invariably have a substituent in the *para*-position, which makes the molecule elongated. When the substituent is in the *ortho*- or the *meta*-position, liquid crystals are no longer formed. Typical of this type of compound is *p*-methoxycinnamic acid.

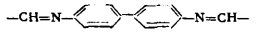
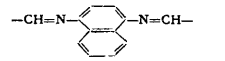
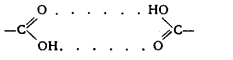
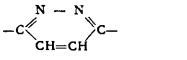
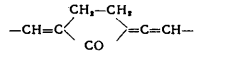
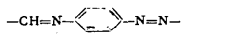
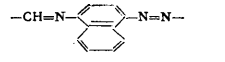
In general, the presence of carboxyl groups in aromatic compounds favours the formation of liquid crystals, but the effect is even more marked when the acid is converted into a salt. Evidently, salt formation from aromatic acids, just as from aliphatic acids, gives rise to additional orientating forces which favour the formation of liquid crystals. For example, sodium benzoate gives liquid crystals over the wide temperature range 410°–430°.

Many compounds known to exist in a liquid-crystalline state contain two or more aromatic nuclei. The nuclei are invariably joined in the *para*-position, and the terminal nuclei are also frequently *para*-substituted.

The tendency to form liquid crystals increases with the number of aromatic nuclei in the molecule. With four benzene rings (quaterphenyl), elongated substituents in the *para*-positions of the end nuclei are no longer necessary, nitro- or amino-groups being sufficient to induce mesomorphism.

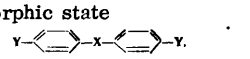
TABLE 3. Composition of central group in aromatic type molecules giving liquid crystals of general formula



X = central group	Type	Typical example
Symmetrical molecules		
—CH=CH—	*trans*-diphenylethylene	*p,p'*-diacetoxystilbene
—N=N—	*trans*-azobenzene	*p*-(*p*-acetoxyazo)benzoic acid
—C≡C—	diphenylacetylene	*p,p'*-diacetoxydiphenylacetylene
—CH=CH—CH=CH—	diphenylbutadiene	*p,p'*-dimethoxydibenzalbutadiene
—CH=N—N=CH—	dibenzalazine	*p,p'*-dimethoxybenzalazine
	dibenzaldiphenyldiamine	dibenzalbenzidine
	dibenzalnaphthalenediamine	*p,p'*-dimethoxydibenzal-1,4-naphthalenediamine
	carboxylic acids* (double molecule)	*p*-butylbenzoic acid (double molecule)
	diphenylpyridazine	*p,p'*-butyldiphenylpyridazine
	dibenzalcyclopentanone	*p,p'*-diethoxybenzalcyclopentanone
Unsymmetrical molecules		
—CH=N—	benzalaniline	*p*-(*p*-cyanobenzal)-anisidine
	phenyl esters of benzoic acid	*p*-(*p*-methoxybenzoxy)-benzoic acid
	azoxybenzene	*p*-azoxyanisole
	benzal-*p*-aminoazobenzene	anisal-*p*-aminoazobenzene
	benzal-1-aminonaphthalene-4-azobenzene	anisal-1-naphthylamino-4-azobenzene

* Other workers, *e.g.* Bennett and Jones[47], are also of the opinion that these molecules are dimeric.

TABLE 4. Composition of end groups in aromatic molecules showing the liquid-crystalline mesomorphic state



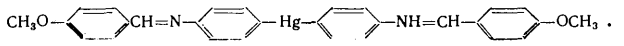
Y = end group	Type
$CH_3(CH_2)_n$—	normal alkyl
$(CH_3)_2CH(CH_2)_n$—	branched alkyl
$CH_3(CH_2)_nO$—	alkoxy
Cl, Br, I	halogen
$CH_3(CH_2)_nCOO$—	carboxylic acid ester
—CN	cyano
$-NO_2$	nitro
$-NH_2$	amino

Most of the aromatic compounds for which evidence of liquid-crystal formation has been obtained contain only benzene rings, but liquid crystals with naphthalene rings are also known. In the latter, however, the tendency towards formation of liquid crystals is much less marked than in benzene derivatives. The liquid-crystalline phases of naphthalene derivatives are often unstable and difficult to study.

In addition to the above, there is another class of these compounds containing the cyclopentylperhydrophenanthrene group with a long side-chain (cholesteryl esters).

The molecular structure of substances which form liquid crystals is often found to consist of two or more benzene nuclei joined by chains of two (or a multiple of two) atoms. Compounds in which the benzene rings are joined by a single atom, or by a chain containing an odd number of atoms, show a negligible tendency to form liquid crystals. Examples of this type of behaviour are provided by the derivatives of diphenylamine, diphenylmethane, diphenylthioether, and diphenyl oxide.

Vorländer explains this effect by pointing out[7] that the bond angles of the atoms linking the nuclei are appreciably different from 180°, and can distort the linearity of the molecule. Nevertheless, the condensation products of aromatic aldehydes with di(*p*-aminophenyl)mercury show mesomorphic properties, *e.g.*



This led Vorländer to propose a linear configuration for the two bonds between the mercury atom and the benzene rings.

Groups joining aromatic nuclei into chains are also of great importance. The following groupings were shown to be particularly effective:

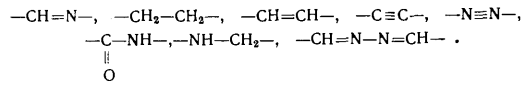
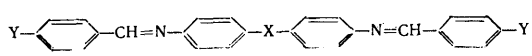


Table 5 gives examples of relatively simple compounds which contain these central groups and readily form liquid crystals.

Table 6, taken from Brown and Shaw's article[10], illustrates the effect of rearranging the end groups in unsymmetrical molecules, and of the change of arrangement of the central group, on the t_1 and t_2 transformation temperatures. Replacement of a methoxy-group by a non-polar phenyl group has relatively little effect on t_2, but the exchange of two polar groups changes it by as much as 20°. The polarity and disposition of the central grouping also affect t_2. If the molecule contains a strong central dipole, such as the azoxy-group, re-orientation of the central group does not appreciably affect t_2, but in the case of a weaker dipole, such as the azo-group, a change in the arrangement of the central grouping gives a large change in t_2 (up to 40°). Further experimental work may, of course, alter the picture.

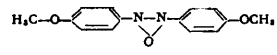
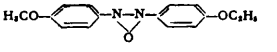
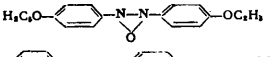
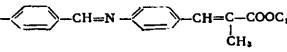
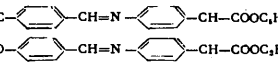
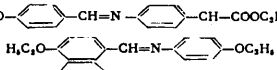
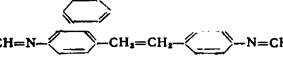
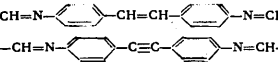
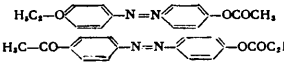
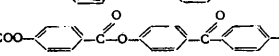
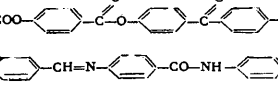
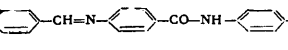
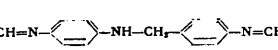
Fig. 2 summarises (after Brown and Shaw) the effect of the central and the end groups on temperature t_2 for a series of compounds having the basic structure:



where X is the central group and Y an end group. Non-polar ($-CH_3$) and polar ($-NO_2$) end groups are considered separately.

These data exemplify the general rule that for any given basic molecular structure, and for a given central group, an increase in the polarity of the end groups decreases t_2.

TABLE 5.

Bond type	Typical compound
	
	
	
 aldimines	
	
	
	
	
	
	
	
	
	
	
	

An exception to this rule is found in the case where the central group is a carboxyl group. The effect of the nature of the central group on the t_2 temperature is also clearly shown by Fig. 2.

Table 7, compiled by Brown and Shaw, illustrates the effect of the central group on the phase transformation

TABLE 6. Effects of the arrangement of the end groups and of the central group on the t_1 and t_2 temperatures.

Compound	t_1, °C	t_2, °C
Change in arrangement of unsymmetrical end groups		
$C_6H_5C_6H_4CH{=}NC_6H_4OCH_3$	176	186
$CH_3OC_6H_4CH{=}NC_6H_4C_6H_5$	161	177
$CH_3COOC_6H_4CH{=}NC_6H_4OCH_3$	112	128
$CH_3OC_6H_4CH{=}NC_6H_4OCOCH_3$	81.5	108
$CNC_6H_4CH{=}NC_6H_4OC_2H_5$	115	132
$C_2H_5OC_6H_4CH{=}NC_6H_4CN$	105	124
Change in arrangement of central group		
	185	292
	226	295
$CH_3C_6H_4CH{=}NC_6H_4N{=}NC_6H_4CH{=}NC_6H_4CH_3$	190	285
$CH_3C_6H_4N{=}CHC_6H_4N{=}NC_6H_4CH{=}NC_6H_4CH_3$	228	297
$CH_3OC_6H_4CH{=}NC_6H_4N{=}NC_6H_4N{=}CHC_6H_4OCH_3$	220	300
$CH_3OC_6H_4N{=}CHC_6H_4N{=}NC_6H_4CH{=}NC_6H_4OCH_3$	257	340

temperatures for the homologues of a series [10,35,48]. It is clearly seen that the differences in the t_2 values decrease with increase in molecular weight. The maximum differences in the t_2 points are observed with the lower-molecular-weight compounds.

Vorländer [7] studied the change in the transformation temperatures with a change in the central grouping for a series of substituted dianisalbenzidines, and found some very large effects (Table 8). He also made a comparative study [49] of derivatives of the type

$$C_6H_5CH = NC_6H_4 - X - C_6H_4N = CHC_6H_5,$$

and showed that the behaviour of analogous central groupings in the two structures was very similar.

Further results [10,50] illustrating the effect of the end groups on the transformation points are summarised in Table 9. They show that if the alkyl of the alkoxy-group in

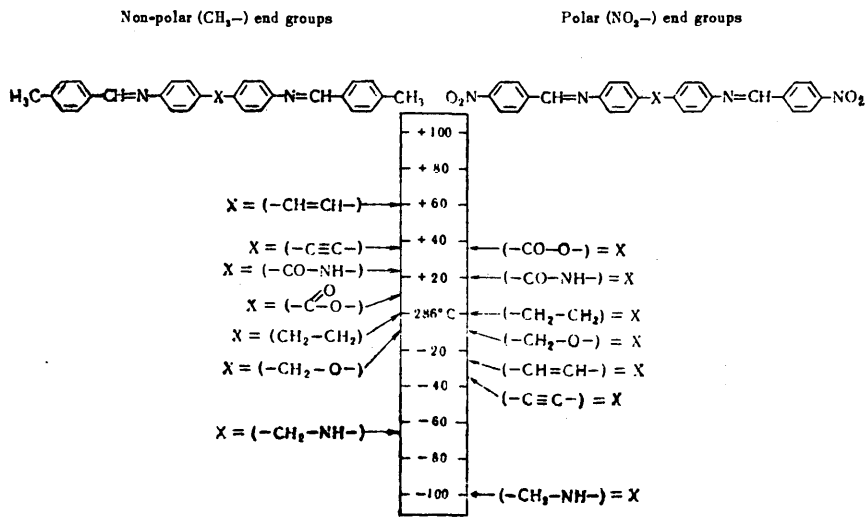


Fig. 2. Effect of end groups and of central group on the melting point of liquid crystals.

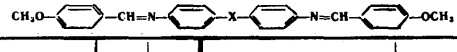
TABLE 7. Transformation points for the azoxyphenol, azophenol, and azomethinephenol ethers*.

Length of side-chain**	Azoxyphenol ethers, °C			Azophenol ethers, °C			Azomethinephenol ethers	
	t_1	t_2	t_3	t_1	t_2	t_3	t_1	t_2
2	116	134	—	165	(110)	—	146	99
3	134	168	—	159	150	—	149	143
4	116	122	—	146	(112)	—	133	(107)
5	107	134	—	135	124	—	125	121
6	82	119	—	113	108	—	113	103
7	81	127	72	102	114	—		
8	74	122.5	92	102	109	97		
9	76	124.5	106	98	—	—		
10	77	121	113	103	107	99		
11	78	123	119.5	106	—	107		
12	78	—	120.5	—	—	—		
13	82	—	122					

* t_1 is the solid→liquid crystal-transformation temperature; t_2 is the temperature of the transformation from nematic liquid crystals to the isotropic liquid; t_3 is the temperature of the transformation from the smectic modification to the nematic or to the isotropic liquid.

** Length of side-chain: 2 = methoxy; 3 = ethoxy; 4 = propoxy, etc.

TABLE 8. Effect of change of the central group of dianisalbenzidine on t_1 and t_2.



X	t_1	t_2	X	t_1	t_2
No central group	253	>345	—OCH_2—CH_2O—	209	298
—CH_2—	not liquid crystalline		—$NHCH_2CH_2NH$—	187	241
			—$COOCH_2CH_2OCO$—	183	197
			—$OCOCH_2CH_2COO$—	183	266
—CH_2—CH_2—	171	312	—C_6H_4—	290	320
—CH_2—CH_2—CH_2—	not liquid crystalline		—O—	not liquid crystalline	
—CH_2—CH_2—CH_2—CH_2—	156	270	—S—	not liquid crystalline	
—CH_2—CH_2—CH_2—CH_2—CH_2—	very small liquid crystallinity		—NH—	239	<239
—CH=CH—	230	>360	—Hg—	209	285
—C≡C—	235	251			
—CH_2O—	209	298			
—C(=O)—O—	206	>310			

TABLE 9. Transformation temperatures of some compounds of the *p*-alkoxybenzal-*p'*-alkylaniline type*.

Compound	Temperature, °C			
	t_1	t_2	t_3	t_4
n-$C_9H_{19}OC_6H_4CH$=$NC_6H_4CH_3$	73	74	70	76
n-$C_9H_{19}OC_6H_4CH$=$NC_6H_4CH_2CH_3$	65	77	74	—
n-$C_9H_{19}OC_6H_4CH$=$NC_6H_4OCH_3$	108	—	—	96
n-$C_9H_{19}OC_6H_4CH$=$NC_6H_4CH_2CH_2CH_3$	51	84	79	—
n-$C_9H_{19}OC_6H_4CH$=$NC_6H_4OCH_2CH_3$	101.5	84	79	115
n-$C_7H_7OC_6H_4CH$=$NC_6H_4OC_7H_7$-n	133	—	—	107
$CH_3OCH_2OC_6H_4CH$=$NC_6H_4OCH_2OCH_3$	47	—	—	—
n-$C_7H_9OC_6H_4CH$=$NC_6H_4OCH_2CH_3$	105.5	—	—	129.5
$CH_3CH_2OCH_2OC_6H_4CH$=$NC_6H_4OCH_2CH_3$	64	—	—	—
n-$C_3H_7OC_6H_4CH$=$NC_6H_4OCH_2CH_3$	125	—	—	123.5
$CH_3OCH_2OC_6H_4CH$=$NC_6H_4OCH_2CH_3$	80.5	—	—	—

* t_1 is the temperature of the transformation from solid crystal to liquid crystal; t_2 and t_3 are temperatures for transformations between different liquid-crystalline modifications; t_4 is the temperature of the transformation from liquid crystal to isotropic liquid.

p-alkoxybenzal-*p*-alkoxyanilines is replaced with an ether (*i.e.* RCH_2CH_2O– with $ROCH_2O$– or $ROCH_2CH_2OCH_2$–) the temperature of the transformation from nematic phase to isotropic liquid will be lowered, or the liquid-crystalline structure will disappear altogether.

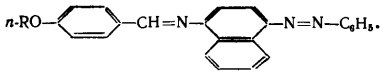
Wiegand's work[51] on dianisalbenzidine and its derivatives illustrates the effect of substituents in different positions of the biphenyl portion of the molecule (Table 10).

Gray and Jones[52,53] have made a similar study of substituted alkoxybenzoic acids and alkoxynaphthoic acids. Their results are set out in Table 11.

The alkoxybenzoic acids and the alkylbenzoic acids afford an interesting series of compounds for comparison of the effect of change of t_1 and t_2 temperatures in a homologous series. These series of compounds give both smectic and nematic structures. In Fig. 3 transformation points are plotted against the chain length of the alkyl or alkoxy-group[10].

It can be seen from Fig. 3 that for the lower-molecular-weight members of the series the smectic and nematic curves show a very similar type of periodicity†, and that the curves tend to flatten out as the length of the molecules increases. The general slope of curves *1* and *3* is negative, that of curve *2* is positive. This type of behaviour is representative of most of the homologous series which have been studied.

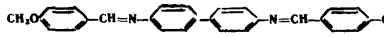
In homologous series exhibiting a distinct periodicity[54], the melting point of the liquid crystals depends on the length of the end chain. An example is the benzalnaphthylamino-azobenzene compounds:



In this system the nematic → isotropic liquid transformation points alternate regularly and strongly between 85° and 100°.

The position of the substituent groups also determines whether the compounds shall form liquid crystals, as work on dianisylnaphthyldiamines has shown[55]. Table 12, after

TABLE 10. Effect of substituents on the nature of the liquid-crystalline state of dianisalbenzidine derivatives



Compound	Temperature, °C	
	t_1	t_2
Dianisalbenzidine	252–253	>345
2,2′-Dichlorodianisalbenzidine	215–216	320–321
3,3′-Dichlorodianisalbenzidine	148–149	>340
2,2′,6,6′-Tetrachlorodianisalbenzidine	217–219 (m.p.)	no liquid-crystalline state
2,2′-Dimethyldianisalbenzidine	172–173	307–308
3,3′-Dimethyldianisalbenzidine	180–181	353
2,2′,6,6′-Tetramethyldianisalbenzidine	212–213 (m.p.)	no liquid-crystalline state

† This statement is not consistent with the description of the curves in the caption to Fig. 3 (Ed. of Translation).

TABLE 11. Influence of substituents on the nature of the liquid-crystalline state of alkoxybenzoic acids and alkoxynaphthoic acids. n = number of carbon atoms in alkoxy--side-chain.

X	Value of n at first appearance of: nematic structure	smectic structure	smectic structure only	Value of n at max. phase interval	Maximum phase interval, °C
Alkoxybenzoic acids					
H	3	7	18	10	57
F	8	9	16	16	16
Cl	8	8	—	16	4.5
6-Alkoxy-2-naphthoic acids					
Cl	3	6	16 and 18	6	42
Br	3	7	16 and 18	7	40
I	4	8	16 and 18	8	25
NO_2	9	12	—	10	1.5

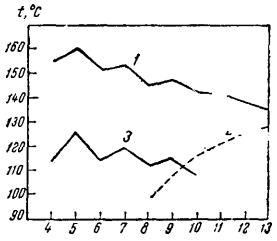


Fig. 3. Transformation points of alkylbenzoic and alkoxybenzoic acids as a function of side-chain length and substituents:
1) nematic → isotropic liquid temperatures for *p*-n-alkoxybenzoic acids;
2) smectic → nematic temperatures for *p*-n-alkoxybenzoic acids;
3) nematic → isotropic liquid temperatures for *p*-n-alkoxybenzoic acids [*p*-n-alkylbenzoic acids (Ed. of Translation)].

TABLE 12. Effect of molecular structure on the liquid-crystalline state.

Compound	Temperature, °C: t_1	t_2
Dianisal-1,4-naphthylenediamine	182.5–184	262–263
Dianisal-1,5-naphthylenediamine	196	282.5
Dianisal-2,6-naphthylenediamine	188.5–189.5	354–356
Dianisal-1,7-naphthylenediamine	142–143 (m.p.)	no liquid-crystalline state
Dianisal-2,5-naphthylenediamine	133–134 (m.p.)	ditto
Dianisal-2,7-naphthylenediamine	204–206 (m.p.)	»

Wiegand, illustrates this effect. Molecules that are rod--shaped, or nearly rod-shaped, can form liquid crystals, whilst molecules lacking a linear structure do not.

Work on the *p*-alkoxycinnamic acids and their halogen derivatives[56,57] gave very similar results. Only the *trans*--form was found to exist in the liquid-crystal state.

Many colloidal systems form structures similar to nematic or smectic liquid crystals. Typical of these are a number of aqueous systems with soap[58,59], the tobacco mosaic virus and other viruses[19], 10-bromophenanthrene--sulphonic acids[60], and some dyestuffs[61,63]. Lawrence[59] classifies these structures as *lyotropic* liquid crystals, since they are formed during dissolution of the solid crystals.

The solvent weakens the intermolecular cohesive forces which hold the crystal lattice together. On dilution, initially these forces are destroyed in one direction only and the substance acquires the properties of a smectic liquid crystal. Increase in dilution causes bond breaking in two dimensions, and the substance becomes nematic. Eventually, at the highest dilutions, the solution becomes isotropic.

The equilibrium diagram of the potassium palmitate–water system, reproduced in Fig. 4, illustrates these lyotropic phase transformations.

It is interesting to consider the formation of these crystals in three-component systems[64–66]. Some organic materials which are insoluble in water are known to dissolve in aqueous soap solutions. These three-component systems (soap–water–insoluble substance) show a liquid--crystal field over some region of the equilibrium diagram. For example, cholesterol melts at 148.5°, but it can exist in a stable liquid-crystalline state at room temperature when mixed with one equivalent of soap solution[66].

Some compounds exhibit several liquid-crystalline modifications[35,67–69]: for example, the dianil obtained from ethyl *p*-aminocinnamate and terephthalaldehyde has four liquid-crystalline modifications, and undergoes the following transformations:

$$\text{IL} \rightleftharpoons \text{LC}_1 \rightleftharpoons \text{LC}_2 \rightleftharpoons \text{LC}_3 \rightleftharpoons \text{LC}_4 \rightleftharpoons \text{SC}.$$

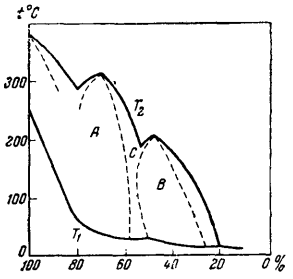
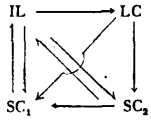


Fig. 4. Equilibrium diagram for the potassium palmitate–water system. The lower curve (T_1) forms the boundary of the region of gels and coagels. The isotropic solution is stable above T_2. The region between T_1 and T_2 defines the liquid-crystalline state.

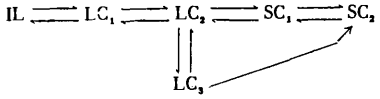
IL is the isotropic liquid, LC the liquid crystals, and SC the solid crystal. The arrows show that the phase transformations can occur in either direction. Consequently, the liquid crystals exhibit *polymorphism*.

In some compounds the liquid-crystalline state is monotropic with respect to the solid state. Thus, cholesteryl acetate never forms liquid crystals when the solid crystals are heated[70,71], but melts at 114° to give an isotropic liquid. On cooling this liquid, however, metastable liquid crystals are formed. At large enough supercooling the liquid crystals are converted into beautiful spherulites (the SC_2 modification), which are themselves monotropic with respect to the stable SC_1 solid modification.

The transformations of cholesteryl acetate are summarised in the following diagram:



Phenyl *p*-azoxyphenetolebenzoate gives this series of transformations:

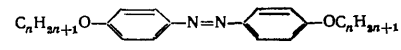


The third liquid-crystalline modification appears only during cooling.

According to Shubnikov[21], the complexity of the conversion scheme and the number of possible modifications increase with the number of thermodynamic variables and can, therefore, be infinitely large.

Small additions of isomorphous impurities can significantly extend the region of existence ($t_1 - t_2$) of liquid crystals. There is a clear analogy between this phenomenon and the formation of crystalline solid solutions: the impurity affects the properties of the liquid crystals as well as the temperature limits of their existence[72].

Arnold and Sackmann[73,74] discuss, with a comprehensive list of references, the isomorphism of liquid-crystalline phases, and point out that mixtures of liquid-crystalline phases should provide examples of both complete and partial miscibility. Two-component systems consisting of pairs of homologues of the series



(4,4′-di-*p*-alkoxyazobenzenes; n = 2, 3, 4, 8, 9, 10, 12) have been studied microscopically. Complete miscibility was observed for mixtures of isomorphous phases (smectic–smectic, or nematic–nematic), and for mixtures of the isotropic liquids, but mixtures of different liquid-crystalline phases or of solid phases did not form a continuous series of solutions.

These observations led to the suggestion that miscibility might be used as a criterion for isomorphism, but further experimental work is needed.

Studies of the factors which determine the miscibility of liquid crystals of a single (or of more than one) class are, unfortunately, only just beginning. The approach is to explore the stability limits of the phases under study by varying the size and shape of the molecules without disturbing the type (or the intensity) of molecular interactions.

3. X-RAY DIFFRACTION BY LIQUID CRYSTALS

Liquid crystals were examined by *X-ray structural analysis* shortly after the discovery of X-ray diffraction. Van der Lingen[75] obtained Laue patterns from *p*-azoxyanisole and *p*-azoxyphenetole, but could only conclude that liquid crystals lack a three-dimensional lattice, since the X-ray diffraction patterns were similar to those of ordinary amorphous liquids.

Hückel[76] confirmed the absence of a crystal lattice after examining the diffraction patterns of *p*-azoxyanisole, *p*-azoxyphenetole, dianisaldazine, cholesteryl propionate, and cholesteryl benzoate. More advanced X-ray techniques, however, enabled Kast to show[77] that the plot of intensity *versus* diffraction angle for the nematic state is slightly displaced relatively to that for the isotropic liquid.

A large proportion of the X-ray work on nematic liquid crystals was done in a magnetic field. According to Kast[78], each swarm gives two interference maxima at right angles to the long axis of the molecules, but since the swarms are randomly oriented the diffraction pattern contains one broad, diffuse ring, as in the case of amorphous liquids. In the presence of a magnetic field the swarms take up an orientation parallel to the magnetic lines of force, and the diffuse ring splits into two crescents corresponding to two interference maxima at right angles to the direction of the field.

Stewart[79–82], using molybdenum $K\alpha$ radiation, found that the diffraction-intensity curves of nematic *p*-azoxyanisole and of the corresponding isotropic liquid differ slightly at the principal maximum, which is approximately 10% higher for the nematic than for the liquid structure. The curvature, and the sharpness of the peak, are also slightly more pronounced in the nematic state. Stewart concludes that the swarms in the liquid crystals are much larger than any similar aggregates in the isotropic liquid. If the latter are assumed to comprise 100–1000 molecules, the swarms in liquid crystals must be thought to contain at least 10^6 molecules.

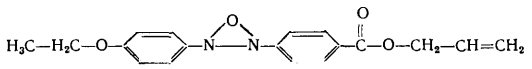
Glamann *et al.*[83] examined *p*-azoxyanisole by X-ray diffraction. Two diffraction rings were found with copper $K\alpha$ radiation, while three rings were obtained with molybdenum $K\alpha$ radiation. In a magnetic field the two diffraction rings obtained using the copper radiation split into crescents.

Recent work by Falgueirettes[84] has shown that nematic *p*-azoxyanisole, oriented in a magnetic field or by contact with mica leaves prepared by Chatelain's method, gives three pairs of crescents in copper $K\alpha_1\alpha_2$ radiation. One pair of crescents is parallel to the optic axis, and is ascribed to intermolecular interference. The two remaining pairs are weaker, perpendicular to the optic axis of the nematic single crystal, and they are produced by intramolecular interferences. Falgueirettes calculated the molecular distribution in the nematic single crystal, $f(\theta)$ as a function of θ, by a microphotometric study of the variation of intensity along the diffraction rings.

Crescent-shaped interference maxima are also found in the diffraction patterns of nematic liquid crystals oriented by an electric field[85]. However, in contrast to the crescents observed in a magnetic field, these can be oriented either parallel or perpendicular to the direction of the electric field. The effect depends on the orientation of the long axes of the molecules, which is determined by the molecular structure[8].

When liquid crystals of *p*-azoxyanisole are placed in a low-frequency a.c. electric field the diffuse ring of the diffraction pattern splits into two crescents whose axes are oriented parallel to the field, showing that the molecules themselves have taken up this orientation. Increase in frequency to 300 c/s destroys the sickle-shaped pattern and restores the diffuse ring, but at still higher frequencies the crescent shape once again appears, with its axis at right angles to the initial direction. Kast[86] accounts for this phenomenon in terms of frictional dispersion: the swarms cannot align themselves with the field once the period of the applied a.c. becomes shorter than the relaxation time involved. The relaxation time of the swarms, evaluated by this method, was found to be 10^{-5} sec, as compared with 10^{-11} sec for a typical isolated molecule.

Numerous X-ray studies[87-89] have confirmed the layer structure of smectic liquid crystals. Herrmann[90] examined a series of cinnamic and of benzoic esters which can give both nematic and smectic liquid crystals. His tabulated results show that the first three compounds exhibit a new kind of interference (immediately above the liquid crystal–solid crystal transformation point) whose origin is ascribed to hexagonal cylindrical packing of the molecules within the smectic layers. Herrmann and Krummacher[91] examined allyl *p*-phenetoleazoxybenzoate



(a compound which can exist in nematic and smectic mesophases), and reported the following transformation points: solid crystal $\underset{66°}{\rightleftharpoons}$ smectic liquid crystal $\underset{77°}{\rightleftharpoons}$ nematic liquid crystal $\underset{95°}{\rightleftharpoons}$ isotropic liquid.

These workers also found that in a magnetic field of 8600 G the diffraction patterns of the smectic and the nematic liquid crystals are practically indistinguishable, and consist of two pairs of crescents. However, the molecules appear to be better aligned in the smectic phase, since the diffraction ring is more sharply resolved into crescents. The results are summarised in Table 13.

The diameter of the outer ring varies with temperature, and therefore also with the amount of intermolecular interference. Herrmann and Krummacher arrived at similar conclusions in their work[92] on the X-ray diffraction of anisal-1,5-diaminonaphthalene.

TABLE 13. X-Ray data on allyl phenetoleazoxybenzoate.

Temperature, °C	Structure	Diameter of outer ring	θ/2	d, Å
	Radiation: Cu Kα (*H* = magnetic field)			
100	liquid, no *H*	32	8°47′	5.0
88	nematic, with *H*	34	9°18′	4.8
79.5	nematic, with *H*	34	9°18′	4.8
75.5	smectic, with *H*	35	9°33′	4.6
72	smectic, with *H*	35	9°33′	4.6
	Radiation: Mo Kα (*H* = magnetic field)			
94	nematic, with *H*	34.4	9°26′	2.16
82	nematic, with *H*	36.5	9°56′	2.04
70	smectic, with *H*	38	10°19′	1.96

Many papers on the X-ray analysis of liquid crystals include diffraction patterns of the same materials in the solid crystalline state. Bernal and Crowfoot's paper[46] on the structure of six crystalline solids able to form liquid crystals is among the most informative.

It is found that molecules with a single active terminal group (or two symmetrical terminal groups) have a tendency to crystallise in layer structures, which yield smectic liquid crystals when the solid crystals are heated. Compounds of this type (*e.g.* ammonium oleate or ethyl *p*-azoxybenzoate) are termed "smectogenic". On the other hand, molecules having central active groups tend to form "nematogenic" solid crystals. These materials (*e.g.* *p*-azoxyanisole or *p*-azoxyphenetole) give nematic liquid crystals on heating.

X-Ray diffraction and other methods of investigation have established the existence of five allotropic liquid-crystalline phases in anhydrous sodium soaps[93,94]. The results of this work are summarised in Table 14.

Many diffraction lines (sometimes more than 20) are found in the centre of the diffraction pattern of each liquid-crystalline phase. Further out, there are diffuse rings with a fine structure which sharpens up when the temperature is lowered.

The first four phases have a two-dimensional, face-centred, rectangular lattice. The structure consists of parallel bands of polar end groups packed in a rectangular lattice, with liquid-like hydrocarbon chains (Fig. 5). The cell dimensions (*a* and *b*) depend on the soap and on the phase (Table 14). The fifth (or "neat") phase has a lamellar structure (Fig. 6*a*).

The X-ray pattern of the isotropic phase a few degrees above the melting point contains two or three fairly sharp rings, confirming that the structure of a melt close to the transformation temperature is not very dissimilar from the structure which is stable below the transformation point.

TABLE 14.*

Structure	*t*	Sodium laurate	*t*	Sodium myristate	*t*	Sodium palmitate	*t*	Sodium stearate
Two-dimensional rectangular	100		107		117		118	
Two-dimensional rectangular	141	*a*=75.2 *b*=30.9 at 166°	141	*a*=80.0, *b*=34.5 at 155°	135	*a*=86.6, *b*=38.3 at 152°	132	*a*=80.0, *b*=40.3 at 140°
Two-dimensional rectangular	182	*a*=68.5, *b*=30.3 at 195°	176	*a*=69.0 *b*=33.6 at 195°	172	*a*=74.2 *b*=36.8 at 195°	167	*a*=72.5 *b*=37.9 at 198°
Two-dimensional rectangular	220	*a*=49.8 *b*=27.0 at 234°	217	*a*=53.8 *b*=29.1 at 233°	208	*a*=56.2 *b*=30.6 at 236°	198	*a*=62.4 *b*=34.4 at 238°
Lamellar	255	*d*=25.3 at 290°	245	*d*=27.5 at 271°	253	*d*=29.1 at 278°	257	*d*=30.6 at 285°
Isotropic melt	336		310		295		298	

* *t* is the phase transformation temperature, *a* and *b* the dimensions of the unit cell in Å, *d* the interplanar spacing.

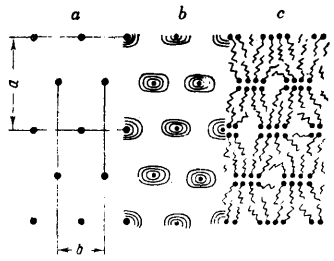


Fig. 5. *a*) Two-dimensional, centred rectangular lattice; *b*) electron density projection along {001}; *c*) schematic of the rectangular phase structure.

A recent paper[94] points out that sodium laurate can form, between the "superwaxy" and the "subneat" phases, yet another new phase with a three-dimensional, face-centred, orthorhombic lattice (lattice constants a = 55.5, b = 28.3, c = 32.7 Å).

Complete conversion of the sample from one form to another takes several hours. This may account for some disagreement between different research groups[93-95].

Many X-ray investigations of lyotropic liquid crystals of soaps and detergents have been published[96-100]. Recent work[101-102] has shown that phase A (Fig. 4) takes the form of smectic double layers of soap molecules. The surfaces of each layer contain the polar ends of the molecules, and the "liquid" hydrocarbon chains are pointed inwards (Fig. 6*a*). At higher soap concentrations the layers of soap molecules become thicker, whilst the intervening water layers become thinner.

Phase B is formed as a hexagonal array of long cylinders (Fig. 6*b*) whose diameter is not a function of concentration at constant temperature.

In addition to these two phases, three intermediate phases have been identified in region C of Fig. 4. These include a complex hexagonal phase (Fig. 6*c*), a distorted variant of phase B showing an orthorhombic lattice, and a cubic (isotropic) phase in which the hydrocarbon chains are arranged in spheres separated by water molecules.

The diffraction patterns of lyotropic liquid crystals of tobacco mosaic virus in water[103,104] have four sharp equatorial spots, which justify the belief that the particles are arranged in a two-dimensional hexagonal lattice (Fig. 7).

The cholesteric lyotropic liquid crystals formed by certain polypeptides have been shown[105] to have a structure similar to that of Fig. 7, but with some additional coiling along the Z axis.

Diffraction studies of aqueous desoxyribonucleic acid and nucleoprotein systems[106,107] have identified a number of phases, including some which are liquid crystalline. Haemoglobin, α-keratin, and many other biologically important substances are able to form liquid crystals.

The theory of X-ray diffraction in similar biological systems has been developed by Hosemann[108,109] [the "ideal paracrystal" model of liquid crystallinity (Ed. of Translation)].

The *nuclear magnetic resonance* (NMR) of liquid crystals has been discussed in a number of recent papers[110-117]. The isotropic melt of p-azoxyanisole in a magnetic field of 7300 G has a resonance line[110] of width 0.1 G. When the temperature is lowered to 135.8° and the specimen is converted into the liquid-crystalline state, the amplitude of the signal decreases and the line is resolved into three components. The separation between the two satallite peaks is approximately 3.3 G; the intensity ratio is 2 : 3 : 2. The NMR line loses its structure when the specimen is converted into the solid-crystalline state.

Comparative NMR results for three compounds are given in Fig. 8 (after Jain *et al.*[112]). The investigation, which was concerned with the effect of temperature on the NMR spectrum of three compounds, established that the NMR signal of 4,4'-dimethoxyazoxybenzene (p-azoxyanisole, PAA) is fairly independent of temperature within the limits of the liquid-crystalline state, but that the peak separation decreases with increasing temperature.

4,4'-Dimethoxy-D_3-azoxybenzene (DPAA) differs from PAA in having the hydrogen atoms of the end groups replaced by deuterium, so that the protons attached to the benzene rings are the only possible source of NMR signals. The signal in this case consists of a strong doublet with a relatively weak central component. Again, the shape of the signal is fairly independent of temperature over the

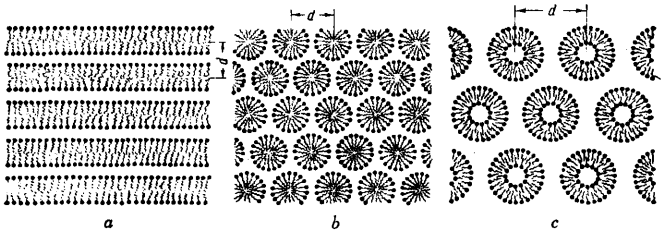


Fig. 6. Structure of the soap–water liquid-crystalline system. *a*) Phase A (see Fig. 4); *b*) phase B; *c*) complex hexagonal phase C. The spaces between the soap micelles are filled with water.

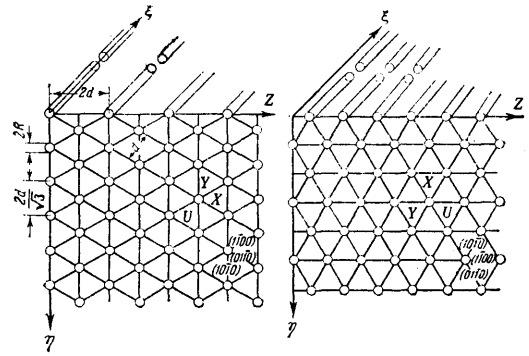


Fig. 7. Structure of the tobacco mosaic virus. $XYZU$ are the crystallographic axes, $\eta\xi$ are the molecular axes.

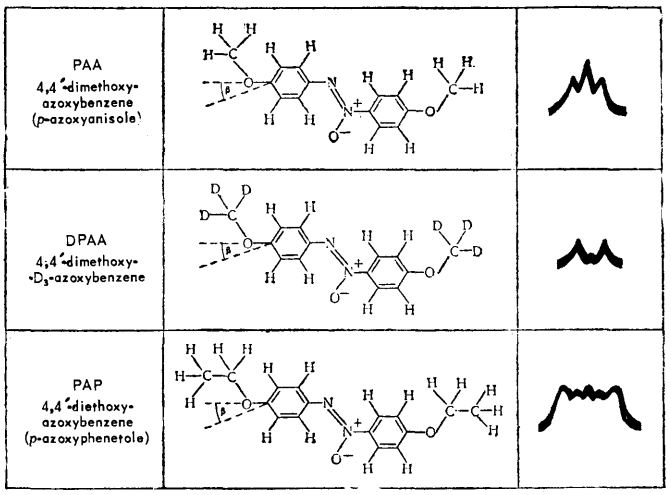


Fig. 8. Molecular structure and shape of proton magnetic resonance signals.

entire liquid-crystalline region, but the peak separation decreases at higher temperatures. However, within 0.5° of the liquid crystal → isotropic liquid transformation point the central component begins to increase rapidly and reaches an amplitude 1.5 times that of the satellite peaks. At the transformation point the satellite peaks disappear and a single narrow line remains.

The NMR line of *p*-azoxyphenetole (PAP) is similar, at the highest temperatures, to that of PAA (Fig. 8). At lower temperatures, however, the central peak begins to shrink and two additional peaks appear (Fig. 8, bottom). This justifies the conclusion that the replacement of methyl groups (PAA) by ethyl groups (PAP) produces a more highly oriented liquid-crystalline phase.

4,4'-Propoxyazobenzene and anisaldazine behave like PAA. Smectic substances, like sodium oleate and sodium stearate, give simple lines of average width at all temperatures between the isotropic-liquid and the solid-crystalline phase [112].

NMR has been used to study transition phenomena in many substances [113]. It has been shown that these phenomena are not symmetrical about the transformation point, and that they depend on the thermal history of the specimen. Frenkel's theory of fluctuations in heterogeneous phases can account for these results if contamination by the thermal decomposition products of the material is considered.

The newest developments in the NMR study of smectic and nematic liquid crystals are due to Lippman [115-117], who has also produced a comprehensive review of the theoretical and experimental aspects of the application of NMR to liquid crystals.

Another recent review article, by Saupe and Maier [118], deals with the methods (including NMR) of studying the degree of ordering in nematic crystals.

4. SOME PROPERTIES OF LIQUID CRYSTALS

Smectic crystals are always uniaxial and positive. A smectic substance, pressed between a microscope glass slide and cover slip, can form large homogeneous areas within each of which the optic axes of the molecules are uniformly oriented (homeotropic texture). Each of these areas is effectively a liquid single crystal.

At temperatures close to the smectic → isotropic liquid transformation point, differences in the strength of attachment of the molecules to the glass surface may cause the smectic layers to move or become disturbed, giving a focal-conic texture (Fig. 9). A discussion of focal-conic textures can be found in the literature [5,119].

When the isotropic melt of a smectogenic compound is cooled, the liquid crystals adopt the shape of elongated rods ["bâtonnets" (Ed. of Translation)] which coalesce at the points of contact, producing spherical bulges at the points of coalescence of a small rod with a larger one (Fig. 10).



Fig. 9. Focal-conic texture. Ethyl *p*-azoxybenzoate. Crossed Nicols.



Fig. 10. Smectic rods of cholesteryl palmitate. Crossed Nicols.

The lack of sphericity of these smectic droplets suggests that their surface tension is anisotropic. On further cooling the rods coalesce completely to form the focal-conic texture.

Smectic liquid crystals produced lyotropically give rise to the same textures. The liquid-crystalline texture shown in Fig. 11, for example, was produced by evaporation of an aqueous alcoholic solution of potassium oleate. It was shown to be stable only between definite limits of concentration and temperature: at higher soap concentrations the texture begins to separate into layers, and gives a slightly different type of focal-conic texture[120] (Fig. 12).

The *nematic* type of liquid crystals can be classified‡ into *true nematic* and *cholesteric* forms. In true nematic liquid crystals dark filaments are visible. If the threads are arranged normally to the slide and coverslip they appear as dark spots, nuclei from which dark lines are seen to radiate when the specimen is viewed between crossed Nicols in a polarising microscope (see Fig. 13*a*). By analogy with dislocations in crystals, these threads can be called dislocation lines, since the orientation of the molecules suffers a sharp discontinuity at these features.

Nematic liquid crystals are uniaxial and positive. They do not rotate the plane of polarisation, but optical activity can be induced by mechanical distortion of the liquid-crystalline specimen.

The cholesteric liquid crystals are thus named because derivatives of cholesterol are this type (Fig. 13*b*). Cholesteryl benzoate, in which liquid crystals were first observed[1], gives cholesteric liquid crystals with $t_1 = 146°$ and $t_2 = 178.5°$.

Amyl cyanobenzalaminocinnamate ($t_1 = 95°$, $t_2 = 105°$) is an example of a cholesteric compound not chemically related to cholesterol.

Cholesteric liquid crystals are uniaxial, negative, and strongly optically active (up to 200 complete rotations of the plane of polarisation per 1 mm thickness). These properties stem from the structure of the liquid crystals, which is twisted in a direction perpendicular to the long axes of the molecules, thus permitting some measure of stratification, which ultimately leads to a focal-conic texture. The pitch of the twisted structure (equal to the thickness of the resulting layers) is of the order of 1000 Å.

The optical properties of liquid crystals can be studied only if the specimens are suitably oriented. Chatelain[121-125] has worked out a simple and reliable method of producing nematic single crystals, by melting the sample between a slide and cover slip previously rubbed with a sheet of paper in a definite direction. This treatment produces a single crystal with its optic axis in the direction of rubbing.

Chatelain and his coworkers used this technique to study the scattering of light by nematic structures, and also the refractive index. Measurements of the refractive index of PAA, summarised in Table 15, show that the enormous birefringence of the liquid crystal decreases gradually on raising the temperature towards the point of transformation

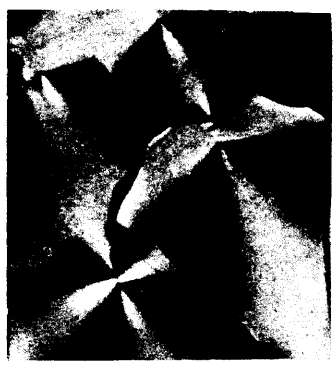


Fig. 11. Liquid-crystalline texture of potassium oleate between slide and cover slip. Crossed Nicols.



Fig. 12. Liquid-crystalline texture obtained by disrupting the texture of Fig. 11. Crossed Nicols.



Fig. 13. *a*) *p*-Azoxyanisole in the liquid-crystalline state. Crossed Nicols. *b*) Cholesteryl cinnamate, showing the focal-conic texture. Crossed Nicols.

‡ The assignment of cholesteric mesophases to the general nematic type, originally due to Friedel[5], is far from universally accepted (Ed. of Translation).

TABLE 15. Refractive indices of liquid crystals of *p*-azoxyanisole. n_0 = ordinary refractive index; n_e = extraordinary refractive index.

Temperature, °C	589 mμ		546 mμ		Temperature, °C	589 mμ		546 mμ	
	n_0	n_e	n_0	n_e		n_0	n_e	n_0	n_e
105	1.558	1.875	1.568	1.907	122	1.564	1.836	1.574	1.872
110	1.559	1.865	1.569	1.898	125	1.566	1.825	1.576	1.862
114	1.560	1.856	1.570	1.890	128	1.569	1.814	1.578	1.850
117	1.561	1.849	1.571	1.884	130	1.571	1.806	1.581	1.843
120	1.563	1.842	1.572	1.877	132	1.576	1.795	1.584	1.833

into isotropic liquid, and suddenly drops to zero at the transformation point.

Studies of the *absorption spectra* of PAA liquid crystals revealed a closer similarity to the solid state than to the isotropic liquid state. The solid and the liquid crystals have an absorption band at 1247 cm^{-1} which is not observed in the isotropic liquid. Differences in the absorption spectra of the solid, liquid-crystalline, and isotropic liquid states [126-128] have been reported also for a number of other substances, both in the visible [126-128] and in the infrared [129-131] and ultraviolet [132] regions of the spectrum.

An anomalous change in *viscosity* has been observed [133-136] near the point of transformation from liquid crystal to isotropic liquid (Fig. 14). Bose [137] ascribes this phenomenon to anisotropy of the viscosity of the liquid-crystalline particles.

Kast and Becherer [138] measured the viscosity of PAA, and reported a linear variation of viscosity with temperature in the liquid-crystalline and the isotropic liquid states, with a sudden discontinuity from 0.0317 to 0.0254 C.G.S. units at the transformation point.

Owing to the anisotropy of viscosity, the rate of flow of liquid crystals through capillaries can be altered by applying an electric or magnetic field [139-143]. Measurements of the anisotropic viscosity of PAA liquid crystals, flowing through a capillary in the presence of a magnetic field and at 122°, gave the following values [139]: $\eta_1 = 0.024$ (molecules parallel to the flow direction); $\eta_2 = 0.092$ (molecules parallel to the velocity gradient); $\eta_3 = 0.034$ (molecules perpendicular to the velocity gradient).

The application of a magnetic field in the same direction as the electric current has been shown [144,145] to increase the electrical conductivity of liquid crystals. It follows that the *electrical conductivity* of a substance in the liquid-crystalline state is anisotropic, with a maximum in the direction of the long axes of the molecules.

Anisotropy of the electrical conductivity has recently been observed, and widely studied, in lyotropic liquid crystals (anisotropic soap solutions) oriented between a fixed and a rotating cylinder [146-149].

Kast [150] showed that the dielectric constant of liquid crystals is affected by a magnetic field, and made a quantitative study of the effect. Several investigators have discussed the dielectric constant [8,150,155]. Typical changes in dielectric constant and dielectric anisotropy are plotted in Fig. 15. [156]

Foix and Royer [157] reported that PAA is diamagnetic, and that the liquid crystals are more weakly diamagnetic than either the solid crystals or the isotropic liquid. The molecules therefore show *anisotropic diamagnetism*. The magnetic susceptibility at constant magnetic field [158] is plotted against temperature in Fig. 16.



Fig. 14. Anomalous change in viscosity at the temperature of the transformation between isotropic liquid and liquid crystals (after Vorländer).

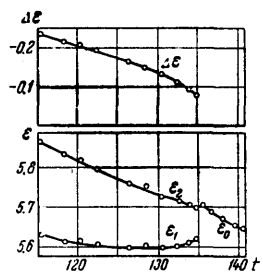


Fig. 15. Temperature dependence of the dielectric constants ϵ_1 and ϵ_2, and of the dielectric anisotropy $\Delta\epsilon$, for *p*-azoxyanisole. The ϵ_0 curve refers to the isotropic melt.

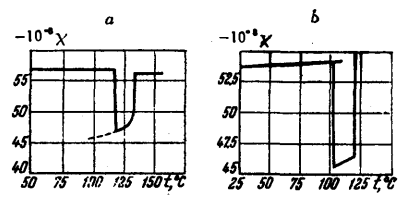


Fig. 16. Effect of temperature on the magnetic susceptibility in a constant magnetic field for: *a*) *p*-azoxyanisole (nematogenic); *b*) ethyl *p*-azoxybenzoate cooled from the isotropic melt (smectogenic).

Systematic studies of the electrical and magnetic properties of liquid crystals, and of their molecular structure, were carried out in Leningrad by Frederiks and his team of physicists [159-163]. More detailed treatments of the properties of liquid crystals are given in the previously mentioned reviews [3-11].

In conclusion, it can truly be said that transformation into the liquid-crystalline state causes important changes in the physical properties of a system.

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VIBRATIONAL SPECTRA OF COMPOUNDS CONTAINING ELEMENTS OF THE CARBON SUBGROUP

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I. INTRODUCTION

This review surveys the experimental results which have accumulated on the vibrational spectra both of organic compounds containing Si, Ge, Sn, and Pb and of inorganic compounds of these elements such as, for example, SiH_4, $HGeCl_3$, etc.

The survey is divided according to the individual bonds and groups representing substitution on silicon, germanium, tin, and lead.

II. COMPOUNDS CONTAINING AN E–H BOND (E = Si, Ge, Sn)

1. Compounds of the Type EH_4 (E = C, Si, Ge)

The molecules CH_4, SiH_4, and GeH_4 belong to the symmetry point group T_d. In conformity with this, they will be expected to have four vibrational frequencies in the Raman spectrum (R), and only the frequencies of the triply degenerate vibrations in the infrared absorption spectrum (i.r.). We shall not consider the methane molecule[1,2] in detail, and say a little only about SiH_4 and GeH_4.

Various workers have described the vibrational spectra of silane and germanium tetrahydride (germane) in several papers, among which must be noted the work of Stitt and Yost[3] on the Raman spectrum of SiH_4, and that of Schäfer and Gonzales-Barredo[4] on the Raman spectrum of GeH_4. The infrared absorption spectra of these compounds have been investigated by Tindal *et al.*[5-7]. Data on the vibrational spectra of SiH_4 and GeH_4 are also available[8-12]. The data in Table 1 and Fig. 1 are based mainly on these papers.

The vibrational spectra of deuterated silanes have been described by Meal and Wilson[13] and Polo and Wilson[14], the first of these papers dealing with the infrared absorption spectra of SiD_4, $SiHD_3$, and SiH_2D_2, and the second with that of SiH_3D. Calculations have also been made on the vibrational spectra of methane[2] and silane[15]. It follows from the calculations that, for compounds of the type EH_4, the force constant of the E–H bond decreases in the sequence E = C, Si, Ge, Sn (calculation of completely symmetrical vibration) (see Fig. 2).

E	$k_{q(E-H)}$, cm^{-2}	r_{E-H}, Å	Refs.
C	$8.34 \cdot 10^6$	1.09	2
Si	$4.67 \cdot 10^6$	1.4798	14,15,17
Ge	$4.3 \cdot 10^6$	1.54	5,16
Sn	$\sim 3.8 \cdot 10^6$	—	16

TABLE 1. Vibration frequencies of molecules of the type EH_4 (symmetry T_d).

ν, cm^{-1}	CH_4 (R and i.r.)[1]	SiH_4 (R)[10]	SiH_4 (i.r.)[5,6]	GeH_4 (R)[a,4]	GeH_4 (i.r.)[5,7]
ν_1 (a)	2914 (R)	2180	—	2089 (10)	—
ν_2 (e)	1526	970	975[c]	920[b] (3)	932[c]
ν_3 (f_2)	3020 (i.r.)(R)	2183	2191	2106 (2)	2114
ν_4 (f_2)	1306 (i.r.)	910	910	816[b] (0)	818

[a] Spectrum of GeH_4 determined at -100°.

[b] The assignment given in Ref. 4 is that $\nu_2(e)$ = 816 cm^{-1} and $\nu_4(f_2)$ = 920 cm^{-1}. From the intensity ratio for these lines and from the infrared spectroscopic data[6,7], a more correct assignment is that shown in Table 1.

[c] The authors of the paper give an explanation for the appearance of the frequency $\nu_2(e)$, which is forbidden in the infrared spectrum.

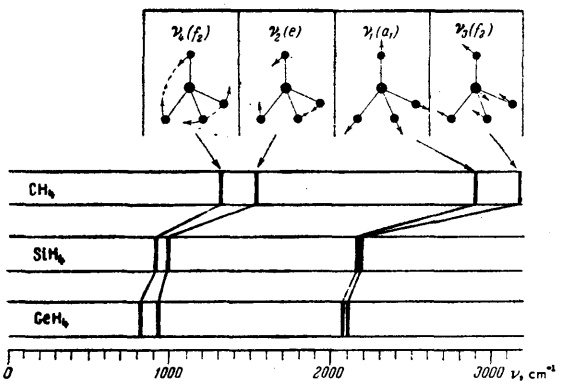


Fig. 1. Molecules of the type EH_4 (symmetry T_d).

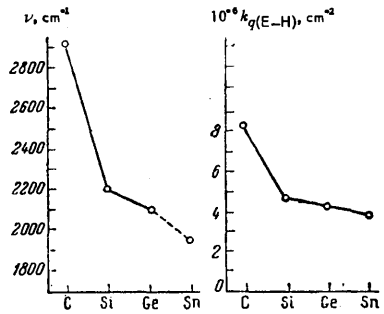


Fig. 2. Vibration frequencies and force constants of E–H bonds in molecules of the type EH_4 (E = C, Si, Ge, Sn).

2. The E–H bond in Halogeno-Derivatives (E = C, Si, Ge)

The chief results for the E–H vibrations in the mono-halogeno-derivatives of methane, silane, and germane are given in Table 2 and also in Fig. 3. Andersen and Bak[22] have examined the infrared absorption spectra of SiD_3Cl, SiH_3F, and SiD_3F. The vibrational–rotational spectrum of monochlorosilane has been studied[23] over the range 650–2200 cm^{-1}. Mayo *et al.*[24] investigated the infrared absorption spectra of SiH_3Br and SiH_2Br_2, the Raman spectra of these compounds having been examined earlier[25].

Results are given for CH_2X_2 and SiH_2X_2 molecules, as examples of dihalogeno-derivatives (Table 3 and Fig. 4).

In the case of the trihalogeno-derivatives the frequencies of the E–H vibrations lie within the ranges indicated in Table 4; the variation in frequency for molecules of type EHX_3 can be judged from Fig. 6.

3. Alkyl, Alkenyl, and Alkenylalkyl Derivatives Containing an E–H Bond (E = Si, Ge, Sn)

Alkylsilanes have been investigated by several workers. Westermark[35] showed that $\geqslant$Si–H groups have intense infrared bands in the region of 2109 cm^{-1}, $>SiH_2$ near 2132–2136 cm^{-1}, and $-SiH_3$ near 2164 cm^{-1}. The values of ν_{Si-H} for $(C_6H_5)_2SiH_2$ and $(C_6H_5)_3SiH$ are 2155 and 2136 cm^{-1} respectively†. Other investigations have been made of the infrared spectra of alkylsilanes containing these same groups[36]. The infrared spectra of triphenylsilane (ν_{Si-H} = 2135 cm^{-1}, δ_{Si-H} = 805 cm^{-1}) and of tripropylsilane (2108 and 820 cm^{-1}) have been investigated by Kaplan[37]. Dialkylsilanes ($RR'SiH_2$) have been investigated by West and Rochow[38], the values of ν_{Si-H} being 2083–2096 cm^{-1} for compounds in which R is an aliphatic radical, and 2096–2118 cm^{-1} where R is aromatic. Studies have also been made[39,40] of the Raman spectra of a series of compounds containing $\geqslant$SiH, $>SiH_2$, and $-SiH_3$ groups, from

TABLE 2. Vibration frequencies of EH_3 groups in molecules of the type EH_3X (E = C, Si, Ge; X = F, Cl, Br, I) (symmetry C_{3v})*

	CH_3F[1]	SiH_3F[18]		CH_3Br[1]	SiH_3Br[18]
$\nu_s(a_1)$	2964	2196		2972	2196
$\nu_{as}(e)$	2982	2206		3056	2200
$\delta_s(a_1)$	1475	990		1305	930
$\delta_{as}(e)$	1471	943		1445	950
	CH_3Cl[1]	SiH_3Cl[18]	GeH_3Cl[19]	CH_3I[1]	SiH_3I[20,21]
$\nu_s(a_1)$	2966	2185	2121	2970	2192
$\nu_{as}(e)$	3042	2201	2129	3060	2205
$\delta_s(a_1)$	1355	949	848	1251	903
$\delta_{as}(e)$	1454	954	874	1440	941

* The types of vibrations and assignment of frequencies are given also in Fig. 3.

† In this paper the infrared spectra of 28 compounds are given (over the range 2–15 μ).

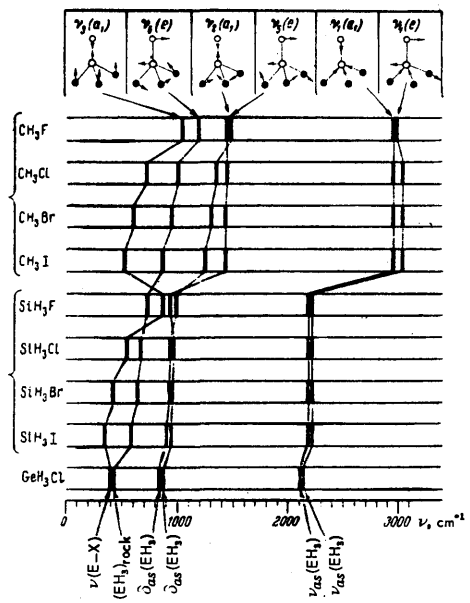


Fig. 3. Molecules of the type EH_3X (symmetry C_{3v}).

TABLE 3. Vibration frequencies of EH_2 groups in molecules of the type EH_2X_2 (symmetry C_{2v}). X = F, Cl, Br, I.

	CH_2F_2(R)[26]		CH_2Br_2(R)[26]	(i.r.)[26]	SiH_2Br_2(R)
$\nu_s(a_1)$	2963		2988	2200	2206
$\nu_{as}(b_1)$	3030		3061	—	2232
$\delta(a_1)$	1509		1388	942	925
$\delta(b_2)$	1509		1133	843	828
	CH_2Cl_2[1]	SiH_2Cl_2(i.r.)[27]	CH_2I_2[28]		
$\nu_s(a_1)$	2984	2200	2968		
$\nu_{as}(b_1)$	3048	2200	3048		
$\delta(a_1)$	1429	953	1348		
$\delta(b_2)$	1255	877	1103		

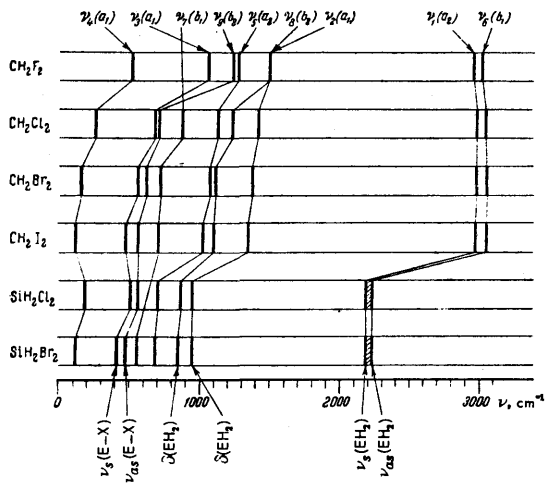


Fig. 4. Molecules of the type EH_2X_2 (symmetry C_{2v}).

TABLE 4. E–H vibration frequencies in molecules of the type EHX_3* (E = C, Si, Ge; X = F, Cl, Br) (symmetry C_{3v}).

	CHF_3(R)[26]	$SiHF_3$(l.s.)[28]	(l.s.)[1] CH_3Cl_3(R)		(l.s.)[29] $SiHCl_3$(R)[30,31]		$GeHCl_3$(R)[32]
ν	3062	2315	3033	3019	2262	2258	2159
δ	1376	851	1205	1215	802	799	699
	$CHBr_3$(R)[26]	$SiHBr_3$(R)[26]	$GeHBr_3$(R)[32]				
ν	3022	2236	2116				
δ	1143	770	674				

* Unfortunately, results[33,34] for the Raman spectra of $SnHX_3$ cannot be used, since the papers do not give frequencies for the Sn–H bond.

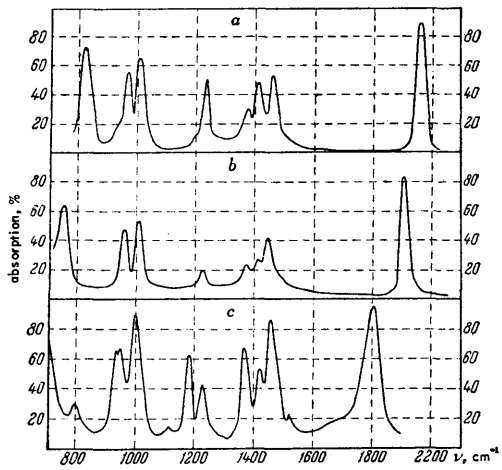


Fig. 5. Infrared absorption spectra of compounds of the type $(C_2H_5)_3EH$: *a*) $(C_2H_5)_3SiH$; *b*) $(C_2H_5)_3GeH$; *c*) $(C_2H_5)_3SnH$.

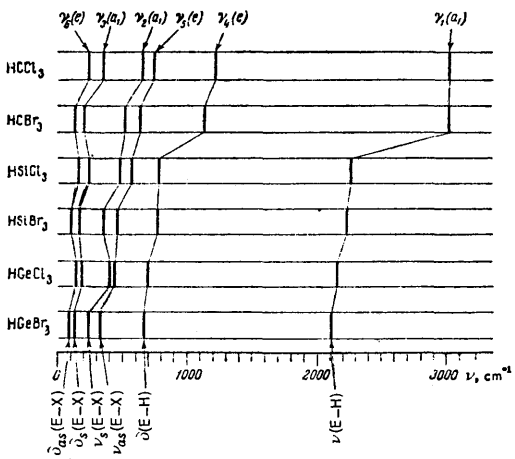
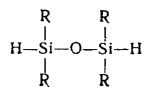


Fig. 6. Molecules of the type EHX_3 (symmetry C_{3v}).

which it follows that the corresponding values of ν_{Si-H} are ~2120, ~2135, and 2155 cm^{-1}. The results of Harvey *et al.*[41] for the infrared absorption spectra of dialkylsilanes of the type $RR'SiH_2$ agree with those of previous work[38].

The values of ν_{Si-H} for alkenylalkylsilanes containing an Si–H bond lie in almost the same regions as those for alkylsilanes[29].

The same relations are observed also with tetrasubstituted disiloxanes having the structure



(where R = CH_3, C_2H_5, $CH:CH_2$, C_6H_5) and with a large number of polymers resulting from their interaction with dienes[29,42,43].

Noteworthy calculations have been made by Kovalev[44-46], showing that the Si–H bond is less stable in alkylsilanes than in SiH_4. With the series $(CH_3)_nSiH_{4-n}$ (n = 0–4) as an example, it has been shown[46] that the strength of the Si–H bond decreases with increasing number of methyl groups on the silicon atom, the corresponding force constant $k_{q(Si-H)}$ becoming smaller (this explains the shift in ν_{Si-H} to lower frequencies).

The halogenosilanes show the reverse relationship, the ν_{Si-H} frequencies becoming higher with increase in the number of halogen atoms attached to the Si in SiH_4 [$k_{q(Si-H)}$ also becomes rather higher]. Information on the Si–H vibrations is also to be found in several other papers, in particular those of Kriegsmann[47,48].

Relatively little work has been done on compounds containing Ge–H and Sn–H bonds. Thus, for example, West[49] gives ν_{Ge-H} = 2040 cm^{-1} in triphenylgermane, and 2060 cm^{-1} in $(CH_3)_2GeH_2$. The infrared absorption spectra of several alkylgermanes[50] of the types R_3GeH, R_2GeH_2, and $RGeH_3$ have been examined (where R represents ethyl and propyl; ethyl, butyl, hexyl, heptyl, and octyl; and pentyl, hexyl, heptyl, and octyl respectively), values of ν_{Ge-H} for the $\rangle GeH$, $\rangle GeH_2$, and $-GeH_3$ groups being respectively 2010, 2035, and 2065 cm^{-1}.

The Ge–H and Sn–H stretching frequencies are lower than the Si–H vibration frequencies, this being clearly shown in the series of compounds[16,51] $(C_2H_5)_3EH$ (E = Si, Ge, Sn) (see Fig. 5).

The frequency of the E–H vibration falls regularly from Si to Sn (the same occurs also with δ_{E-H}, from ~810 to ~700 cm^{-1}).

Mention must be made also of work on compounds of the type H_3E-EH_3, disilane and digermane. In the former, investigated by Gutowsky and Stejskal[52], ν_{Si-H} lies in the range 2154–2181 cm^{-1}, and δ_{Si-H} in the range 843–910 cm^{-1}. In the case of digermane[53] ν_{Ge-H} lies between 2078 and 2114 cm^{-1}. It is noted that the vibrational frequencies fall steadily on passing from ethane to disilane and digermane.

A calculation made by Kovalev[54] shows that $k_{q(Si-H)}$ for disilane is 4.51×10^6 cm^{-2}, which is very close to the value in silane. Results for ν_{Si-H} in disilylacetylene[55] are close to those in disilane[52].

Trisilylamine has been investigated by Ebsworth *et al.*[56], and a value of 2168 cm^{-1} has been found[47] for ν_{Si-H} in this compound.

Smith and Angelotti[57] have attempted to correlate the Si–H vibration frequencies with molecular structure, and from their work it follows that the shift in ν_{Si-H} depends on the electronegativity of the substituents attached to the silicon atom, and is almost proportional to the change in electronegativity.

Finally, it is interesting that the E–H vibration bands (E = Si, Ge, Sn) are separated from the rest of the spectrum and are fairly intense. They lie in a frequency range which is separated both from the C–H stretching vibrations and from vibrations involving other functional groups (bonds). Such isolation considerably facilitates the task of identifying compounds containing these bonds (groups). The region of E–H vibrations includes only the C≡C and C≡N stretching vibrations.

It follows from the results given in the present section that in general the bands due to Si–H stretching vibrations lie within the frequency range 2100–2300 cm^{-1}, those due to Ge–H at about 2000–2200 cm^{-1}, and those due to Sn–H at about 1800–2000 cm^{-1}.

The regular decrease in frequency of the E–H vibrations in the sequence C, Si, Ge, Sn is noteworthy. The greatest changes in frequency occur on passing from C to Si, those in the series Si, Ge, Sn being less marked. The chief reason for the change in frequency is a change in the force constants of the E–H bonds. The latter also show the most marked change from C to Si, the value of $k_{q(C-H)}$ being almost double that of $k_{q(Si-H)}$.

The E–H vibration frequencies are somewhat higher in the halogeno-derivatives than in the alkyl and alkenylalkyl derivatives (mainly of silanes, since very extensive data are available for them). This is associated with a rather higher value of the force constants of the E–H bond in the halogenosilanes.

The alkyl and alkenylalkyl derivatives of silicon show little difference in frequency, which indicates fairly convincingly that the Si–H vibrations are quite characteristic of these classes of compounds. The same applies also to the Ge–H vibrations.

III. COMPOUNDS CONTAINING E–Alk AND E–C_6H_5 GROUPS (E = Si, Ge, Sn, Pb; Alk = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9)

Let us consider the frequency range 1150–1270 cm^{-1}, which shows the most specific influence of the central atom (E = Si, Ge, Sn, Pb) on the frequencies of C–H deformation vibrations in the alkyl groups attached to E.

Reference must first be made to work on molecules of the type $E(Alk)_4$. Among the early experimental investigations are those of Kettering and Sleator[58] [although they have only recorded the infrared absorption spectra of $Sn(CH_3)_4$, $Pb(CH_3)_4$, and $Ge(C_2H_5)_4$, without any assignment of the frequencies or interpretation of the results], Rank[59,60] [the first paper on the Raman spectrum of $C(CH_3)_4$, the second on $Si(CH_3)_4$], Duncan and Murray[61] on the Raman spectrum of $Pb(CH_3)_4$, and Anderson[62], who examined the Raman spectra of $C(CH_3)_4$, $Si(CH_3)_4$, $Si(C_2H_5)_4$, $Sn(CH_3)_4$, $Pb(CH_3)_4$, and $Pb(C_2H_5)_4$. More recent investigations include those of Young *et al.*[63] [who examined the infrared absorption spectra of $C(CH_3)_4$, $Si(CH_3)_4$, and $Ge[CH_3)_4]$, and Rank *et al.*[64] on the vibrational spectra of $C(CH_3)_4$, $Si(CH_3)_4$, and their monodeuterated derivatives. Sheline and Pitzer[65] give results on the infrared absorption spectrum of $Pb(CH_3)_4$.

Lippincott and Tobbin[66] investigated the infrared and Raman spectra of $Ge(CH_3)_4$, $Sn(CH_3)_4$, and $Pb(CH_3)_4$, and calculated the thermodynamic functions of these molecules. Data on compounds of the type $E(CH_3)_4$ are given also in several other papers[67-71].

A great deal of work has been done on compounds containing E–Alk groupings, among which must be mentioned investigations[72] on Si–CH_3 and on the infrared spectra of cyclic siloxanes[73] having the structure

$$-[-Si(Alk)_2-O-]_n- ,$$

where Alk = CH_3, C_2H_5, C_6H_5. Compounds containing Si–CH_3 groupings have been investigated also by Richards and Thompson[74], Rank *et al.*[64], Frisch *et al.*[75], Tatlock and Rochow[76], Horak *et al.*[77], Egorov and Bazhulin[78], and the reviewer[42]. Compounds containing the Si–CH_2–R (R = H, CH_3, C_2H_5, n-C_3H_7) grouping have been investigated by the reviewer[29], Kaye and Tannenbaum[36], Harvey *et al.*[41], Plate *et al.*[79], and also Durgar'yan *et al.*[80] Compounds containing Si–CH_3, Ge–CH_3, Sn–CH_3, Pb–CH_3, Si–C_6H_5, Ge–C_6H_5, Sn–C_6H_5, and Pb–C_6H_5 groupings have been investigated[81], and also[16] those containing Sn–CH_3 and Sn–C_2H_5. The above papers show good agreement among themselves in the sense that data on the frequencies of the E–Alk groupings coincide. Thus Si–CH_3 is characterised by the presence of absorption bands and Raman lines within the range 1250–1258 cm^{-1} (in the case of methylchlorosilanes[29] the frequency rises to 1265–1267 cm^{-1}), with Ge–CH_3 the frequency, in the case of alkyl- and alkenylalkyl-germanes, lies at about 1240–1242 cm^{-1} (also rising slightly in the methylchlorogermanes)[51], with Sn–CH_3 at 1190–1195 cm^{-1}, and with Pb–CH_3 at 1170 cm^{-1}.

TABLE 5. Vibration frequencies of E–Alk and E–C_6H_5 groupings[16,29,51].

Grouping	ν, cm^{-1}	Grouping	ν, cm^{-1}
Si–CH_3	1250–1258	Si–n-C_3H_7	1205, 1215 doublet
Ge–CH_3	1238–1242		
Sn–CH_3	1190–1195	Si–n-C_4H_9	1180, 1190 doublet
Pb–CH_3	1170		
Si–C_6H_5	1235–1240	Si–C_6H_5	1110–1120 (1103)*
Ge–C_6H_5	1230–1235	Ge–C_6H_5	1080 (1084)*
Sn–C_6H_5	1183–1190	Sn–C_6H_5	— (1068)*
Pb–C_6H_5	1158	Pb–C_6H_5	— (1055)*

* According to Noltes *et al.*[81]

Table 5 gives the E–Alk and E–C_6H_5 vibration frequencies, where E = Si, Ge, Sn, Pb, and Alk = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9. The following generalisations can be made for the absorption bands and Raman lines due to E–Alk groupings: frequencies decrease (1) in the sequence E = Si, Ge, Sn, Pb, and (2) in the sequence CH_3, C_2H_5, n-C_3H_7, n-C_4H_9.

In contrast, in the assignment of the vibrations having the above frequencies, there is no unity of the sort shown by the agreement between the frequencies. Several workers give different interpretations of the results, but many investigators are inclined to regard the above frequencies as due to symmetrical C–H deformation vibrations. This question can be completely cleared up only by sufficiently careful calculations.

It should be noted[29] that the intensity of the infrared absorption bands due to Si–Alk groupings (the reviewer has made measurements of the integral intensities of the bands for organosilicon compounds) may serve as a measure of the number of alkyl groups attached to the silicon atom.

IV. GROUPS CONTAINING MULTIPLE BONDS

1. Compounds Containing E–CH=CH_2 and E–CH_2–CH=CH_2 Groupings (E = Si, Ge, Sn). The C=C Bond and Terminal Methylene (=CH_2) Groups

A large proportion of the work on alkenyl derivatives of Si, Ge, Sn has been done by Soviet investigators, among which must be mentioned the work of Egorov *et al.*[78,82–85] on the Raman spectra. The infrared absorption spectra of several alkenyl derivatives have also been examined[16,29,43,51,86,87]. Some allyl derivatives of silicon had been investigated earlier by Scott[75,88] (i.r.).

The Raman spectrum of methyltriallylsilane has been examined by Malkovich and Kolesova[89]. Tetravinyltin has been investigated[90]. The principal C=C vibration frequencies are given in Table 6.

The variation in intensity of C=C vibrational bands is extremely interesting. In the sequence C → Sn the vinyl derivatives show a decrease in intensity of these absorption bands, and the allyl derivatives, on the other hand, an increase. Several workers[83–87] have made detailed studies of the laws governing the changes in intensity and frequency of the C=C vibrations.

TABLE 6. C=C vibration frequencies in vinyl and allyl derivatives* of C, Si, Ge, Sn.

Compound	ν, cm^{-1}	Compound	ν, cm^{-1}
$(CH_3)_3C$–CH=CH_2	1645	$(CH_3)_3C$–CH_2–CH=CH_2	1648
$(CH_3)_3Si$–CH=CH_2	1595	$(CH_3)_3Si$–CH_2–CH=CH_2	1633
$(CH_3)_3Ge$–CH=CH_2	1590	$(CH_3)_3Ge$–CH_2–CH=CH_2	1633
$(CH_3)_3Sn$–CH=CH_2	1583	$(CH_3)_3Sn$–CH_2–CH=CH_2	1628

* In the case of olefins[91] infrared absorption bands in the range 1620–1680 cm^{-1} correspond to an isolated double bond.

Perfluorovinyl derivatives of Si, Ge, Sn have been investigated by Stafford and Stone[92]. Fluorine atoms adjacent to a C=C bond increase $\nu_{C=C}$ appreciably, right up to 1700–1800 cm^{-1}.

With regard to methylene (=CH_2) groups, the C–H stretching vibrations (ν_{as}) for E–CH=CH_2 groupings lie within the range 3040–3050 cm^{-1} in the cases of Si, Ge, Sn. With E–CH_2–CH=CH_2, $\nu_{as(C-H)}$ = 3070–3080 cm^{-1}.

Data on frequencies and intensities of infrared absorption bands and Raman lines due to vibrations of C=C and =CH_2 groups may provide a valuable criterion of the presence of a particular alkenyl group in the compound.

2. Acetylenic Derivatives. The C≡C Bond

The following compounds containing an acetylenic bond have been investigated:

$SiH_3C{\equiv}CSiH_3$ (I) (infrared and Raman),[55]
$Si(CH_3)_3CH_2CH_2C{\equiv}CH$ (II),[93]
$C_2H_5Si(CH_3)_2C{\equiv}CH$ (III),[29]
$Si(CH_3)_3C{\equiv}CSi(CH_3)_3$ (IV),[29]
$C_2H_5SiH(CH_3)C{\equiv}CSiH(CH_3)C_2H_5$ (V) (infrared).[29]

Values of $\nu_{C\equiv C}$ for I–III are 2132, 2116, and 2050 cm^{-1} respectively. In the cases of IV and V, the C≡C vibration frequencies did not appear in the infrared absorption spectra owing to the symmetry of the molecules. We may note that $\nu_{C\equiv C}$ has the values 1974 cm^{-1} (R) for HC≡CH, 2100–2150 cm^{-1} for monosubstituted acetylenic derivatives of the type AlkC≡CH, and 2200–2250 cm^{-1} for disubstituted derivatives RC≡CR. For the terminal ≡C–H bonds $\nu_{\equiv C-H}$ has the values 3305 cm^{-1} (II) (R) and 3280 cm^{-1} (III) (i.r.).

Especially noteworthy is the curious fact that the frequencies and intensities of C=C and C≡C vibrations located α to Si, Ge, and Sn undergo the most significant changes, which indicates that the specific effect of these elements on the above bonds in the molecule is qualitatively different from that found with olefins.

The vibration frequencies of terminal methylene groups also undergo some change compared with olefins, this being especially noticeable in the case of vinyl derivatives.

V. THE E–C BOND (E = Si, Ge, Sn, Pb)

Of the papers on alkyl derivatives of Si, Ge, Sn, Pb noted in Section III, a considerable number are concerned with the compounds $E(CH_3)_4$.[58,60–65,67,94,95] The most complete data on vibrations of this type of molecule are given by Young *et al.*[63]‡ The frequencies of skeletal vibrations of these molecules, taken from this paper, are listed in Table 7.

A considerable number of calculations have been made on $E(CH_3)_4$ molecules, among them being the papers by Wall and Eddy[96] and Silver[97,98] [though these workers determined the frequencies of the $Si(CH_3)_4$ skeleton by regarding the methyl groups as atoms of atomic weight 15], and also by others[65,67,69,99]. The most complete calculation is that of the $Si(CH_3)_4$ molecule made by Kovalev[100].

‡ Data on Raman spectra from other papers are used in this work[63].

TABLE 7. Frequencies of the skeletal vibrations of molecules of the type[63] $E(CH_3)_4$ (E = C, Si, Ge, Sn, Pb).

ν, cm^{-1}	$C(CH_3)_4$	$Si(CH_3)_4$	$Ge(CH_3)_4$	$Sn(CH_3)_4$	$Pb(CH_3)_4$
$\nu(a_1)$	733	598	540	506	460
$\nu(e)$	335	202	110	100	100
$\nu(f_2)$	925	696	590	526	473
$\nu(f_2)$	414	239	200	152	130

Force constants for the Si–C bonds in $Si(CH_3)_4$ from different sources are given in Table 8. Values of k_{E-C} for the $E(CH_3)_4$ series given by Siebert[99] are reproduced in Table 9. Data are available on the infrared absorption spectra[101] and on the Raman spectra[102]. Some results for methylsilicon derivatives are given in Table 10.

In compounds containing $Si-CH_3$ groupings ν_{Si-C} lies within the range 700–760 cm^{-1}.

Thus the frequency range for stretching vibrations of the Si–C bond in methyl derivatives is 600–800 cm^{-1}. In the case of methylgermanium compounds ν_{Ge-C} lie within the ranges[51] ν_s = 570–600 cm^{-1} and ν_{as} = 610–650 cm^{-1}. The Sn–C vibration frequencies in methyltin derivatives[16] are still lower: $\nu_s \simeq$ 510–525 cm^{-1} and ν_{as} = 520–550 cm^{-1}.

Estimated E–C vibration frequencies (for $E-CH_3$ groupings) are compared in Table 11. Information on regularities in the variation of E–C vibration frequencies in ethyl derivatives $E(C_2H_5)_4$ is provided by the data in Table 12. Japanese workers[105] assign the frequency 736 (3) cm^{-1} to $\nu(f_2)$, but Malkovich and Kolesova[89] and Batuev *et al.*[106] have adopted the frequencies 640 (3 w) and 630 (3 w) cm^{-1}§ respectively. The correctness of the assignment[62] is evident from a comparison of the frequency differences $\nu(f_2)-\nu(a_1)$ for molecules of types $E(CH_3)_4$ and $E(C_2H_5)_4$ (see Table 13)

TABLE 8. Force constant k_{Si-C} for $Si(CH_3)_4$.

	$10^{-5}k_s$, dyn cm^{-1}	$10^{-5}k_d$, cm^{-2}	References
k_{Si-C}	3.31	5.20	96
k_{Si-C}	3.31	5.20	98
k_{Si-C}	2.93	4.60	99
k_{Si-C}	2.92	4.62	100

TABLE 9. k_{E-C} for compounds of the type $E(CH_3)_4$ according to Siebert[99].

Compound	$10^{-5}k_s$, dyn cm^{-1}
$C(CH_3)_4$	4.22
$Si(CH_3)_4$	2.93
$Ge(CH_3)_4$	2.72
$Sn(CH_3)_4$	2.24
$Pb(CH_3)_4$	1.90

§ w = wide.

TABLE 10. Frequencies of Si–C stretching vibrations* in $Si(CH_3)_4$ groups.

	ν_s(Si–C)	ν_{as}(Si–C)	References
$(CH_3)_3SiH$	623	718	103
$(CH_3)_3Si-Cl$	640	700	104
$(CH_3)_3SiCH=CH_2$	—**	696	
$(CH_3)_3SiCH_2-CH=CH_2$	627	702	
$(CH_3)_2SiCH_2CH_2CH=CH_2$	626	697	
$(CH_3)_2SiCH_2CH_2CH_2CH=CH_2$	—**	700	

* See also Ref. 48.

** It is difficult to make a definite assignment of the lines.

The infrared absorption spectra of $Si(C_2H_5)_4$ have been examined[29,35], though within the range 2–15 μ, and information on the infrared spectrum of $Ge(C_2H_5)_4$ is available[107].

The Raman spectra of some alkyltrichlorosilanes[108] indicate that the Si–C vibration frequency in Si–Alk groupings decreases in the sequence CH_3, C_2H_5, n-C_3H_7, n-C_4H_9 (see Table 14).

Since the E–C vibration frequencies have the lowest value in the case of allyl groups (see Table 11), the Si–C stretching vibrations can be assumed to lie within the range 550–800 cm^{-1}, Ge–C at 500–650 cm^{-1}, Sn–C at 450–550 cm^{-1}, and Pb–C at 420–480 cm^{-1}.

The authors of some papers on the infrared absorption spectra of organosilicon compounds[72,74,91] assume that the Si–C stretching vibrations lie within the range 800–900 cm^{-1}: this is incorrect. This range contains the

TABLE 11. Frequencies of E–C stretching vibrations (E = Si, Ge, Sn) from infrared spectra.

Type of vibrations	$(CH_3)_3SiCH_2CH=CH_2$	$(CH_3)_3GeCH_2CH=CH_2$	$(CH_3)_3SnCH_2CH=CH_2$
A	555	524	480
A	635	573	512 } ν_s $E(CH_3)_3$
E	701	602	527 } ν_{as}

TABLE 12. Frequencies of the skeletal vibrations of $E(C_2H_5)_4$ molecules.

Type of vibrations	$Si(C_2H_5)_4$[62]	$Ge(C_2H_5)_4$*	$Sn(C_2H_5)_4$[16]*	$Pb(C_2H_5)_4$[16]*
A	553 (10)	530 (80) (R)	475 (125) (R)	443 (320) (R)
F	625 (3)	577 (40) (R and i.r.)	500 (84) (R and i.r.)	458 (200) (R and i.r.)

* Intensities (numbers in parentheses) were measured relative to the CCl_4 line at 458 cm^{-1}, the intensity of which was taken as 100.

TABLE 13. $\Delta\nu = \nu(f_2) - \nu(a_1)$ for compounds of the types $E(CH_3)_4$ and $E(C_2H_5)_4$.

Type of compound	Si $\Delta\nu$	Ge $\Delta\nu$	Sn $\Delta\nu$	Pb $\Delta\nu$
$E(CH_3)_4$	98	50	20	13
$E(C_2H_5)_4$	72	47	25	15

TABLE 14. Si–C vibration frequencies[108].

Compound	ν_{Si-C} (I)
CH_3SiCl_3	757 (5)
$C_2H_5SiCl_3$	712 (3d)
n-$C_3H_7SiCl_3$	698 (0d)
n-$C_4H_9SiCl_3$	705 (0s)
n-$C_6H_{13}SiCl_3$	695 (0)

rocking vibrations of CH_3 groups in Si–CH_3, etc. groupings. Experiment shows that definite assignment of E–C vibration frequencies requires data on both infrared and Raman spectra. The frequencies of the E–C deformation vibrations lie within the range 100–300 cm^{-1}, falling regularly in the sequence[109] Si, Ge, Sn, Pb.

The problem of the E–C vibrations is the most important in the identification of organosilicon, organogermanium, and organotin compounds, for the E–C bond characterises the above as definite classes of heteroorganic ("organoelemental") compounds. The E–C bonds are more polar than the C–C bond, and as a result the task of finding and assigning E–C vibrations in the spectra is somewhat easier than the analogous problem in the case of hydrocarbons.

Nevertheless, as already noted, several different views exist concerning the frequency range of E–C vibrations. Several recent papers on the vibrational–rotational spectra of the simplest methyl derivatives of silicon again indicate that the frequency range 800–900 cm^{-1} is that of CH_3 rocking vibrations. Incidentally, the frequencies of these vibrations are very close for both Si–CH_3 and Ge–CH_3, around 800 cm^{-1}. However, the difference in Si–C and Ge–C vibration frequencies in the ranges 550–800 and 500–600 cm^{-1} is ~100 cm^{-1}. For example, the values of ν_{Si-C} and $\nu_{(CH_3)rock}$ for CH_3SiCl_3 are 760 and 800 cm^{-1}, while the corresponding values of ν_{Ge-C} and $\nu_{(CH_3)rock}$ for CH_3GeCl_3 are 633 and 824 cm^{-1}.

VI. THE E–X BOND (E = Si, Ge; X = F, Cl, Br, I)

Table 15 gives the frequencies of Si–X stretching vibrations for the groups SiX, SiX_2, and SiX_3, together with references to the original papers. Table 16 gives corresponding data for compounds containing GeX, GeX_2, and GeX_3 groups. For the spectra of $HSiCl_3$, see Refs. 118 and 119; trimethylchlorosilane has been investigated by Duchesne[120] (for monochlorosilane, see Ref. 121). Methylchlorosilanes have been investigated by Goubeau *et al.*[122], Simanouti *et al.*[102], Smith[104], and Ignat'eva *et al.*[101] Murata and Hayashi[112] have investigated the methylbromosilanes. Data on trichlorosilane are given by Collins and Nielsen[123]. The Raman spectra of ethylchlorosilanes have been investigated by Batuev *et al.*[106], and also by Murata *et al.*[105] The Sn–X stretching vibrations (X = Cl, Br) should be sought[33,34,118] within the range 300–400 cm^{-1}.

Several calculations have been made by various workers: for example, Simanouti[124] determined k_{Si-X} for molecules of the type SiX_4 (X = F, Cl, Br)¶. Shimizu and Murata

¶ In this section we shall not discuss the tetrahalides (for which see Ref. 26).

TABLE 15. Si–X stretching vibration frequencies.

Si–X compound	ν, cm^{-1}	Ref.	SiX_2 compound	ν_s	ν_{as}	Ref.	SiX_3 compound	ν_s	ν_{as}	Ref.
H_3SiF	874	22	—	—	—	—	—	—	—	—
D_3SiF	885	22	—	—	—	—	—	—	—	—
$(CH_3)_3SiF$	912	110	$(CH_3)_2SiF_2$	818	899	114	—	—	—	—
$(C_6H_5)_3SiF$	852	111	$(C_6H_5)_2SiF_2$	681	918	111	$(C_6H_5)SiF_3$ (soln.)	862	970	114
H_3SiCl	551	18	H_2SiCl_2	531	592	115	$HSiCl_3$	493	589	29
$(CH_3)_3SiCl$ (gas)	487	104	—	—	—	—	$DSiCl_3$	489	555	48
$(CH_3)_3SiCl$ (liq.)	467	102	$(CH_3)_2SiCl_2$	469	538	29	CH_3SiCl_3	450	572	29
$(C_2H_5)_3SiCl$	464	106	$(C_2H_5)_2SiCl_2$	458	?	105	$C_2H_5SiCl_3$	447	580	105
							n-$C_3H_7SiCl_3$	448	588	108
$(CH_3)_2$n-C_4H_9SiCl	481	29	$(CH_3)C_2H_5SiCl_2$	467	540	29	iso-$C_3H_7SiCl_3$	458	586	29
$(C_2H_5)_2$n-C_3H_7SiCl	484	29	—	—	—	—	n-$C_4H_9SiCl_3$	448	588	108
$(CH_3)_2(CH_2{=}CH)SiCl$	477	86	$CH_3(CH_2{=}CH)SiCl_2$	462	562	86	$CH_2{=}CHSiCl_3$	453	599	86
$(CH_3)_2(CH_2{=}CH{-}CH_2)SiCl$	476	86	$CH_3(CH_2{=}CH{-}CH_2)SiCl_2$	470	548	86	$CH_2{=}CH{-}CH_2SiCl_3$	455	590	86
$(C_6H_5)_3SiCl$ (soln.)	550	111	$(C_6H_5)_2SiCl_2$	472	553	104	$C_6H_5SiCl_3$ (soln.)	518	593	111
H_3SiBr	430	18	H_2SiBr_2	393	456	115	$HSiBr_3$	360	468	26
$(CH_3)_3SiBr$	374	112	$(CH_3)_2SiBr_2$	355	426	112	CH_3SiBr_3	314	453	112
H_3SiI	355	20								
D_3SiI	351	113								
$(CH_3)_3SiI$	331	116								

TABLE 16. Frequencies of Ge–X stretching vibrations.

GeX		Ref.	GeX_2			Ref.	GeX_3			Ref.
compound	ν, cm^{-1}		compound	ν_s	ν_{as}		compound	ν_s	ν_{as}	
H_3GeCl	423	19	$BrHGeCl_2$	350	432	32	$HGeCl_3$	409	438	32
$(CH_3)_3GeCl$	360–70	117	$(CH_3)_2GeCl_2$	385	428	51	$(CH_3)GeCl_3$	393	427	51
Br_3HGeCl	419	32	$(C_2H_5)_2GeCl_2$	380	420	51	$(C_2H_5)GeCl_3$	397	423	51
Cl_2HGeBr	309	32	$ClHGeBr_2$	290	320	32	$HGeBr_3$	235	325	32
—	—	—	$(CH_3)_2GeBr_2$	272	297	117	CH_3GeBr_3	263	314	117

have made calculations on CH_3SiCl_3,[125] $(CH_3)_2SiCl_2$,[126] and $(CH_3)_3SiCl$.[127] Goubeau *et al.*[122] determined the force constants of Si–Cl bonds for the series $(CH_3)_nSiCl_{4-n}$ (n = = 0–4). Kovalev's calculation[128] is also concerned with this series of compounds. Table 17 gives values of the force constants of Si–Cl bonds in methylchlorosilanes taken from various sources.

Force constants of Si–X bonds for the series $(CH_3)_nSiF_{4-n}$ and $(CH_3)_nSiBr_{4-n}$ are given by Murata[129] and also in Ref. 48. The values of k_{Si-X} are approximately, in 10^5 dyn cm^{-1}, 5.8–6.4 for Si–F, 2.5–3.2 for Si–Cl, and 2.0–2.5 for Si–Br (according to the results of different workers for various compounds).

A series of papers recently published by Kovalev[130-134] gives a fairly detailed numerical analysis of the vibrational spectra of methylchlorosilanes and methylbromosilanes of the structure $(CH_3)_nSiX_{4-n}$ (X = Cl, Br; n = 1–4).

The infrared absorption spectra and the Raman spectra of the complete series of methylchlorostannanes $(CH_3)_nSnCl_{4-n}$ (n = 0–4) have been examined by Edgell and Ward[135], from whose work it follows that for $(CH_3)_3SnCl$ the stretching vibration frequency is ν_{Sn-Cl} = 318 cm^{-1}, for $(CH_3)_2SnCl_2$ $\nu_{s\ and\ as(Sn-Cl)}$ = 344 cm^{-1}, and for CH_3SnCl_3 $\nu_{s\ and\ as(Sn-Cl)}$ = = 363 cm^{-1}.

Among alkylchlorosilanes and alkylchlorogermanes which have the greatest practical application, alkenylalkylchlorosilanes containing one Si–Cl bond usually have infrared absorption bands and Raman lines lying within the range 465–485 cm^{-1}, which can be detected fairly easily. Compounds containing two Si–Cl bonds ($SiCl_2$ groups) are characterised by two fairly intense absorption bands, ν_s in the range 460–470 cm^{-1} and ν_{as} in the range 540–565 cm^{-1}. Compounds containing $SiCl_3$ groups also have two absorption bands due to Si–Cl stretching vibrations, ν_s in the range 445–460 cm^{-1} and ν_{as} at 580–600 cm^{-1}. The difference in the infrared absorption bands of $SiCl_2$ and $SiCl_3$ groups is quite appreciable. This difference is evident primarily in the value of $\Delta\nu = \nu_{as} - \nu_s$, which is greater for $SiCl_3$ than for $SiCl_2$, 140 cm^{-1} compared with 80 – 100 cm^{-1}. Moreover, in the Raman spectra $\nu_{as(Si-Cl)}$ is somewhat more clearly developed with $SiCl_3$ than with $SiCl_2$. In the case of compounds containing $GeCl_2$ groups $\nu_{s(Ge-Cl)}$ = 380 cm^{-1} and $\nu_{as(Ge-Cl)}$ = 420–430 cm^{-1}, while for compounds containing $GeCl_3$ groups $\nu_{s(Ge-Cl)}$ = = 390 cm^{-1} and above, and $\nu_{as(Ge-Cl)}$ = 420–430 cm^{-1} (nearer to 430 cm^{-1}). In the Raman spectra ν_{as} is also more clearly developed with $GeCl_3$ than with $GeCl_2$ groups.

TABLE 17.

Compound	$10^{-5}k_{Si-Cl}$, dyn cm^{-1}		
	Ref. 116	Refs. 125–127	Ref. 128
$(CH_3)_3SiCl$	2.4	2.59	2.54
$(CH_3)_2SiCl_2$	3.7	2.59	2.69
CH_3SiCl_3	3.8	2.59	2.87

TABLE 18. Lengths of E–X bonds, Å.

Compound	r_{E-X}, Å (X = F, Cl)	References
H_3SiF	1.593±0.002	136
H_3SiCl	2.050±0.001	136
D_3SiCl	2.0486	136
$(CH_3)_3SiCl$	2.03	137
$HSiCl_3$	2.021±0.002	137
CH_3SiCl_3	2.021	137
$HGeCl_3$	2.1139±0.0010	138

The variation in the E–X vibration frequencies for molecules of the types EH_3X and EH_2X_2 is quite well seen from Figs. 3 and 4. For molecules of type EHX_3 this dependence is shown in Fig. 6 (the forms of the vibrations for molecules of symmetry C_{3v} are given in Fig. 3).

Table 18 lists the lengths of Si–X and Ge–X bonds in several molecules, these data having been taken from papers on microwave spectra[136-138].

VII. THE E–O BOND (E = Si, Ge)

A large proportion of papers on compounds containing E–O bonds are devoted to disiloxanes and alkoxysilanes, both monomers and polymers. Among the early investigations reference must be made to the work of Wright and Hunter[72] and Young *et al.*[73] The former workers noted that in the methylpolysiloxanes the Si–O stretching vibration frequencies lie in the neighbourhood of 1052 cm^{-1}.

In disubstituted cyclic siloxanes of the type

$$[-Si(Alk)_2-O-]_n,$$

ν_{Si-O} = 1020 cm^{-1} in the case of trimers (n = 3), the value for tetramers being 1081 cm^{-1}. The infrared absorption spectra of several alkylsiloxanes have been examined by McMahon[95], who gives the frequency $\nu_{Si-O-Si}$ = 1075 cm^{-1} for the Si–O–Si grouping. Lord *et al.*[139] investigated the vibrational spectra and the structure of disiloxane (I) and hexadeuterodisiloxane (II), and found that $\nu_{Si-O-Si}$ lie near 606 and 1107 cm^{-1} in the case of (I), and at 555 and 1094 cm^{-1} in the case of (II). They conclude that the SiOSi angle is either equal or close to 180°. McKean, however, considers[140] that this angle lies between 135° and 155°. It has been estimated[141] as 155°. Electron diffraction examination of the structure of $(CH_3)_3SiOSi(CH_3)_3$ suggests[142] that the SiOSi angle is 130° ± 10°.

A considerable number of papers on this question are due to Kriegsmann, who investigated the vibrational spectra of cyclic siloxanes[143] of the type $[(CH_3)_2SiO]_n$ ($n = 4-6$) and compounds of the type $(CH_3)_3SiXSi(CH_3)_3$ (X = O, NH, CH_2, S)[144]. Kriegsmann and Licht[145] examined alkoxy--compounds of the types $Si(OAlk)_4$ and $Ti(OAlk)_4$, where Alk = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9. Compounds of the structure $(CH_3)_2XSiOSiX(CH_3)_2$ (X = OH, Cl, C_6H_5) have been investigated[146]. Data are available[147] on the infrared absorption spectra and Raman spectra of $[(CH_3)_3SiO]_3$ and $[(CH_3)_3SiNH]_3$. It follows from the above work of Kriegsmann that in different compounds $\nu_{s(SiOSi)}$ lies within the range 500–550 cm^{-1}, and $\nu_{as(SiOSi)}$ in the region of 1070–1080 cm^{-1}.

The same result follows from the work of Kirei and Lisitsa[148] on the infrared absorption spectrum of hexaethyldisiloxane, and also that of Lazarev *et al.*[149] The general conclusion from work on organosilicon compounds containing an Si–O bond is that $\nu_{s(SiOSi)}$ = 500–550 cm^{-1}, $\nu_{as(SiOSi)}$ = 1060–1080 cm^{-1} (the frequencies being rather lower for cyclic polysiloxanes), δ_{SiOSi} = 250 cm^{-1}, and $\angle$ SiOSi $\neq$ 180°.

Goubeau and Hiersemann[154] examined the Raman spectra of

$(CH_3)_3SiSH$, Cl_3SiSH, $(CH_3)_3SiSSi(CH_3)_3$,
$Cl_3SiSSiCl_3$, $(CH_3)_2SiS_2Si(CH_3)_2$, and $Cl_2SiS_2SiCl_2$.

Kriegsmann and Clauss[155] investigated $[(CH_3)_2SiS]_2$ and $[(CH_3)_2SiS]_3$. Disilyl sulphide and bistrideuterosilyl sulphide have been investigated by Linton and Nixon[156]. From these papers it follows that $\nu_{s(SiSSi)} \simeq 400-450$ cm^{-1}, $\nu_{as(SiSSi)} = 480-520$ cm^{-1}, $\delta_{Si-S} \simeq 175$ cm^{-1}, and the angle SiSSi is close to 100°. The silicon cyanates $(CH_3)_nSi(NCO)_{4-n}$, where $n = 0-4$, have been investigated by Goubeau *et al.*[157] Simon and Arnold[158] investigated $(CH_3)_3SiOOSi(CH_3)_3$ and $(C_2H_5)_3SiOOSi(C_2H_5)_3$. Table 19 compares the Si–O vibration frequencies[158] for $(CH_3)_3SiOSi(CH_3)_3$ and $(CH_3)_3SiOOSi(CH_3)_3$.

Extremely interesting data on the angles and force constants of the Si–X bonds in SiXSi groups (X = O, NH, CH_2, S) have been obtained by Kriegsmann[144] (see Table 20).

Among the work on germanium derivatives mention must be made of that of Johnson and Fritz[159], who investigated the infrared absorption spectra of several alkoxygermanes $Ge(OAlk)_4$ (Alk = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}) as well as tetracyclohexyloxygermane. These compounds are characterised by strong absorption bands at 1040 and 680 cm^{-1}, which are attributed to the group



In compounds containing Si–O–C groupings (for example tetraethoxysilane) $\nu_{(Si-O-C)}$ = 1090–1100 cm^{-1}.[29] The

TABLE 19.

Compound	$\nu_{s(Si-O)}$, cm^{-1}	$\nu_{as(Si-O)}$, cm^{-1}	$\nu_{s(SiC_3)}$, cm^{-1}
$(CH_3)_3SiOSi(CH_3)_3$	522	1055	660
$(CH_3)_3SiOOSi(CH_3)_3$	768	1254	614

TABLE 20. Force constants and angles[144] of Si–X–Si groupings (X = O, NH, CH_2, S).

Compound	$10^{-5}k$, dyn cm^{-1}	$\angle$SiXSi
$(CH_3)_3SiOSi(CH_3)_3$	4.65	150°
$(CH_3)_3SiNHSi(CH_3)_3$	3.84	131°
$(CH_3)_3SiCH_2Si(CH_3)_3$	2.77	120°
$(CH_3)_3SiSSi(CH_3)_3$	2.20	104°

frequency 1040 cm^{-1} can most probably also be assigned to the grouping Ge–O–C in the formula denoted by the asterisk. For example, in the case of $(C_6H_5)_3GeOGe(C_6H_5)_3$,[51] $\nu_{Ge-O-Ge}$ = 855 cm^{-1}.

Thus it can be seen that the infrared absorption spectra of the siloxanes contain intense bands in the range 1020–1100 cm^{-1}, which a great many facts show to be due to antisymmetric (ν_{as}) Si–O–Si vibrations. The $\nu_{Si-O-Si}$ frequency is lowest in the case of trimeric cyclic siloxanes, when its value is close to 1020 cm^{-1}. In all other cases — cyclic siloxanes containing more than three Si–O–Si units, and also linear siloxanes and polysiloxanes — this frequency is close to 1060–1070 cm^{-1} and is quite constant, being independent of substituents (alkyl, alkenyl, aryl) on the silicon atoms.

An extremely interesting and important fact is that a large proportion of investigators have reached the conclusion that the Si–O–Si angle is not 180°, its most probable value being 150°.

Little information is as yet available on Ge–O–Ge vibrations, and further data must be accumulated.

VIII. COMPOUNDS CONTAINING AN E–E BOND

Relatively little work has been done on compounds containing an E–E bond. Disilane[52], digermane[53], and hexamethyldisilane[152,153,160] has been investigated. Data on hexachlorodisilane are given by Morino[161], Katayama *et al.*[162], and Stitt and Yost[163]. The work by Brown *et al.*[109] on compounds of the type $(CH_3)_3E-E(CH_3)_3$ (E = Si, Ge, Sn), which has been mentioned before, merits special attention. The principal results on the E–E vibration frequencies and the force constants of E–E bonds are given in Table 21. Kovalev[54] has made a calculation on disilane, and found $k_{Si-Si} = 1.75 \times 10^5$ dyn cm^{-1}.

Of the work on organosilicon compounds which has not been mentioned in the previous sections we would like to enumerate briefly the following. Clark *et al.*[164] investigated the infrared absorption spectra of substituted arylmethylsilanes, Gelkey and Tyler[165] give data on those of 1- and 2-naphthyltrichlorosilanes. The question of hydrogen bonds in silanols has been discussed[166]. Spectroscopic characteristics of individual groups have been given[167] for the range 2–10 μ on the basis of an investigation of the infrared absorption spectra of various classes of organosilicon compounds. Curry[168] notes that $SiCH_2CH_2Si$ groups can be detected from absorption bands at 8.85 and 9.50 μ. The question of the configurations of 1,2-disilylethylenes

TABLE 21.

Compound	$\nu_{E-E'}$, cm^{-1}	$10^{-5} k_{E-E'}$, dyn cm^{-1}	$r_{E-E'}$, Å	References
$H_3Si—SiH_3$	434.5	1.7	2.32	52
$H_3Ge—GeH_3$	—	1.3	2.41	53
$(CH_3)_3Si—Si(CH_3)_3$	404	1.3	—	109
$(CH_3)_3Ge—Ge(CH_3)_3$	273	1.34	—	109
$(CH_3)_3Sn—Sn(CH_3)_3$	190	1.01	—	109

has been cleared up by Egorov *et al.*[169] According to Goubeau and Reyhing[170], $\nu_{C\equiv N}$ in $(CH_3)_3SiC\equiv N$ is 2187 cm^{-1}; these workers have also examined[171] silicon thiocyanates. Grenoble and Launer[172] have made qualitative and quantitative analyses of phenylchlorosilanes over the range covered by the CsBr prism (up to 40 μ). Egorov[173] has devoted a paper to the effect of the nature of substituents attached to the silicon atom on the frequency of the completely symmetrical Si−C stretching vibration. Rao *et al.*[174] have investigated the absorption spectra in the infrared (and also in the near ultraviolet) of polyphenyl derivatives of elements of Groups IV and Vb. The vibration frequencies of various groups in organosilicon compounds have been noted[175], and a spectroscopic examination has been made[176] of the influence of the silicon atom on multiple bonds in organosilicon compounds. Further information on the silanes can be obtained also in a review paper by Janz and Mikawa[177].

Two papers which could be included in Section III deal respectively with compounds containing multiple bonds (C≡C and C=C)[178] and compounds of the type $R_3M-C\equiv C-R$ (M = Si, Sn)[179].

Yakovleva *et al.*[180] have examined the vibrational spectra of alkenynyltin derivatives of the type $Alk_3SnC\equiv C-CH\equiv CH_2$, where Alk = CH_3, C_2H_5, particularly with regard to the vibration frequencies and intensities of the multiple bonds.

The dependence of the vibration frequencies of the Ge−C bond in the spectra of alkylgermanes on the nature of the substituents has been discussed[181], the paper resembling to some extent that noted earlier[173].

Harran *et al.*[182] have examined the question of identifying phenyl derivatives of elements in Groups IVb and Vb from the infrared absorption spectra in the range 2−35 μ.

Investigations of the vibrational−rotational spectra of compounds containing elements of the carbon subgroup are of some interest. Thus Randić[183] has examined the vibrational−rotational spectrum of CH_3SiH_3 in the gaseous state, and Ebsworth *et al.*[184] that of H_3SiNCS. From the structure of the vibrational−rotational bands, it was concluded[184] that the heavy atoms in the H_3SiNCS molecule are arranged linearly, from which it follows that the molecule has the symmetry C_{3v} and is a symmetrical top.

In conclusion, we may mention a recent paper by Kriegsmann[185], on the problem of measuring the intensities of the Si−O−Si bands in siloxanes, which contains a complete list of papers by this author on the vibrational spectra of organosilicon compounds.

Furthermore, extremely interesting and important results have been obtained by Wilson and Rhee[186] on compounds of the type GeH_3X and GeD_3X (X = F, Cl, Br, I), and also by Goldfarb and Sujushi[187], who investigated the infrared absorption spectra of $(H_3Ge)_2O$, $(H_3Ge)_2S$, $(D_3Ge)_2O$, and $(D_3Ge)_2S$. From an analysis of the rotational structure of a series of bands, the latter workers concluded that in $(H_3Ge)_2O$ the GeOGe angle is 108° ± 12°, and in $(H_3Ge)_2S$ the GeSGe angle is 112° ± 10°. A useful paper has also been published by Smith[188].

Summarising what has been said above, we must note the following points.

The E−H vibrations (E = Si, Ge, ...) are very characteristic, as shown by the constancy of their frequencies in the case of alkyl and alkenylalkyl derivatives containing the same number of E−H bonds.

Differences in the E−H vibration frequencies (E = C, Si, Ge, Sn) are to be attributed mainly to variation in the force constants of the E−H bonds; the change in mass of the elements E will make a very small contribution.

It is interesting that, whereas for SiH_4 $k_{q(Si-H)} = 4.67 \times 10^6$ cm^{-2}, it is rather higher for halogenosilanes and rather lower for alkylsilanes, the same generalisation applying to the variation in the ν_{Si-H} frequencies. This is valid also for derivatives of germane GeH_4.

The effect of the central atom (E = Si, Ge, Sn, Pb) on the various vibrations in the spectra of organosilicon, organogermanium, organotin, and organolead compounds is most specific in the frequency range below 1270 cm^{-1}. In the first place we must note how extremely characteristic are the vibration frequencies in the range 1150−1270 cm^{-1} due to E−Alk groups (E = C, Si, Ge, Sn, Pb; Alk = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9). The presence of $E-CH_3$ groups can be further confirmed by the occurrence in the infrared spectrum of bands in the range 800−850 cm^{-1}, due to rocking vibrations of the CH_3 groups. The presence of C_2H_5 groups is characterised by absorption bands at about 735−740 cm^{-1}.

The absorption bands and Raman lines due to E−C vibrations have, of course, the greatest analytical value. As has been seen (Section V), many papers have been published on molecules of the type $E(CH_3)_4$. Quite a lot of work has been done also on methyl derivatives of organosilicon compounds, less on other alkyl derivatives of silicon. In the case of organogermanium and organotin compounds considerably less research has been published on the E−C vibrations than with organosilicon compounds. Nevertheless, available data on E−C bonds enable the frequency ranges of their stretching vibrations to be quite clearly isolated: $\nu_{Si-C} \simeq 550-800$ cm^{-1}; $\nu_{Ge-C} \simeq 500-650$ cm^{-1}; $\nu_{Sn-C} \simeq 450-550$ cm^{-1}; and ν_{Pb-C} lies within 420−480 cm^{-1}. The E−C vibration frequencies are seen to fall regularly on passing from Si to Pb, this being associated with a decrease in the force constants of the E−C bonds.

The intensity of the Raman lines of the E−C stretching vibrations increases on passing from Si to Pb, which may be due to the greater polarisability of the Pb−C bond compared with Si−C, Ge−C, and Sn−C.

Published results on E−X vibrations (E = Si, Ge, Sn; X = F, Cl, Br) are most comprehensive for the chlorosilanes.

Considerably less information is available on the chlorogermanes. This can be inferred, say, from the number of mathematical papers, which are always based on the experimental vibrational spectra of the molecules. Whereas for the chlorosilanes (and also fluoro- and bromo-silanes)

quite a large number of calculations have been made on the molecular vibrations, hardly any have been made on the chlorogermanes (or organogermanium compounds in general): *i.e.* a few years ago insufficient experimental data were available.

The frequency ranges of the E–Cl stretching vibrations (E = Si, Ge, Sn) are: ν_{Si-Cl} = 450–600 cm^{-1}; ν_{Ge-Cl} = = 360–440 cm^{-1}; and ν_{Sn-Cl} = 315–370 cm^{-1}.

Quite a large number of papers have dealt with compounds containing an Si–O bond, from which it follows that no difficulty is involved in identifying compounds containing Si–O–Si and Si–O–C groupings. A very important fact is that, according to the results in most of these papers, the Si–O–Si angle in siloxanes can be accepted as ~150°.

It must be noted that most of the work has been done on organosilicon compounds, and considerably less on derivatives of germanium and tin.

The present survey by no means claims to give a completely exhaustive account of the work which has been done. No doubt several communications may have been omitted, but it seems to the reviewer that the survey may prove a real help to those who are working on organosilicon, organogermanium, and organotin compounds.

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STEREOCHEMISTRY OF THE PERHYDROINDENE SYSTEM

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I. INTRODUCTION

The development of the chemistry of steroids and the introduction of conformational analysis have given rise to interest in the stereochemistry of perhydroindene. The reviews published several years ago[1,2] examined together the properties of perhydroindene itself and more complex steroid systems. Recent advances in conformational analysis of cyclopentane have explained a number of important specific stereochemical properties of perhydroindene and have formed a basis for their quantitative estimate.

The information at present available on the stereochemistry of perhydroindene has been successfully applied in the investigation of steroid and related polycyclic systems. The bicyclic perhydroindene systems constitute a combination of cyclopentane and cyclohexane rings in which each acquires new properties due to the effect of the neighbouring ring, the changes in properties being associated exclusively with steric factors. The study of the stereochemistry of perhydroindene thus broadens our ideas about such mutual influences within a molecule. The study of the stereochemistry of perhydroindene was begun by Hückel[3] who in 1926 achieved a stereospecific synthesis of both perhydroindene-2-one stereoisomers and established that the *cis*-isomer is more energy-rich than the *trans*-isomer.

The present review deals with a wide variety of specific stereochemical properties of perhydroindene and fills the gap which has existed in this field in the Soviet literature. An attempt is made at a systematic presentation of the available literature data on the stereochemistry of perhydroindene derivatives, from the point of view of modern ideas about the conformations of ring systems.

II. STEREOCHEMISTRY OF THE RING FUSION IN THE PERHYDROINDENE SYSTEM

According to the numerous determinations[4-7] of the heats of combustion of *cis*-perhydroindene and *trans*-perhydroindene, the *cis*-isomer is richer in energy than the *trans*-isomer, although this difference is appreciably smaller than for the two isomeric decalins. The most exact measurement of ΔH gave 0.74 ± 0.5 kcal mole^{-1}.[7] When the pure isomers are heated with palladised charcoal below 193°, *trans*-perhydroindene predominates in the equilibrium mixture, whereas at an even slightly higher temperature the *cis*-isomer is predominant. The calculated enthalpy of isomerisation at 279° is -1.07 ± 0.09 kcal mole^{-1} and the entropy -2.30 e.u.[8] For the analogous process in the decalin series ΔH = -2.7 kcal mole^{-1} and ΔS = -0.55 e.u.[9] The isomerisation of *cis*-perhydroindene to *trans*-perhydroindene under the action of aluminium bromide, discovered

by Zelinskii [10], is probably associated with the higher thermodynamic stability of the *trans*-isomer.

Nevertheless it is widely known that *trans*-perhydroinden-1-ones and *trans*-perhydroinden-4-ones are readily converted into the corresponding *cis*-isomers under the action of acids, bases, high temperature, and light. Furthermore, it is known that in ring closure yielding a five-membered ring forming a 1,2-junction with a six-membered ring, *cis*--cyclisation takes place more readily than *trans*-cyclisation and the resulting *cis*-bicyclic systems are usually more stable than the corresponding *trans*-isomers. In order to resolve these contradictions, it is necessary to examine the conformations of the stereoisomeric perhydroindenes (Scheme I).

Two conformations (Ia) and (Ib) are theoretically possible for the *trans*-perhydroindene molecule, but the latter is energetically so unfavourable that it can be disregarded. In conformation (Ia) the six-membered ring is present in the chair form and the five-membered ring is in conformation C_2 ("half-chair") in which the bridging carbon atoms lie on different sides of the plane containing the $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$ atoms. With such a conformation unsubstituted *trans*-perhydroindene as a whole has a diad symmetry axis [11].

Comparison of the infrared spectra of 1-chloro- and 1-bromo-*trans*-perhydroinden-2-one and the unsubstituted *trans*-perhydroinden-2-one shows that the five-membered ring is indeed present in conformation C_2. [12] The presence of the C_2 conformation of the D ring in steroids was demonstrated from a study of the infrared spectra and the rotatory dispersion curves of the stereoisomeric 16-bromo-3β--hydroxy-5α-androstan-17-ones and 17-bromo-3β-hydroxy--5α-androstan-16-ones [13].

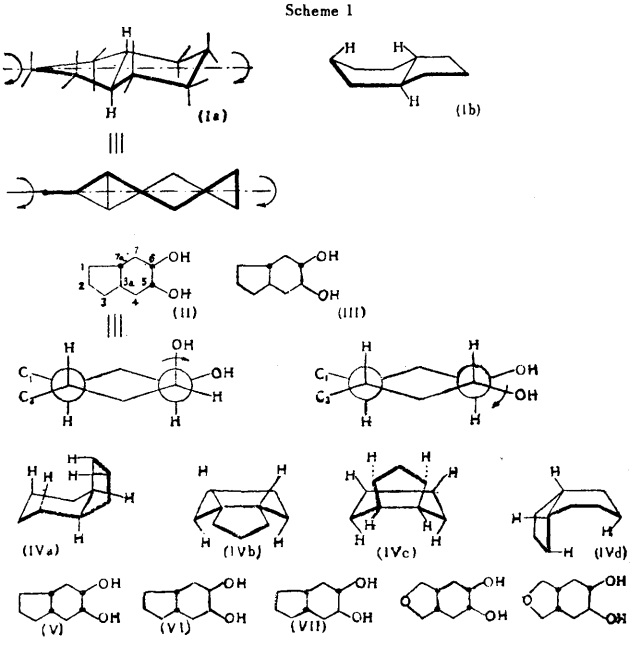
The chair conformation of the six-membered ring in the *trans*-perhydroindene system has been confirmed by the kinetic data for the oxidation of the stereoisomeric *trans*--perhydroindenediols [14]. The rate constant ratio $K^{25^\circ}_{cis}/K^{25^\circ}_{trans}$ for the two diols (II) and (III) is of the same order as for the *cis*- and *trans*-cyclohexane-1,2-diols (76 and 23 respectively). The *cis*-diol (II) is oxidised more rapidly and the *trans*-diol (III) more slowly than the corresponding cyclohexane-1,2-diols and therefore in the *trans*-perhydroindene system the projection angle between the *cis*-*ortho*--groups in the six-membered ring is less than 60°, whereas that between the equatorial *trans*-*ortho*-groups is greater than 60°. Examination of the projection formulae (Scheme I) shows that in both cases the change in the angle between the substituents is associated with repulsion of the axial groups at $C_{(5)}$ and $C_{(6)}$ from the angular hydrogen atoms. It is evident that in the *trans*-perhydroindene system the axial 1,3-substituents are closer together than in the unstrained cyclohexane or *trans*-decalin systems. Examination of the rotatory dispersion curves of *trans*-decalones and *trans*-perhydroindenones [15,16], which have similar structures, confirms the conclusion that the chair conformation of the six-membered ring in the *trans*-perhydroindene system is slightly deformed.

In the *cis*-perhydroindene molecule the six-membered ring can theoretically exist in four conformations (IVa–IVd); the number of possible conformations is even greater when substituted *cis*-perhydroindenes are considered [2]. Conformations (IVc) and (IVd) are improbable, being energetically unfavourable. The only unfavourable thermodynamic factor in conformation (IVb) is the boat form of the six-membered ring (here the five-membered ring is made up of equatorial bonds lying in the plane of the sides of the "boat"). Finally, in the chair conformation (IVa) there are three energetically unfavourable 1,3-diaxial interactions between the methylene groups. Thus both conformations (IVa) and (IVb) are probable for the *cis*-perhydroindene molecule.

The proof of the chair conformation of the six-membered ring in the *cis*-perhydroindene system was obtained in the same way as in the case of *trans*-perhydroindene (Scheme I). The rate constant ratio for the oxidation of the *cis*-*cis*--diols (V) and (VI) and the *cis*-*trans*-diol (VII) by lead tetraacetate is of the same order as for the two isomeric cyclohexane-1,2-diols. [17]. The absolute rate of oxidation of all the three diols (V–VII) is higher and the energy of activation lower than for both cyclohexane-1,2-diols. Hence it was concluded that in the *cis*-perhydroindene system the six-membered ring exists in the "flattened" chair conformation in which the distance between the axial 1,3-substituents is greater than in cyclohexane. The flattening of the chair conformation of the six-membered ring and the weakening of the 1,3-diaxial interaction in the *cis*-2-oxaperhydroindene system have been clearly demonstrated by Eliel and Pilar [18].

The chair conformation of the six-membered rings in the *cis*-perhydroindene system was also confirmed by an examination of the rotatory dispersion curves for certain *cis*-perhydroindenones [16,19] obtained in an investigation of the bromination kinetics of *cis*-perhydroinden-5-one, [20] and by the results of the study of the deamination of the epimeric 4- and 5-amino-*cis*-perhydroindenes and the saponification of the esters of the epimeric *cis*-4- and *cis*-5--decalols [21]. The greater distance between the axial substituents and the weakening of the 1,3-diaxial interaction in

Scheme 1



such a "flattened" six-membered ring behave as favourable thermodynamic factors, partly compensating the interaction between non-bonded methylene links in *cis*-perhydroindene.

Introduction of an angular methyl group in the perhydroindene framework alters the order of stability: the *cis*--isomer becomes somewhat more stable than the *trans*--isomer. This finding may be explained by the fact that although formally the number of interactions between non--bonded methylene links in 3a-methyl-*trans*-perhydroindene (VIII) is smaller than in the *cis*-isomer, which can exist in two conformations (IXa) and (IXb), the severity of these interactions will increase when the rings are joined in the *trans*-position and will decrease when they are joined in the *cis*-position, in consequence of the specific properties of the six-membered ring (described above) in the perhydroindene system.

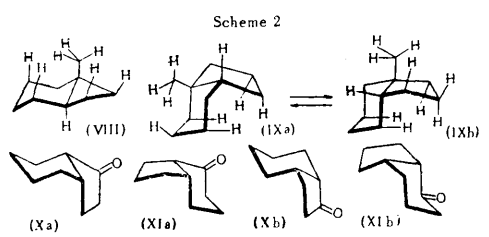
The oxime of 3a-methyl-*trans*-perhydroinden-1-one, which cannot be converted into the *cis*-isomer by an enolisation mechanism, is in fact converted into the *cis*-isomer in the presence of palladised charcoal[22]. The formation under the action of radiation of lumisteroids with rings C and D joined in the *cis*-position is also known[23].

Like *cis*-decalin, *cis*-perhydroindene can be converted from one conformation to another[24], probably *via* the boat conformation of the six-membered ring[3]. The results of the alkaline hydrolysis and epimerisation of the dimethyl esters of *cis-syn-cis*- and *cis-anti-cis*-perhydroindene--4,5-dicarboxylic acids confirm this conclusion[25]. The most favourable conformation for 3a-methyl-*cis*-perhydroindene is (IXb), where the methyl group is oriented equatorially in relation to the six-membered ring (Scheme 2). Investigation of the rotatory dispersion of 3a-methyl-*cis*--perhydroinden-6-one[16] confirms this conclusion.

The question of the relative stability of *cis*- and *trans*--perhydroindenones, with the oxo-group next to the angular hydrogen atom, which is thus capable of enolisation, is of interest. As a rule the *cis*-form is the more stable, *trans*-perhydroinden-1-ones and *trans*-perhydroinden-4--ones being converted into the *cis*-analogues by acids and bases, heat, ultraviolet irradiation, and sometimes spontaneously. This distinguishes the perhydroinden-1-ones from 1-decalones, whose *trans*-isomers are the more stable.

The stability of *cis*-perhydroinden-1-ones can be explained by the following two causes: (1) the preferential *cis*-ring junction due to thermodynamic factors[8]; (2) the 2-alkylketone and 3-alkylketone effects[3]. The first of these causes will be examined in the following section of the review and here we shall consider only the alkylketone effects.

Scheme 2



The angle between the equatorial methyl group and the carbonyl group in the 2-methylcyclohexanone molecule is only 15° and therefore their mutual repulsion is very powerful. With axial orientation of the methyl group in 2-methylcyclohexanone the angle between this group and the carbonyl group is 105° and there is no non-bonding interaction between them. According to Klyne's calculations[26], the elimination of interaction between the methyl and carbonyl groups reduces the energy of the molecule by 1 kcal mole^{-1} and as it were compensates for the energy of the diaxial 1,3-interaction between the methyl group and the methylene links in the ring. The interaction between the equatorial alkyl group and the carbonyl oxygen constitutes the 2-alkylketone destabilising effect.

In the axial conformation of 3-methylcyclohexane there is only one 1,3-diaxial interaction between the methyl group and the methylene link, since the carbonyl group in the other *meta*-position does not interact with the methyl group. Therefore 3-methylcyclohexanone is more stable than methylcyclohexane to the extent of one 1,3-diaxial methyl--methylene interaction (about 0.9 kcal mole^{-1}). Such relative stabilisation is called the 3-alkylketone stabilising effect.

A quantitative estimate of the 2-alkyl- and 3-alkyl--ketone effects for perhydroindenones containing the oxo--group in the five-membered ring is difficult at present. By a semiempirical procedure it has been estimated as 0.4 kcal mole^{-1}.[26] However the concept of these effects is extremely useful for a qualitative estimate of the stability of stereoisomeric perhydroindenones[3].

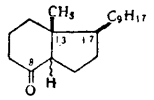
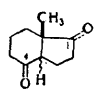
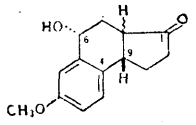
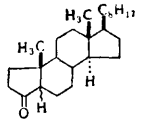
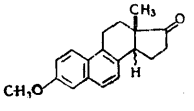
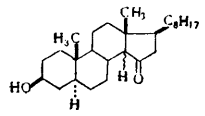
Although only one conformation is possible for *trans*--perhydroinden-1-one, *cis*-perhydroinden-1-ones can exist in two conformations, differing in the nature of the bond joining the carbonyl group with the bridging carbon atom (see Scheme 2). The latter can be either equatorial [*eq*-conformations (Xa) and (XIa)] or axial (*ax*-conformations (Xb) and (XIb)].

The importance of both alkylketone effects in the perhydroinden-1-one series is greater the lower the energy barrier between the *cis*- and *trans*-perhydroindene systems. The data in Table 1 demonstrate the validity of the alkylketone effects as criteria of the stability of the isomeric perhydroindenones.

Apart from the influence of the thermodynamic factor and the alkylketone effects, the equilibrium between the *cis*- and *trans*-forms of the more complex perhydroinden--1-ones greatly depends on fine steric effects acting over short, medium, and long distances[26,40-42]. The question of the stability of the *trans*-junction between the C and D rings in certain 15-oxosteroids is of interest. The evidence quoted by Barton and coworkers[39] in favour of the greater stability of the *trans*-ring fusion in such systems is consistent with the predictions based on an estimate of the alkylketone effects. However, many other 15-oxosteroids exist almost entirely as the *cis*-isomers in alkaline or acid media[26,43,45]. Conformational transmission has no effect on the equilibrium between steroid perhydroindenes[46].

Recently the unusual conversion of *cis*-Δ^5-hexahydroinden-1-one into *trans*-Δ^5-hexahydroindene has been observed in the Wolff–Kischner reduction[47], indicating the intermediate formation of *trans*-Δ^5-hexahydroinden-1-one

TABLE 1.

Perhydroindenone		Ketone effect: 2-alkyl	Ketone effect: 3-alkyl	Stable isomer: theoretical	Stable isomer: experimental	References
Perhydroinden-1-one						
trans-		O—C_1—C_8—C_7	—	*cis-eq*	*cis*	5, 27
cis-eq		—	—			
cis-ax		O—C_1—C_8—C_7	—			
Perhydroinden-4-one	*trans*-	O—C_4—C_9—C_3				27–31
	cis-eq	O—C_4—C_9—C_3				
	cis-ax	—	—	*cis-ax*	*cis*	
8-Methylperhydroinden-1-one						
trans-		O—C_1—C_8—C_7	—			
cis-eq		O—C_1—C_8—CH_3	—		*cis*	22
cis-ax		O—C_1—C_8—C_7				
Degradation product of vitamin D						32–34
	*trans*-	O—C_8—C_{14}—C_{15}	O—C_8/C_{13}—CH_3			
	cis-eq	O—C_8—$C_{14}C_{15}$	O—C_8/C_{13}—C_{17}		*cis*	
	cis-ax		O—C_8/C_{13}—CH_3	*cis-ax*		
	*trans*-	O—C_1—C_8—C_7	O—C_4/C_8—CH_3			
	cis-eq (C_8-C_1)	O—C_4—C_9—C_3				
		O—C_1—C_8—CH_3	O—C_4/C_8—CH_3	*cis-eq*	*cis*	
	cis-ax (C_8-C_1)	—	—			35, 36
		O—C_1—C_8—C_7				
		O—C_4—C_9—C_3				
	*trans*-	O—C_1—C_8—C_7	—			37
	cis-eq	—	—	*cis-eq*	*cis*	
	cis-ax	O—C_1—C_8—C_7	—			
	*trans*-	O—C_2—C_3—C_5	O—C_3/C_{10}—CH_3		*cis*	38
	cis-ax	O—C_2—C_3—C_9	O—C_3/C_{10}—C_9			
	*trans*-	O—C_{17}—C_{13}—C_{12}	—		*cis* (luminiequilenin or isoequilenin)	22, 23
	cis-eq	O—C_{17}—C_{13}—C_{12}	—			
	cis-ax	O—C_{17}—C_{13}—CH_3				
	*trans*-	O—C_{15}—C_{14}—C_9	O—C_{15}/C_{15}—CH_3	*trans*	*trans*	39
	cis-	O—C_{15}—C_{14}—C_9	—			

under alkaline conditions. In view of this finding it is necessary to treat with caution the alkylketone effects as stability criteria.

III. EFFECT OF THE THERMODYNAMIC FACTOR ON THE RELATIVE STABILITIES OF THE *cis*- AND *trans*--ISOMERS

From the point of view of the second law of thermodynamics, the fact that although *cis*-perhydroindene systems have higher heats of combustion *cis*-perhydroindene-1-ones are nevertheless the more stable[48] is not paradoxical. Since the free energy of a process is given by

$$\Delta F = \Delta H - T\Delta S,$$

it is not permissible to identify the difference in heat content with the free energy change determining the mode of isomerisation. In those systems where the role of the entropy factor is small (for example, in decalin) ΔF may be regarded as approximately equal to ΔH. If, however, the entropy factors of two isomers differ significantly from each other, the second term in the equation cannot be disregarded. In particular if the entropy of the *cis*-perhydroindene system is higher than that of the *trans*-perhydroindene system, the free energy of isomerisation at high temperatures will favour the formation of the *cis*-isomer although the latter has the higher heat content.

Thermochemical investigation of the equilibrium between *cis*- and *trans*-perhydroindene[8] confirms this hypothesis. The low value of ΔH (about -1 kcal mole^{-1}) is explained by the appreciable strain in *trans*-perhydroindene, unlike its homologue *trans*-decalin. The low value of the energy difference between *cis*- and *trans*-perhydroindenes is satisfactorily consistent with the fact that in the *trans*-perhydroindene system 1,3-diaxial interaction is more intense and in the *cis*-perhydroindene system less intense than in the unstrained chair conformation of the 6-membered ring.

The value $\Delta S = -2.3 \pm 0.1$ e.u. is of particular significance for the perhydroindene system. if the entropy is regarded as a function of the order of symmetry of the molecule (which ideally is two for *trans*-perhydroindene and one for *cis*-perhydroindene), the maximum value of ΔS can be only 1.4 e.u. The high value of the observed ΔS implies that in the *trans*-isomer the five-membered ring is more stretched and flattened than in the *cis*-isomer. Therefore *cis*-perhydroindene should show a greater capacity for pseudorotation of the five-membered ring. The presence of such an additional degree of freedom appears to be in fact responsible for the high entropy of the *cis*-isomer.

Allinger *et al.*[26] proposed an interesting empirical method for the calculation of the energy content of perhydroindene derivatives differing only in the type of ring junction. The properties of substituted perhydroindenes may be predicted provided that the properties of the corresponding pair of decalins and the "perturbation constant" (difference between the values of ΔF for the isomerisation of decalin and perhydroindene), which includes an entropy factor, are known. This method of calculation of the energy barrier between the *trans*- and *cis*-forms of perhydroindene, based on the "perturbation constant" (about 2.3 kcal mole^{-1}), gave satisfactory results for five pairs of steroid perhydroindenones. It must, however, be mentioned that in the calculation of the energy content of the isomers the 2-alkylketone effect for perhydroindenones was arbitrarily estimated as 0.4 kcal mole^{-1}.

There are many examples supporting the view that five-membered ring closure reactions of 1,2-disubstituted cyclohexanes and the analogous pyranoside systems occur readily with the *cis*-isomers but not with the *trans*-isomers. This also applies to reactions which while not forming cyclic products nevertheless take place *via* a transition state with a five-membered ring. Thus lead tetraacetate oxidises *cis*-cyclohexane-1,2-diol 22 times faster than the corresponding *trans*-isomer. This is because the five-membered transition complex forms more readily in the case of the *cis*-isomer[49]. The same phenomenon is observed in the oxidation of these diols by periodic acid[50]. Examination of the hydrogen-bond bands in the infrared spectra of stereoisomeric cyclohexane-1,2-diols[51] shows that the stability of the hydrogen bonded five-membered ring is greater with the *cis*-diol than with the *trans*-diol. Electron diffraction study of these diols[52] leads to the same finding.

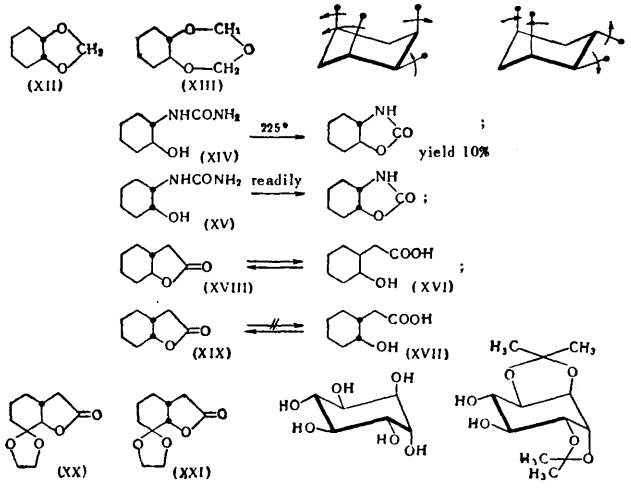
Reactions of the stereoisomeric cyclohexane-1,2-diols with carbonyl compounds are good examples of the preferential *cis*-cyclisation. Reaction of formaldehyde with the *cis*-diol yields *cis*-hexahydrobenzo-1,3-dioxolane (XII) in 74% yield, whereas the *trans*-diol is converted under analogous conditions into compound (XIII) in only 19% yield[53]. Mousseron *et al.*[54] noted differences in the ease of formation of cyclic sulphites from the isomeric cyclohexane-1,2-diols. They also showed that there are differences in the ease of cyclisation of the epimeric 2-hydroxycyclohexylureas (XIV) and (XV) into hexahydrobenzoxazole derivatives[55]. Investigation of the acyl rearrangement of the stereoisomeric *cis*- and *trans*-2-benzamidocyclohexanols, involving a five-membered transition complex, showed that the *cis*-isomer undergoes this reaction much more readily than does the *trans*-isomer[56].

Whereas *trans*-1-hydroxycyclohexane-2-acetic acid (XVI) is stable, its *cis*-isomer (XVII) does not exist in a free state because of spontaneous lactonisation. The *trans*-lactone (XVIII) undergoes ring-opening on hydrolysis, whereas the *cis*-lactone (XIX) resists hydrolysis[57]. Similar relations are observed in the hydrolysis of the γ-lactones (XX) and (XXI) where the hydroxy-acid corresponding to the *cis*-lactone (XXI) cannot be isolated from the alkaline solution due to relactonisation[58].

Angyal and Macdonald made an interesting study of the formation of the acetonides of inositol and epiinositol[59]. They showed that the acetone groups in the mono- and di-acetonides of these alcohols are combined only with the *cis*-hydroxy-groups, whereas the third acetone molecule is capable of binding also *trans*-*ortho*-groups. On the basis of this reaction, the hypothesis was put forward for the first time that *cis*-cyclisation takes place preferentially because in this process the axial *meta*-substitutents move away from one another and there is a decrease in 1,3-diaxial interactions. Conversely, in *trans*-cyclisation the axial *meta*-substituents approach one another due to "wrinkling" of the cyclohexane ring and such cyclisation is therefore unfavourable.

The above findings show that the formation under cyclisation conditions of a *cis*-junction between five- and six-membered rings is thermodynamically more favourable than the formation of a *trans*-linked system. Although this situation applies strictly only to systems where there are no appreciable repulsive forces between the links in the five-membered ring and the adjacent bridging atoms or axial hydrogen atoms in the six-membered ring [for example in dioxolane (XII)], it is reasonable to suppose that it does apply to the perhydroindene system.

Scheme 3



IV. STEREOCHEMISTRY OF PERHYDROINDENE DERIVATIVES

1. Solvolysis and Deamination

Solvolysis of esters has been throughly investigated only in the case of the *cis*-perhydroindenols. In the analysis of the results obtained account must be taken of the possibility

of a change in conformation of the *cis*-perhydroindene system. The results of the alkaline hydrolysis of hydrogen succinates and hydrogen phthalates of the isomeric *cis*-perhydroindenols[60], with corrections based on a reexamination of the configurations of the initial alcohols[24], are presented in Table 2. It is evident from a comparison of these data with the results of hydrolysis of the stereoisomeric *cis*-1-decalol and *cis*-2-decalol[60,61] that there is an analogy in the behaviour of the stereoisomeric *cis*-decalols and *cis*-perhydroindenols.

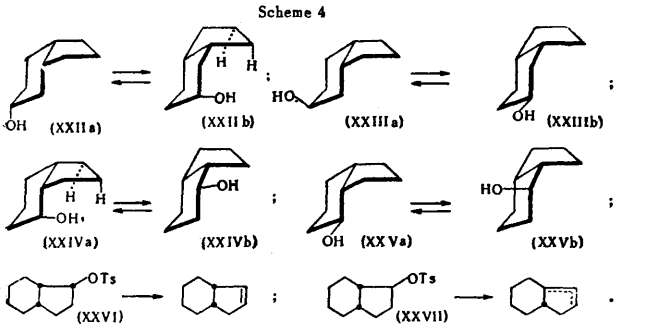
The hydrogen succinate of *cis*-*cis*-perhydroinden-5-ol (XXII) is hydrolysed appreciably more rapidly than the hydrogen succinate of the *cis*-*trans*-isomer (XXIII). This shows that the *cis*-perhydroindene system has the capacity for change in conformation similar to that observed for the *cis*-decalin system. The *cis*-*cis*-isomer exists preferentially in one (equatorial) conformation (XXIIa), whereas the energy barrier between the conformations of *cis*-*trans*-perhydroinden-5-ol (XXIIIa) and (XXIIIb) is much less. A characteristic feature is that weakening of 1,3-diaxial interactions reduces the differences in the rates of hydrolysis of the esters of *cis*-*cis*- and *cis*-*trans*-perhydroinden-5-ols compared with those of the corresponding decalols. It is reasonable to expect that *cis*-perhydroinden-4-ols will also exhibit a similar capacity for change in conformation. However, the relative behaviour of the isomers in this case is more complex. The rates of hydrolysis of the isomeric hydrogen succinates and hydrogen phthalates are similar, but among the former the hydrolysis of the *cis*-*trans*-isomer (XXV) takes place at a higher rate whereas among the latter that of the *cis*-*cis*-isomer (XXIV) is more rapid. Evidently the weakening of the 1,3-diaxial interactions in the perhydroindene system reduces in this case the energy difference between the pairs of conformers (XXVa ⇌ XXVb) and (XXVIa ⇌ XXVIb) and the slight predominance of one or other conformation in the mixture depends on the nature of the ester group.

Perhydroinden-1-yl toluene-*p*-sulphonate (XXVI) (m.p. 18°) hydrolyses so rapidly that the rate of hydrolysis cannot be measured, yielding *cis*-Δ^2-hexahydroindene. The epimeric toluene-*p*-sulphonate (XXVII) is hydrolysed at the same rate as the toluene-*p*-sulphonate of *trans*-2-methylcyclopentanol forming a mixture of olefins in more than 90% yield[62]. The exclusive formation of *cis*-Δ^2-hexahydroindene from the toluene-*p*-sulphonate (XXVI) confirms the *cis*-*cis*-configuration of the corresponding alcohol. Similar observations were made in the hydrolysis of the stereoisomeric *cis*-perhydroinden-4-ols. Here too the most stable is the toluene-*p*-sulphonate of the *cis*-*cis*-isomer in which the orientation of the toluene-*p*-sulphonyloxy-group (OTs) is favourable for scission according to Markovnikov's rule[63].

TABLE 2.

Initial alcohol	M.p., °C	Hydrolysis of hydrogen succinate, $K_{40°} \times 10^3$	Hydrolysis of hydrogen phthalate, $K_{50°} \times 10^3$
cis-cis-Perhydroinden-5-ol	43	1.172	—
cis-trans-Perhydroinden-5-ol	20	0.955	—
cis-cis-Perhydroinden-4-ol	16—31	0.5067	0.0349
cis-trans-Perhydroinden-4-ol	liq.	0.5264	0.0311
cis-cis-Perhydroinden-1-ol	liq.	0.768	0.0467
cis-trans-Perhydroinden-1-ol	18	0.943	0.0536
cis-cis-Perhydroinden-2-ol (?)	5	0.850	—
cis-trans-Perhydroinden-2-ol (?)	21	1.133	

Scheme 4

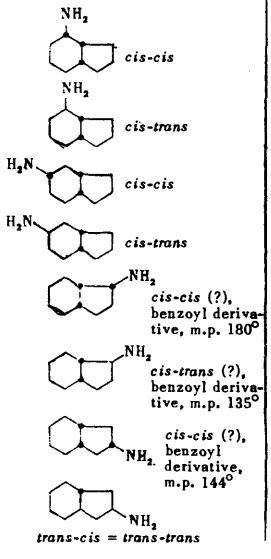
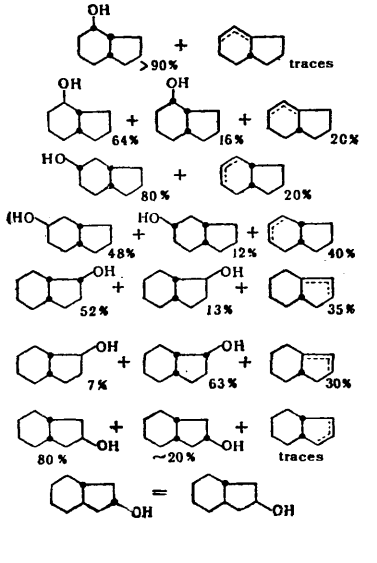


The action of nitrous acid on the amines of the *cis*-perhydroindene series was investigated by Hückel[21]. The results of deamination, allowing for corrections based on a reexamination of the configurations[24], are presented in Table 3.

Results for the deamination of 4-amino- and 5-amino-*cis*-perhydroindenes have been compared with those for the deamination of 1-amino- and 2-amino-*cis*-decalins[21,61]. An obvious analogy was found between the behaviour of aminoperhydroindenes with the amino-group in the six-membered ring and aminodecalins.

In all cases the main product of the deamination of amines with the *cis*-*cis*-configuration is the alcohol with the same configuration as the initial amine. This shows that the amino-group in these isomers behaves as an equatorial substituent, which in turn is satisfactorily consistent with the concept of the ease of conversion from one conformation to another in the *cis*-perhydroindene system, by a

TABLE 3.

Initial amine	Deamination products
	

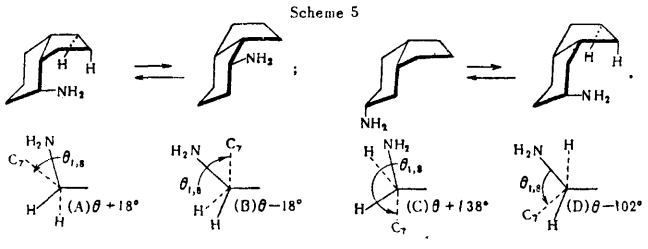
virtue of which the most bulky substituent tends to assume an equatorial orientation. However, depending on the configuration of the molecule, one of the conformers may predominate or both forms, with axial and equatorial orientation of the amino-group, may be present. In the case of the *cis*-*cis*-isomer one of the conformations predominates and the amine reacts almost entirely in this form (with the equatorial position of the amino-group) (see Scheme 5).

With *cis*-*trans*-isomers the difference in stability of the conformers is slight and therefore they behave as a mixture of equatorial and axial amines, *i.e.* their deamination yields together with the alcohol having the initial configuration an appreciable amount of the alcohol with the inverted configuration and an olefin.

In order to interpret the results of deamination of the stereoisomeric 1-amino-*cis*-perhydroindenes, it is necessary to bear in mind the following considerations[64]. If the projection formulae of 1-aminoperhydroindenes are considered from the side of their five-membered ring (see Scheme 5)†, then in the *cis*-*cis*-isomer steric compression will be the same in both conformations (A) and (B). In contrast to this, in the *cis*-*trans*-isomer smaller steric compression will be observed in conformation (C), as a result of which the substituent in the preferred conformation will possess quasi-axial character (the projection angle θ, which is 0° for the *cis*-isomer and 120° for the *trans*-isomer, can vary within ±18° in a planar model of the five-membered ring). In conformity with this finding, deamination of *cis*-*trans*-1-aminoperhydroindene yields 63% of the alcohol with the inverted configuration and 30% of olefins. In the case of the *cis*-*cis*-isomer the relative contribution of the "equatorial character" is reflected in a reduced yield of the alcohol with the inverted configuration. Thus 1-amino-*cis*-perhydroindenes react similarly to 1-amino-*cis*-decalins. The reactivity of the amino-group in 2-amino-*cis*-perhydroindenes is similar to that of aliphatic amines: deamination of the single known 2-amino-*cis*-perhydroindene results in formation only of alcohols with inverted and initial configurations.

The only amine of the *trans*-perhydroindene series investigated is 2-amino-*trans*-perhydroindene which on deamination is quantitatively converted into *trans*-perhydroinden-2-ol.[5] It appears[64] that here we have 100% inversion of configuration. The lack of data on deamination of *trans*-perhydroindene amines is partly compensated by the work of Shoppee[64,65] on deamination of norsteroid amines. It is known that reaction of nitrous acid with steroids having axial amino-groups does not yield alcohols with inverted configuration (in contrast to the amines of the cyclohexane and decalin series), only the corresponding axial alcohols and olefins being formed.

Scheme 5



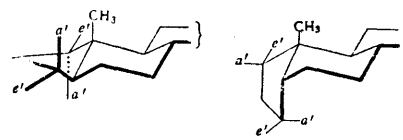
† Scheme 5 appears, however, to relate to 4- and 5-amino-perhydroindenes (Ed. of Translation).

In the presence of a fixed cyclopentane ring in the rigid norsteroid system the quasi-axial and quasi-equatorial character of the bonds at atoms adjoining bridge atoms should be very pronounced, unlike that of the bonds at the more distant fifth atom. The difference between the *cis*- and *trans*-ring fusion is now unimportant. It may be expected therefore that the quasi-axial norsteroid amines will behave like the truly axial steroid amines, *i.e.* will form either the alcohol with the same configuration or an olefin, whereas quasi-equatorial norsteroid amines will yield equatorial alcohols. In those cases where the amino-group is distant from the ring junction it will react like an aliphatic amino-group, *i.e.* will yield mainly the alcohol with the inverted configuration. The results of deamination of steroid amines confirm this hypothesis (see Table 4).

Table 4 shows that the amino-group in the rigidly fixed five-membered ring indeed exhibits more clearly its axial or equatorial properties (examples 2, 4, and 5 and to a lesser extent example 1). The amino-group distant from ring junction behaves as in aliphatic amines (example 3).

The relative stability of the epimeric alcohols or amines formed on reduction of perhydroindenones or their oximes may be estimated by determining the equilibrium position between both forms on boiling with sodium in xylene. Hückel[21] compared the results obtained in the *cis*-perhydroindene and *cis*-decalin series. The results, allowing for later corrections to the configurations[24,61], are presented in Table 5.

TABLE 4.



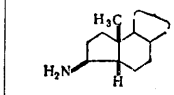
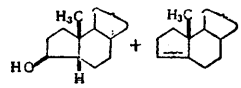
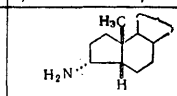
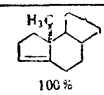
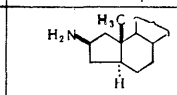
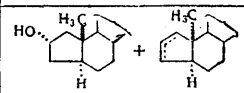
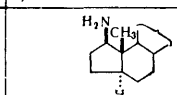
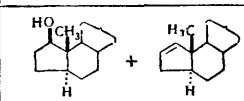
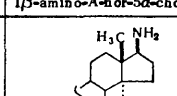
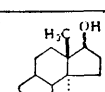
No. of example	Initial amine	Orientation of NH_2 group	Reaction products and their yield
1	 3β-amino-A-nor-5β-cholestane	e′	 40% 59%
2	 3α-amino-A-nor-5β-cholestane	a′	 100%
3	 2β-amino-A-nor-5α-cholestane	as in aliphatic amines	 93% 3%
4	 1β-amino-A-nor-5α-cholestane	e′	 80% 20%
5	 17β-amino-5α-androstane and 17β-amino-androst-6-en-3β-ol	e′	 100%

TABLE 5.

Initial ketone	Method of reduction and alcohol formed		Composition of mixture of alcohols after boiling with Na
	Na in alcohol	H_2/Pt in CH_3COOH	
cis-1-Decalone	*trans-trans*-1-decalol (epimerisation at $C_{(5a)}$)	*cis-cis*-1-decalol (~100%)	*trans-trans*-1-decalol
cis-Perhydroinden-4-one	*cis-trans*-perhydroinden-4-ol (~100%)	*cis-cis*-perhydroinden-4-ol (~100%)	*cis-trans* (80%) + + *cis-cis* (20%)
cis-Perhydroinden-1-one	*cis-cis*-perhydroinden-1-ol (~80%)	*cis-cis*-perhydroinden-1-ol (~100%)	*cis-cis* (50%) + + *cis-trans* (50%)
cis-2-Decalone	*cis-cis*-2-decalol (80%)	*cis-cis*-2-decalol (~100%)	*cis-cis* (80%) + + *cis-trans* (20%)
cis-Perhydroinden-5-one	*cis-trans*-perhydroinden-5-ol (80%)	*cis-cis*-perhydroinden-5-ol (~100%)	*cis-trans* (80%) + + *cis-cis* (20%)
cis-Perhydroinden-2-one	*cis-trans*-perhydroinden-2-ol (? 75%)	*cis-trans*-perhydroinden-2-ol (? 90%)	not established

As with perhydroinden-5-ol, in the case of perhydroinden-4-ol the most stable are the *cis-trans*-isomers (XXIII) and (XXV), where the interaction between the hydroxy--group and the methylene link is a minimum in any of the conformers, not exceeding that in cyclohexanol. However, the predominance of *cis-trans*-perhydroinden-5-ol in the equilibrium mixture has no analogy among the *cis*-2-decalols where the *cis-cis*-isomer is the most stable. This is probably due to different strengths of the 1,3-diaxial interactions in the *cis*-perhydroindene and *cis*-decalin systems.

Reduction of *trans*-perhydroinden-5-one with sodium in alcohol or with lithium aluminium hydride yields *trans--cis*-perhydroinden-5-ol with an equatorial hydroxy-group, whereas catalytic hydrogenation of this ketone results in the formation of only 25% of the *trans-trans*-isomer with an axial hydroxy-group. On heating with sodium, the latter is readily epimerised to the *trans-cis*-isomer[66].

Reduction of the oximes of the ketones yields amines whose configuration has been confirmed by means of the deamination reaction (see above). The results obtained[21] are presented in Table 6.

Tables 5 and 6 show that reduction of ketones and their oximes under similar conditions does not always give alcohols and amines with the same configuration. However, the configuration of the amines obtained under similar conditions from the oximes of *cis*-1- and *cis*-2-decalones and *cis*-perhydroinden-4-one and *cis*-perhydroinden--5-one are identical.

TABLE 6.

Initial ketone	Method of reduction of oxime and configuration of amines	
	Na in alcohol	H_2/Pt in CH_3COOH
cis-1-Decalone	*cis-trans*	*cis-cis*
cis-Perhydroinden-4-one	*cis-trans*	*cis-cis*
cis-Perhydroinden-1-one	m.p. of benzoyl derivative 135°	m.p. of benzoyl derivative 180°
cis-2-Decalone	*cis-cis*	mixture of *cis-cis* + + *cis-trans**
cis-Perhydroinden-5-one	*cis-cis*	*cis-trans*
cis-Perhydroinden-2-one	m.p. of benzoyl derivative 133°–139°	m.p. of benzoyl derivative 144°

* Yield of amine mixture 9%.

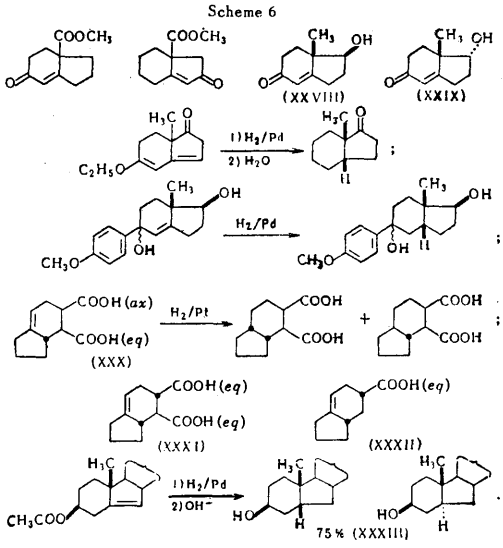
2. Catalytic Hydrogenation

Catalytic hydrogenation of systems such as $\Delta^{1(9)}$-octalin and Δ^4- and Δ^5-unsaturated steroids results mainly in isomers in which both six-membered rings are *trans*-linked. The main product of hydrogenation of 9-ethoxycarbonyl-Δ^4--3-octalone is 9-ethoxycarbonyl-*trans*-3-decalone[67]. Hydrogenation of 9-methyl-*cis*-$\Delta^{4(10),5}$-1-hexalinol and 5-ethoxy-9-methyl-$\Delta^{4(10),5}$-1-hexalinone also yields only *trans*-decalin derivatives[68]. In the catalytic hydrogenation of cholesterol in a neutral medium the yield of 5α-cholestanol exceeds 90%.[69] Similar results were obtained in the hydrogenation of numerous Δ^4- and Δ^5-steroids[70-73].

The situation is different in the case of perhydroindene compounds with the same structure. Here catalytic hydrogenation of the double bond at the ring junction results in preferential formation of the *cis*-perhydroindene system regardless of the reduction conditions. Reduction of $\Delta^{3a(4)}$-hexahydroinden-5-one over a palladium catalyst yields *cis*-perhydroinden-5-one.[74,75]. The *cis*-perhydroindene system is also formed on hydrogenation of 7a-methyl--$\Delta^{3a(4)}$-hexahydroinden-5-one [76] and 6-ethoxycarbonyl--$\Delta^{3a(4)}$-hexahydroinden-5-one[77]. It was shown recently that regardless of conditions hydrogenation of 7a-methoxycarbonyl-$\Delta^{3a(4)}$-hexahydroinden-5-one invariably yields only 7a-methoxycarbonyl-*cis*-perhydroinden-5-one. On catalytic hydrogenation of 7a-ethoxycarbonyl-$\Delta^{3(3a)}$-hexahydroinden-2-one in a neutral, acid, and alkaline medium, 7a-ethoxycarbonyl-*cis*-perhydroinden-2-one is invariably obtained[78]. Hydrogenation of the epimeric-1-hydroxy-7a--methyl-$\Delta^{3a(4)}$-hexahydroinden-5-ones (XXVIII) and (XXIX) forms only products with *cis*-linked rings whatever the mutual disposition of the methyl and hydroxy-groups[79].

Boyce and Whitehurst[80] studied the behaviour of $\Delta^{3a(4)}$--hexahydroindene-1,5-dione, 1-hydroxy-$\Delta^{3a(4)}$-hexahydroinden-5-one, $\Delta^{3a(4)}$-hexahydroindene-1,5-diol (two epimers), and certain other $\Delta^{3a(4)}$- and $\Delta^{3(3a)}$-hexahydroindenes under conditions of catalytic hydrogenation and reduction with lithium in liquid ammonia. In all cases *cis*-perhydroindene derivatives were the only reaction products (see Scheme 6).

Scheme 6



Hydrogenation of $\Delta^{3(3a)}$-hexahydroinden-3-carboxylic acid yields only *cis*-perhydroindene-1-carboxylic acid[81]. Despite the screening of the double bond by the axial carboxy-group in *cis*-*anti*-Δ^{7}-hexahydroindene-4,5-dicarboxylic acid (XXX) the principal product of hydrogenation is *cis*-*anti*-*cis*-perhydroindene-4,5-dicarboxylic acid, *i.e.* the *cis*-perhydroindene system is formed by addition of hydrogen from the sterically hindered side[25]. In those cases where the screening of the double bond is equal on either side, as for example in acids (XXXI) and (XXXII), hydrogenation results in the formation of only the *cis*-perhydroindene system[25,82].

The preferential formation of the isomer with *cis*-junction between rings A and B is also observed in the hydrogenation of B-norcholesterol acetate; the *trans*-A/B-configuration initially ascribed to the reaction product (XXXIII) was later corrected[83,84].

When an oxo-group adjoins the ring junction, it is reasonable to expect that hydrogenation of the double bond will result in the formation of *cis*-perhydroindenone under any conditions. Indeed catalytic hydrogenation of $\Delta^{3a(7a)}$-hexahydroinden-1-one and three of its higher analogues both in acid and alkaline media yields only isomers in which the rings are *cis*-linked[85].

The data discussed above show that in the reduction of systems of the type of $\Delta^{3a(4)}$- and $\Delta^{3(3a)}$-hexahydroindene addition of hydrogen can occur from the most screened side so that the main reaction product is the isomer with *cis*-linked rings. The general validity of this rule suggests that in the reduction of the above systems the entropy factor, favouring the formation of the *cis*-perhydroindene system, is decisive.

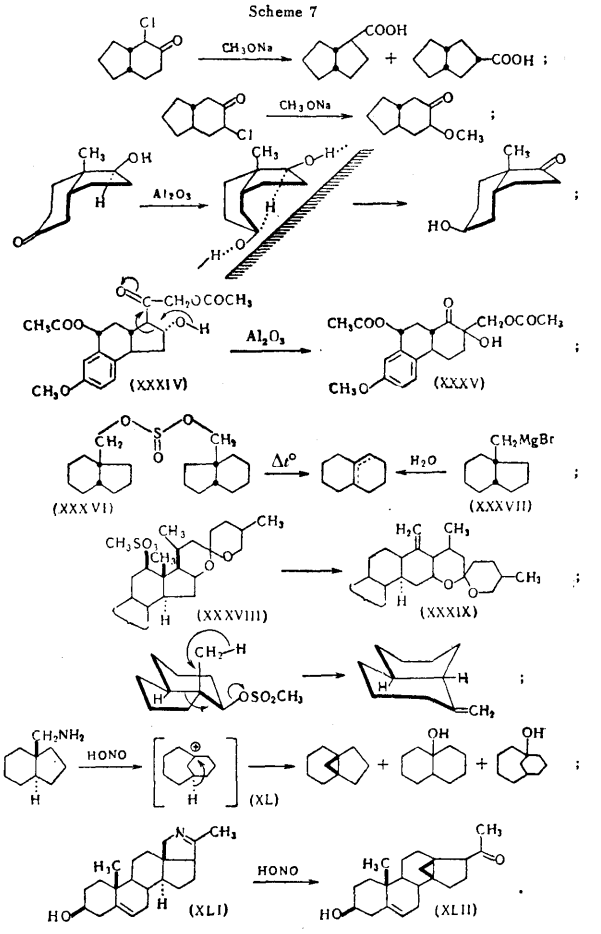
3. Rearrangement of Perhydroindene Derivatives

The influence of steric factors on the mode and nature of rearrangement of the perhydroindene system has been observed in only a few cases. Action of sodium methoxide on 4-chloro-*cis*-perhydroinden-5-one results in 78% yield of equal amounts of *cis*-*trans*-bicyclo[3,3,0]octane-2-carboxylic and *cis*-*cis*-bicyclo[3,3,0]octane-3-carboxylic acids[86]; the formation of both these products is consistent with the usual course of the Favorskii rearrangement. However, the action of sodium methoxide on 5-chloro-*trans*-perhydroinden-6-one does not result in reduction of ring size, since the *trans*-bicyclo[3,3,0]octane system would be very strained. The main reaction product is 5-methoxy-*trans*-perhydroinden-6-one.[87] 7a-Methyl-*cis*-*trans*-1-hydroxyperhydroinden-5-one (but not its *cis*-*cis*-isomer) readily undergoes, on activated alumina under mild conditions, an interesting rearrangement into 7a-methyl-*cis*-*trans*-5-hydroxyperhydroinden-1-one[79]. By virtue of the *cis*-junction between the rings the boat conformation arises on sorption, in which intramolecular and intermolecular shifts occur simultaneously (see Scheme 7); the *trans*-annular 1,5-transfer of hydrogen is in this case the same as in the cyclononane system. It is noteworthy that the isomerisation results in the formation of a system with a trigonal hydrogen atom in the five-membered ring and a tetrahedral atom in the six-membered ring. 3a-Methyl-*cis*-*trans*-1-hydroxy-6-decalone does not undergo a similar rearrangement. Another interesting rearrangement on alumina involves the expansion of the five-membered ring in compound (XXXIV) with formation of structure (XXXV).[37]

A rearrangement of the neopentyl type was observed on distillation of the sulphite (XXXVI) or in the hydrolysis of the organomagnesium compound (XXXVII); in both cases a mixture of $\Delta^{1(9)}$- and Δ^{9}-octalins was formed[88]. A very interesting rearrangement occurs during solvolysis of recogenine 12β-methylsulphonate (XXXVIII), resulting in the formation of C-nor-D-homosapogenin (XXXIX); this reaction is interesting from the point of view of the biosynthesis of certain steroid alkaloids[89]. It would be of interest to investigate the possibility of a similar rearrangement in the case of the simplest model — 8-methyl-*trans*-*trans*-perhydroinden-4-yl methylsulphonate (see Scheme 7).

The action of nitrous acid on 3a-aminomethyl-*trans*-perhydroindene results in a mixture of 74% of tricyclo[4,3,1,$0^{1,5}$]decane, 16% of 9-hydroxydecalin, and 6% of bicyclo[4,3,1]decane-1-ol instead of 7a-hydroxymethyl-*trans*-perhydroindene[90]; apparently the reaction proceeds *via* the intermediate formation of the ion (XL). This reaction also occurs in the steroid series. Thus action of nitrous acid on *N*-desmethylcona-5,*N*(20)-dien-3β-ol yields 14β,18-cycloprogesterone[90,91]. Deamination of 5-aminomethyl-*cis*-perhydroindene results in only one of the possible hydroxyazulenes. On deamination of 5-aminomethyl-6-methyl-*cis*-perhydroindene (the configurations at $C_{(5)}$ and $C_{(6)}$ are unknown), a mixture of both isomeric azulene alcohols is formed[92].

Scheme 7

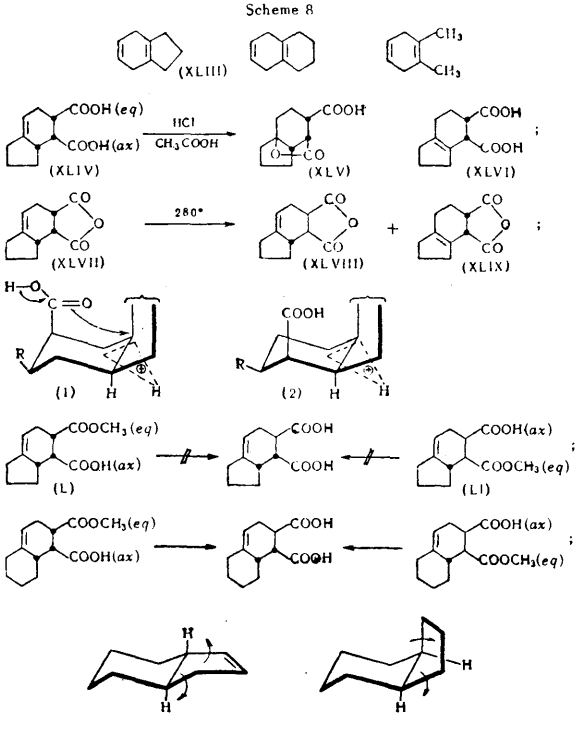


4. The Double Bond in the Perhydroindene System

The relation between the steric factors and the position and nature of the double bond in the perhydroindene system is of considerable interest. Comparison of the reactivity of cyclohexene (for which two half-chair conformations are possible) and *trans*-Δ^5-hexahydroindene (in which the six-membered ring is rigidly fixed by the five-membered ring in a single half-chair conformation) showed that the rate of epoxide formation is the same with both substances, but that hydrogenation of *trans*-Δ^5-hexahydroindene is slower[93]. There are data showing that the intercyclic $\Delta^{3a(7a)}$-double bond in the perhydroindene system is the most stable. Thus when indane is reduced with lithium in liquid ammonia the only reaction product is $\Delta^{3a(7a)5}$-tetrahydroindene (XLIII), virtually free of the possible byproduct of $\Delta^{4,7}$-tetrahydroindene[94]. Pyrolysis of the oxalate of *cis*-perhydroinden-7a-ol results in smooth formation of only $\Delta^{3a(7a)}$-hexahydroindene[95]. Earlier literature[96-98] quotes several instances in which the double bond in unsaturated perhydroindene derivatives was displaced to a "deeper" position (ultimately to the 3a,7a-position) by the action of both alkaline and acid reagents.

Lactonisation of *cis-cis*-Δ^7-hexahydroindene-4,5-dicarboxylic acid (XLIV) by hydrogen chloride in acetic acid yields γ-lactone acid (XLV) and, in addition, *cis*-$\Delta^{3a(7a)}$-hexahydroindene-4,5-dicarboxylic acid (XLVI). The orientation of the double bond in the last compound was demonstrated by a number of reactions. On heating with hydrogen chloride the γ-lactone acid (XLV) is itself slowly converted into the *cis*-carboxylic acid (XLVI), which is evidence of the stability of the latter[99]. Thermal isomerisation of the anhydride of *cis-cis*-Δ^7-hexahydroindene-4,5-dicarboxylic acid (XLVII) to the *cis-trans*-anhydride (XLVIII) is also accompanied by the formation of a very small amount of the *cis*-anhydride (XLIX) due to migration of the double bond[100].

Scheme 8



In order to account for the difference between the *cis-cis*-dicarboxylic acid (XLIV) and the analogous *cis-cis*-Δ^4-octalin-1,2-dicarboxylic acid (which is only lactonised by hydrogen chloride[101]), it was suggested that both the lactonisation and the double bond isomerisation take place *via* a common non-planar carbonium ion with a quasi-*cis*-junction between the rings (see Scheme 8). In the Δ^7-hexahydroindene series this reduces the probability of lactonisation [shift (1)] because of the increase in the distance between the axial *meta*-substituents which occurs in the *cis*-perhydroindene system. If lactonisation is excluded for steric reasons, the mode of reaction will be determined solely by shift (2), *i.e.* by the displacement of the double bond from the *exo*-position (in relation to the unsubstituted ring) to the intercyclic *endo*-position. A shift of this kind occurs more readily in the cyclopentane than in the cyclohexane system[102,103]. Therefore isomerisation involving displacement of the double bond across the ring junction is more probable in the perhydroindene than in the octalin series. Indeed, acids cause easy migration of the double bond from the Δ^7- to the $\Delta^{3a(7a)}$-position in perhydroindene[82,99,100]. It is noteworthy that the $\Delta^{3a(7a)}$-double bond in $\Delta^{3a(7a),5}$-tetrahydroindene (XLIII) is more reactive than the analogous bond in $\Delta^{2,8a}$-tetrahydronaphthalene or in 1,2-dimethylcyclohexa-1,4-diene.[104]

The influence of the Δ^7-double bond on the conformational flexibility of the monoesters of *cis-cis*-Δ^7-hexahydroindene-4,5-dicarboxylic (L) and *cis-trans*-Δ^7-hexahydroindene-4,5-dicarboxylic (LI) acids is interesting. Whereas the monoesters of the octalin series with a similar structure undergo epimerisation of the equatorial methoxycarbonyl group under the action of sodium methoxide[105], the monoesters (L) and (LI) are hydrolysed to the initial acids. This is interpreted as due to lack of conformational changes in the Δ^7-hexahydroindene series so that the equatorial methoxycarbonyl group cannot assume the axial orientation necessary for epimerisation[100]. It may be expected that as a result of the influence of the six-membered ring the strain in the cyclopentene ring in conformation C_s in the Δ^2-hexahydroindene system will be respectively somewhat greater and smaller than in cyclopentene itself when the rings are *trans*- and *cis*-linked. In the first case the $C_{(3)}$ and $C_{(7a)}$ atoms tend to come out of the plane of the double bond whereas in the second the influence of the six-membered ring favours their retention in this plane. As a result, the relative stabilisation on transition from *trans*-perhydroindene to *trans*-Δ^2-hexahydroindene is smaller and on transition from *cis*-perhydroindene to *cis*-Δ^2-hexahydroindene greater than on transition from cyclopentane to cyclopentene. Indirect support is lent to this conclusion by the low tendency of *trans*-perhydroinden-2-ol to dehydrate[5], the ease of isomerisation of *trans*-Δ^2-hexahydroindene-2-acetic acid to *trans*-2-carboxymethyleneperhydroindene[96], and the exclusive formation of *cis*-Δ^2-hexahydroindene on solvolysis of *cis-trans*-perhydroinden-1-yl toluene-*p*-sulphonate[62].

5. Other Reactions

The effect of the orientation of ring fusion on the reactivity of isomeric derivatives of perhydroindene is clearly

shown in the difference between *trans*- and *cis*-perhydroinden-2-ones. Thus the *trans*-isomer condenses with cyanoacetic ester in the presence of ammonia to yield more than 60% of the spirane (LII) whereas in the second case the yield of the analogous compound (LIII) does not exceed 5%. The same condensation in the presence of piperidine results in the formation of *trans*-2-(carboxycyanomethylene)perhydroindene (LIV) in more than 70% yield, whereas the yield of the corresponding *cis*-isomer (LV) is very low. Addition of hydrocyanic acid to the isomers (LVI) and (LV), involving the transition of the $C_{(2)}$ atom in the perhydroindene ring from the trigonal to the tetragonal configuration, takes place much more slowly in the case of the *cis*--isomer (LV). Finally, the Reformatskii reaction between perhydroinden-2-ones and ethyl bromoacetate proceeds much more readily with the *trans*-isomer than with the *cis*--isomer[104].

The relative reactivity of the isomeric *trans*- and *cis*--perhydroindene-2,2-diacetic acid towards Volhard–Zelinskii bromination is also of interest[105]. In the *trans*-isomer the two bromine atoms are equally distributed between both chains with formation of the acid (LVI), whereas in the *cis*-isomer both bromine atoms turn up in one side chain, and after hydrolysis compound (LVII) is formed.

These differences in the reactivities of *trans*- and *cis*--perhydroinden-2-ones and their derivatives can be readily explained on the basis of steric models of 2,2-disubstituted perhydroindenes (see Scheme 9). The transition of the $C_{(2)}$ atom from the trigonal to the tetrahedral configuration in the *trans*-isomer does not result in any appreciable interaction between the R_1 and R_2 substituents and the axial hydrogen atoms in the six-membered rings. However, in the *cis*-isomer such transition is inhibited because of the repulsion between the R_1 group and one of the axial hydrogen atoms in the six-membered ring. A similar effect operates when the size of R_1 is increased, as can be seen from the formation of (LVI) and (LVII), for example.

Several cases are known in which the five-membered and six-membered rings of the perhydroindene system behave independently and follow the same steric rules as those found for cyclopentanes and cyclohexanes. Thus in

Scheme 9

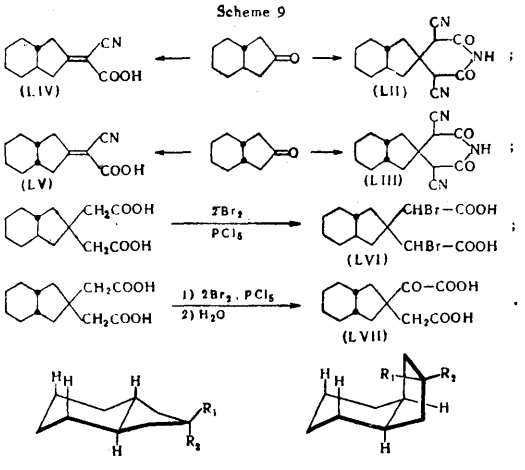
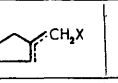
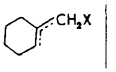
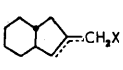
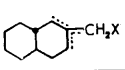


TABLE 7.

Electronegative substituent	Percentage of αβ-isomer in equilibrium mixture			
				
—COOH	14	12	90	12
$-COOC_2H_5$	60	38	98	40
$-COCH_3$	77	23	100	35

their investigation of the percentage formation of a hemiketal in alcoholic medium, Djerassi and coworkers[15] established that whereas 7a-methyl-*trans*-*cis*-5-hydroxyperhydroinden-1-one is converted into the hemiketal only to the extent of 25%, 7a-methyl-*trans*-perhydroinden-5-one yields 74% of the hemiketal. These yields are close to those found for 3-methylcyclopentanone and 3-methylacyclohexanone. The rearrangement[79] of 7a-methyl-*cis*-*trans*--1-hydroxyperhydroinden-5-one to 8-methyl-*cis*-*trans*-5--hydroxyperhydroinden-1-one takes place according to the principle that the location of a trigonal carbon atom in the five-membered ring is more favourable than in the six--membered ring. In the Clemmensen reduction of 3a--methyl-*cis*-perhydroindene-1,4-dione under conditions designed for the reduction of only one oxo-group, the oxo--group in the six-membered ring is reduced exclusively and 7a-methyl-*cis*-perhydroinden-1-one is formed[35].

Comparison of the relative extents of three-carbon tautomerism of the similar α,β- and β,γ-unsaturated compounds of the cyclopentane, cyclohexane, *trans*-decalin, and *trans*-perhydroindene series[96] shows that in the *trans*--perhydroindene system the tendency of the double bond to occupy the exocyclic α,β-position is much more pronounced than in the remaining compounds (Table 7).

It is clear from the foregoing review that the concept of perhydroindene as a system containing a six-membered ring in the chair conformation (or half-chair conformation) and a non-planar five-membered ring is in good agreement with the available experimental data. The role of the thermodynamic (entropy) factor is more clearly shown in the reactivity of the perhydroindene system than in the related decalin system. The similarities and differences between these two systems can be briefly summarised as follows: (a) in both systems the conformations in which the six-membered ring has the chair form are preferred; (b) on the whole *trans*-fusion between the rings is the more stable in the decalin system, while in the perhydroindene series one may speak of either latent or explicit preference for the *cis*-fusion; (c) both *cis*-decalin and *cis*-perhydroindene possess conformational mobility (they are capable of undergoing changes in orientation of all the substituents); the conformational mobility of substituted Δ^7-hexahydroindenes appears to be less pronounced than that of substituted Δ^1-octalins; (d) when a trigonal carbon atom is present at the ring junction (enolic form of an α-ketone or an olefin), its conversion to the tetrahedral state (ketonisation or catalytic hydrogenation) results in the *trans*-fusion between the rings in the decalin system and the *cis*-fusion in the perhydroindene system; (e) the double bond in the perhydroindene system shows a greater tendency towards displacement to the intercyclic position than in the decalin system.

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PYRAZOLIDINE-3,5-DIONES, THEIR SYNTHESIS AND PHARMACOLOGICAL IMPORTANCE

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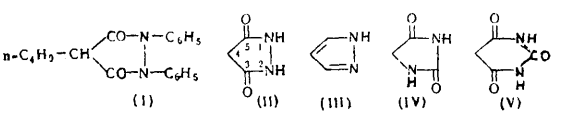
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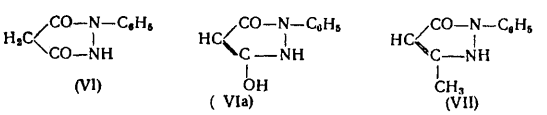
I. INTRODUCTION

The discovery of the valuable therapeutic properties of 4-n-butyl-1,2-diphenylpyrazolidine-3,5-dione[1] (Butazolidine, Phenylbutazone, Butadione†) (I) promoted the development of the chemistry of this group of compounds. Thus, whereas a total of about 25 papers appeared in the 60 years after the synthesis of the first pyrazolidine-3,5-diones[2], in the last decade, and mainly during the last five years, no fewer than 300 papers and patents dealing with this group of substances have been published, not counting the hundreds of papers connected with the study of Butadione itself.

At the present time various methods of synthesising pyrazolidine-3,5-diones have been developed and many of their properties have been studied but these results are dispersed in numerous articles and it is difficult for the research worker to cover them. Much material present in dissertations (*e.g.* that of Têng[3]) is not accessible and the section on pyrazolidine-3,5-diones in Jacobs' article in the recently issued Volume V of the Collection "Heterocyclic Compounds"[4] is very short and to some extent out-of-date, because only references up to 1954 are included. The present review is an attempt to survey the published material on the chemistry of pyrazolidine-3,5-diones and their applications.



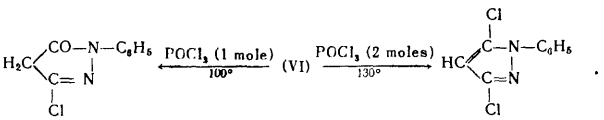
Pyrazolidine-3,5-dione (II) is the 3,5-dioxo-derivative of completely hydrogenated pyrazole (III). It is isomeric with hydantoin (IV) and is structurally related to barbituric acid (V), and also to pyrazolones.



Thus, the enol form (VIa) of 1-phenylpyrazolidine-3,5-dione (VI) differs from 3-methyl-1-phenylpyrazol-5-one (VII)

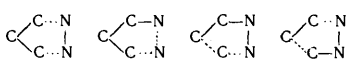
† Trivial name used in USSR (Ed. of Translation).

only in having a hydroxyl group in place of the methyl. The conversion of pyrazolidine-3,5-diones to pyrazolones and pyrazoles was described in 1898.[5]



II. METHODS OF PREPARATION

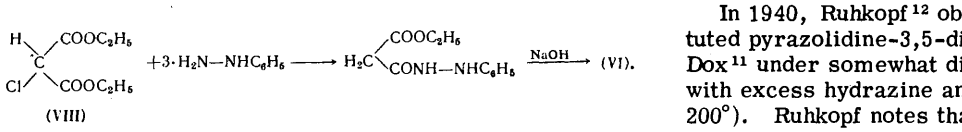
The many methods of synthesising pyrazolidine-3,5--diones can be divided, according to the types of bond being formed in the reaction (C–N, N–N, C–C, and their combinations), into the following four groups‡:



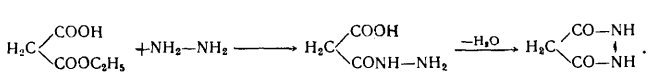
In addition, the preparation of pyrazolidine-3,5-diones from 3-imino-5-oxopyrazolidines forms a fifth group.

1. Formation of Two C...N Bonds. Preparation from Derivatives of Malonic Acid and Hydrazine

In 1891 Burmeister and Michaelis[2] described the preparation of 1-phenylpyrazolidine-3,5-dione (VI) from diethyl chloromalonate (VIII) and phenylhydrazine:

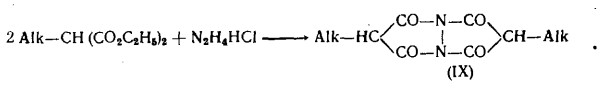


1-*p*-Tolylpyrazolidine-3,5-dione was prepared similarly[6]. This method was not used further because the use of chloromalonic ester (VIII) was found to be not essential. Rothenburg[7] prepared the unsubstituted pyrazolidine-3,5--dione (III) by heating monoethyl malonate with hydrazine hydrate; water is lost and the ring is closed on distilling:



This is the only reference to the preparation of (III). Rothenburg's results have been questioned by other investigators[8]. Syntheses of pyrazolidinediones without condensing agents are now rarely encountered[9].

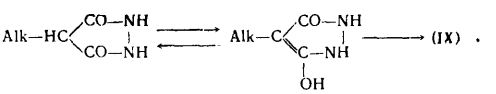
Condensation in the presence of alkaline agents was found more convenient. Conrad and Zart[10] obtained 1-mono- and 1,2,4-tri-substituted pyrazolidine-3,5-diones in satisfactory yields using sodium metal, its amide, or alkoxide and carrying out the reaction at 110°–120° for 12 h. This method has found wide application in view of the ready availability of substituted malonic esters. Dox showed[11] in 1932 that it can be used to prepare 4,4-dialkylpyrazolidine-3,5-diones. Under the same conditions monoalkyl malonates, in contrast to dialkyl malonates, invariably gave 1,3,5,7-tetraoxopyrazo[1,2-*a*]pyrazoles (IX) with hydrazine:



The author considered a possible reason for the different behaviour of mono- and di-substituted malonates to be the presence in 4,4-disubstituted pyrazolidine-3,5-diones of lactim-lactam tautomerism, which makes further condensation with a second dialkyl malonate molecule at the nitrogen impossible:

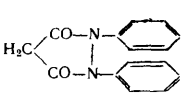


Keto-enol tautomerism in the monoalkylpyrazolidine--3,5-diones does not prevent formation of a compound of type (IX):



Further work, which shows that the hydrogen atom at C_4 is more mobile than that at the nitrogen, supports this hypothesis.

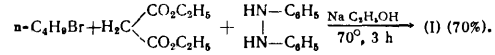
In 1940, Ruhkopf[12] obtained a number of 4,4-disubstituted pyrazolidine-3,5-diones, which had been described by Dox[11] under somewhat different reaction conditions, *viz.* with excess hydrazine and at a higher temperature (180°–200°). Ruhkopf notes that, as the carbon chain of the substituent in the malonic ester lengthens, the tendency to ring-closure is reduced; the same is observed when the hydrazine molecule is "enlarged" by various substituents. For example, he could not achieve ring-closure of ethyl phenyl malonate with phenylhydrazine. He also showed that Conrad and Zart's method is applicable to the preparation of 1,2-diphenylpyrazolidine-3,5-dione (X). 1,2,4-Trisubstituted pyrazolidine-3,5-diones were synthesised by this method in 1950 by Stenzl[13]. The synthesis of a number of 4-monosubstituted 1,2-diphenyl-3,5-dioxopyrazolidines has also been described in patents[14,15]. The last 15 years has been a period of intensive research on pyrazolidine-3,5--diones and particularly on the 1,2-diphenyl derivatives. In 1953 Büchi and coworkers[16] noted the great possibilities of Conrad and Zart's method for the preparation of mono-, di-, and tri-substituted pyrazolidine-3,5-diones. At the same time, they considered the preparation of 1,2,4,4-tetrasubstituted pyrazolidine-3,5-diones by this method to be impossible. The work of Khaletskii, Pesin, and Têng[3,17] showed that, although the tetrasubstituted pyrazolidine-3,5--diones are actually unstable in an alkaline medium, they can all be isolated in 2–3% yield. There are also indications in patents[18] that the 1,2,4,4-tetrasubstituted compounds can be prepared by this method but the yields are not quoted.



(X)

‡ The full lines signify bonds in the pyrazolidine-3,5-dione skeleton which are already present and the dotted lines those being formed in the reaction.

In the last decade, many variations of the method described have been published, differing in the solvents used, the reaction temperature, and condensing agents. Sodium butoxide[19-21] and piperidine[22] have been used as condensing agents, and ethanol or xylene, butanol[20,23], mineral oil[24], cyclohexanol[25,26], polyethyleneglycol[27], etc., as solvents. A fortunate choice of solvent often affects the product yield markedly[28]. Whereas in older work the reaction was often carried out at high temperatures (up to 200°), recently lower temperatures (100°–120° and even 85°[18]) have usually been used. The combining of condensation with alkylation has been suggested[29,30].



The yield is raised by carrying out the reaction in a nitrogen atmosphere[31].

In 1907 Michaelis and Schenk[32] achieved the condensation of a number of mono- and di-substituted malonic acids with monosubstituted hydrazines in the presence of phosphorus trichloride. In subsequent work[33] they described the preparation of 1,4-disubstituted and 1,2,4,4-tetrasubstituted pyrazolidine-3,5-diones by the same method; the applicability of the method was confirmed in 1942,[34] but it is comparatively rarely used now. The preparation of 1,4-diphenylpyrazolidine-3,5-dione and 2-alkyl-1,4-diphenylpyrazolidine-3,5-diones has been described[35,36]. Substituted malonyl chlorides are much more frequently used. Rothenburg[7] was the first to report the use of malonyl chloride as a very active product for the formation of pyrazolidine-3,5-diones. Two years later, the preparation of 1-tolylpyrazolidine-3,5-dione in low yield from malonyl chloride and *p*-tolylhydrazine was described[6]. 4,4-Diethylpyrazolidine-3,5-dione was synthesised from hydrazine and diethylmalonyl chloride by the same method[37]. The method was studied in greater detail by Kaufmann[38], who used dimethylaniline to combine with the acid produced and obtained a number of 1,2,4,4-tetrasubstituted pyrazolidine-3,5-diones in yields up to 60%.

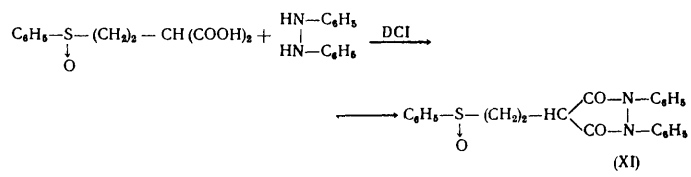
Tsumaki[39] used the same method, but without condensing agents, to obtain for the first time 1,2-diphenylpyrazolidine-3,5-dione (X) in 30% yield.

This method has been used repeatedly in recent years to prepare various pyrazolidine-3,5-diones. The reaction is usually carried out at a low temperature (0°) in a solvent inert with respect to the acyl chloride (benzene, ether) in the presence of an organic tertiary base (pyridine, dimethylaniline)[15,40,41]. By thus maintaining mild condensation conditions, tetrasubstituted pyrazolidine-3,5-diones containing bromine at C_4[42-44] and also an acetyl derivative of *p*-hydroxyphenylbutadione[45,46] were prepared. Good yields (80–90%) were obtained by Linnel and Khalifa[47] in the synthesis of 4-monoalkyl-1,2-diarylpyrazolidine-3,5-diones containing substituents such as $-NO_2$, $-NHCOCH_3$, $-CO_2H$, and $-OCOCH_3$ in the *para*-position of the benzene rings, by heating the hydrazo-compound with a small excess of the acyl chloride in benzene for 3 h at 70°–80° and then distilling off the benzene and excess acyl chloride. Lower yields (50–70%) are observed when the reaction is carried out in the presence of acetic anhydride (as solvent) in a nitrogen atmosphere. The preparation of 4-butyl-1-phenylpyrazolidine-3,5-dione from butylmalonyl dichloride and phenylhydrazine has also been described[48].

The above method has been widely used to synthesise a large number of *N*-substituted pyrazolidine-3,5-diones[49-52].

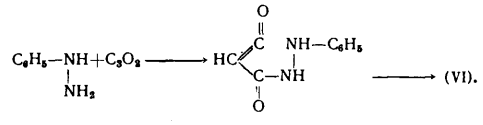
To prepare Butadione, butylmalonic anhydride is condensed with hydrazobenzene in the presence of pyridine or triethylamine in ether or chlorine-containing hydrocarbons; the yield of Butadione reaches 93%.[53]

The use of dicyclohexylcarbodiimide (DCI) for preparing pyrazolidine-3,5-diones with optically active substituents is of great interest. By this means Pfister[36] obtained two optically active forms of 1,2-diphenyl-4-(2-phenylsulphinylethyl)pyrazolidine-3,5-dione (XI):

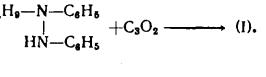


(XI)

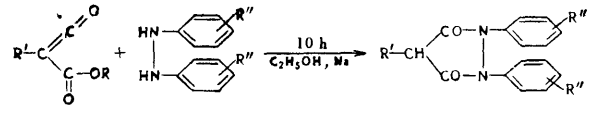
Van Alphen showed[54] in 1924 that 1-phenylpyrazolidine-3,5-dione (VI) is formed in the reaction of equivalent quantities of carbon suboxide and phenylhydrazine in ether. The reaction occurs in two stages:



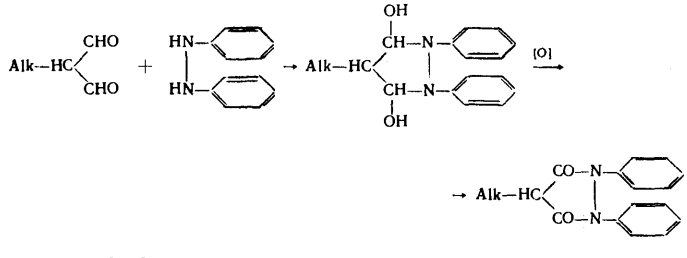
Excess phenylhydrazine leads to formation of by-products. Tsumaki[39] obtained 1,2-diphenylpyrazolidine-3,5-dione (X) in this way. The preparation of pyrazolidine-3,5-diones using carbon suboxide and hydrazine, its alkyl, cycloalkyl, aryl, and arylalkyl derivatives, is described in patents[55,56]; the reaction is carried out at -2° in an anhydrous inert solvent (xylene). Of trisubstituted hydrazines, only those with at least one alkyl radical with not more than four carbon atoms are suitable. For example, Butadione is obtained in 85% yield by this method:



When derivatives of keten are used it is necessary to heat to 110° in the presence of sodium metal[57].

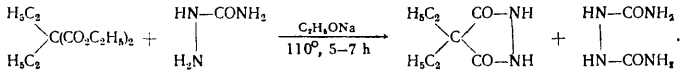


Malonyldialdehyde can also be used to synthesise pyrazolidine-3,5-diones[58]:

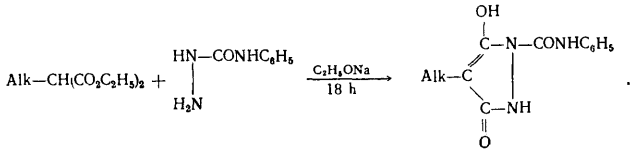


Many hydrazo-compounds are used in the reactions described: hydrazine, mono- and di-substituted alkyl-, aryl-, arylalkyl-, pyridyl-, cycloalkyl-, naphthyl-, and other

hydrazines. Dox showed[11] that a by-product of the reaction of disubstituted malonic esters with semicarbazide is hydrazodicarbonamide:

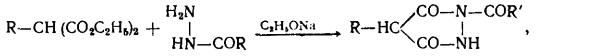


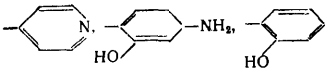
The reaction of monoalkylmalonic esters with 4-phenylsemicarbazide takes place differently[58]:



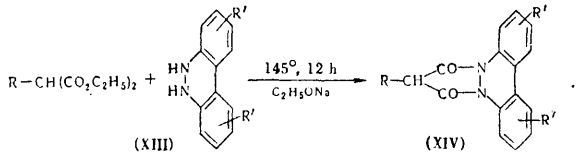
Semicarbazides, and thiosemicarbazides and di(ethoxycarbonyl)hydrazine, also react with malonyl dichloride and its derivatives to form pyrazolidine-3,5-diones in good yields[59-61].

Condensation of the hydrazides of a number of aromatic and heterocyclic acids with esters of monoalkylmalonic acids in the presence of sodium ethoxide occurs with satisfactory yields[62]:



where R = H, C_2H_5, C_4H_9; R' =  .

The preparation of derivatives of *NN'*-malonyldihydrobenzo[*c*]cinnoline (XIV) by the usual methods from 5,6-dihydrobenzo[*c*]cinnoline (XIII) is reported in many patents[63-67]:



The use of *N*-mono- and *NN*-di-acetylated derivatives of hydrazobenzene leads to higher yields[68].

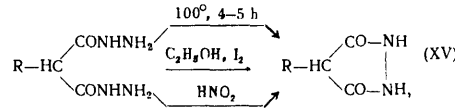
The use of azo-compounds is apparently very promising[69-71]. Thus, Butadione is obtained in 90% yield from organometallic compounds of azobenzene and butylmalonyl dichloride.

The substituents in the malonic acid (or its ester) which are used in reactions of this type are very various. Substances used include esters of numerous alkylmalonic acids[72] with up to 18 carbon atoms in the chain, and of straight chain and branched chain, arylalkyl-, and alkenyl--malonic acids, and also those with bicyclic[73,74] and heterocyclic radical substituents[75,76]. Many substituents containing a sulphur, oxygen, or nitrogen atom[9,75,77-79], an ester group[80], a shielded hydroxy-group[81], etc., in the side chain are used.

The effect of substituents in the molecule of the esters of monosubstituted alkylmalonic acids on their condensation with *o*-, *m*-, and *p*-chlorophenylhydrazines is of interest. The latter takes place, according to Gagnon's results[82], only if there are more than three carbon atoms in the substituent. To achieve condensation of esters of unsubstituted or methyl-, ethyl-, or propyl-malonic acids, they must be fused with the hydrazines at 165° and heated until the alcohol is distilled off completely.

2. Formation of an N...N Bond. Preparation from Dihydrazides and Dianilides§

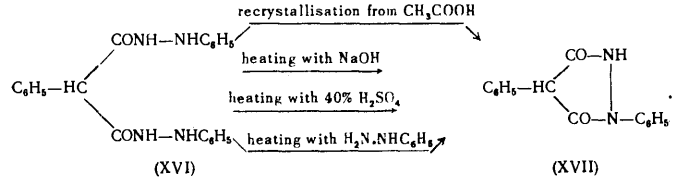
In 1916 Curtius described[83] the conversion of some 4-monosubstituted malonhydrazides into 4-monosubstituted pyrazolidine-3,5-diones (XV):



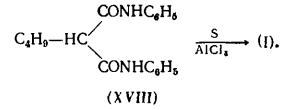
where R = $C_6H_5CH_2$, CH_3, C_6H_4, CH_2.

In subsequent investigations Curtius[84] noted that analogous compounds are formed as by-products.

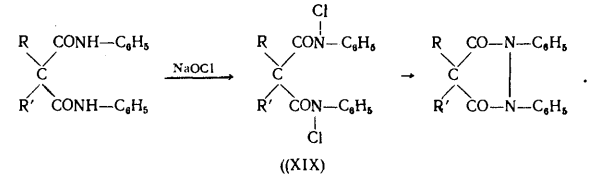
No other ways of preparing compounds of type (XV) have been described. The bisphenylhydrazide of phenylmalonic acid (XVI) behaves similarly:



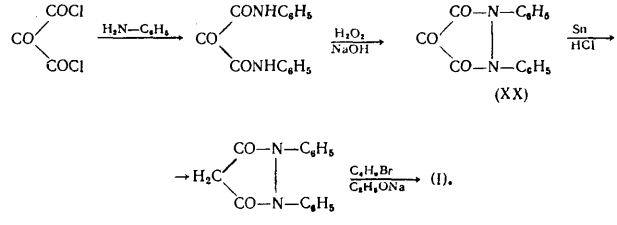
Diamides are the starting materials in some original methods of preparing pyrazolidine-3,5-diones. According to a patent[85], Butadione (I) is formed by treating the dianilide of butylmalonic acid (XVIII) with sulphur and aluminium chloride in dry benzene:



In another patent, the reaction of the dianilide of a disubstituted malonic acid with hypochlorite or chloramine, followed by catalytic dehalogenation of the intermediate *NN'*-dichloro-derivative (XIX) and ring-closure, is described[86]:



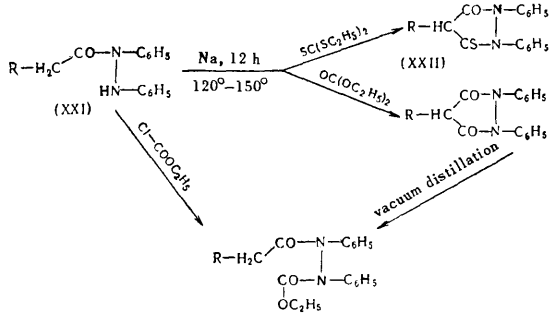
Butadione is also obtained *via* 1,2-diphenylpyrazolidine--3,4,5-trione (XX), by the following scheme[87]:



§ In some of the reactions described in this section it is unlikely that an N . . . N bond is formed (Ed. of Translation).

3. Formation of C...C...N Bonds. Preparation from Phenylhydrazides of Monobasic Carboxylic Acids

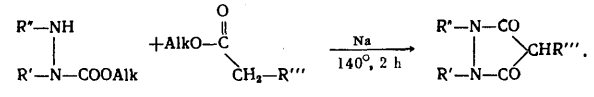
In 1957 Hallman reported[88-91] that pyrazolidine-3,5--diones are formed by the condensation of the *NN'*-diphenylhydrazides of carboxylic acids (XXI), which are easily obtained in good yields from hydrazobenzene and the acyl chloride, with diethyl carbonate or ethyl chlorocarbonate in the presence of alkaline agents. 1,2-Diphenyl-5-thiopyrazolid-3-ones (XXII) are formed when diethyl trithiocarbonate is used:



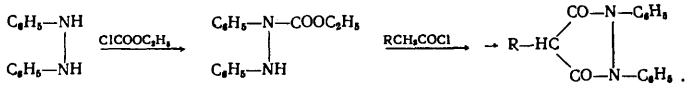
Similar methods are described in a number of patents[92].

4. Formation of C...C and C...N Bonds. Preparation by Condensing *N*-Carboxyhydrazines with Esters of Fatty Acids

The method is described in a Hungarian patent[93]:

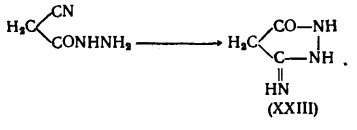


The following synthesis described in work mentioned above[88] occurs by the same scheme:

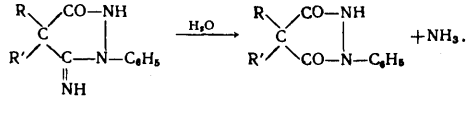


5. Preparation from 3-Iminopyrazolid-5-ones

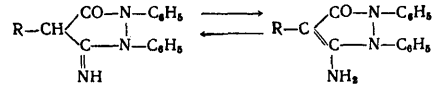
3-Iminopyrazolid-5-ones were first prepared from cyanoacetic ester and phenylhydrazine in the presence of sodium[10]. Unsubstituted 3-iminopyrazolid-5-one (XXIII) is obtained by treating cyanoacetylhydrazine with a 40% solution of sodium hydroxide[94]:


(XXIII)

Syntheses of these compounds and study of their structure, tautomerism, and conversion into pyrazolidine-3,5--diones have been described in a number of papers[95-104]. The conversion takes place when they are hydrolysed by alkalis or acids:



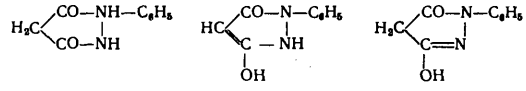
A number of authors, for example Stenzl[13], have demonstrated the existence of tautomerism between 3-iminopyrazolid-5-ones and 3-amino-Δ^3-pyrazolin-5-ones (XXV):

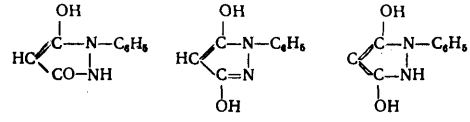

(XXIV) (XXV)

Study of the hydrolysis of 3-iminopyrazolid-5-ones[13] showed that, in contrast to compounds disubstituted or unsubstituted at the 4-position, compounds of type (XXIV) are only hydrolysed with difficulty. This can be explained by the stability of the tautomeric form (XXV).

III. TAUTOMERISM IN THE PYRAZOLIDINE-3,5-DIONE SERIES

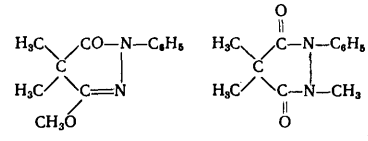
The existence of a number of tautomeric forms of pyrazolidine-3,5-diones is possible. Even for the first compound of the series which was obtained, 1-phenylpyrazolidine-3,5-dione (VI), Burmeister and Michaelis[2,105] were compelled to consider which of the possible structures should be ascribed to it:


(VI) (VIa) (XXVI)



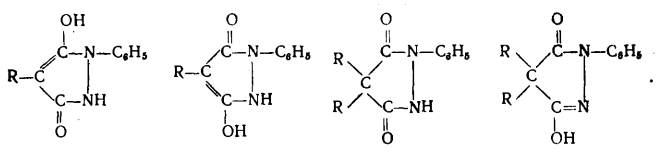
From the ease with which the substance reacts with aldehydes and ketones the presence of a methylene group in the molecule was suggested, and therefore formula (XXVI) was adopted. To confirm this the reaction of compound (XVI) with phosphoryl chloride and methyl iodide was studied. The *O*-methyl ether structure (XXVII) was ascribed to the methylation product.

Later, however, a substance identical with the methylated product (XXVII) was obtained in the condensation of *N*-methyl-*N'*-phenylhydrazine acetate with dimethylmalonic acid. These results[33] proved that the initial substance (VI) and its methylation product are 3,5-dioxo-compounds, (VI) and (XXVIII):


(XXVII) (XVIII)

Thus, confirmation was already obtained of the existence of the diketo-form of pyrazolidine-3,5-diones early in their study, but the existence of enol forms was also indicated[7] by the formation by these compounds of salts with only one equivalent of metal and by the coloration with $FeCl_3$.

The use of ultraviolet and infrared spectroscopy permitted a deeper study of the tautomerism. By studying the ultraviolet spectra of 1,4-disubstituted pyrazolidine-3,5-diones Gagnon and coworkers[106] established the presence of two tautomeric forms (XXIX) and (XXX):



(XXIX) (XXX) (XXXI) (XXXII)

They also concluded, from the ultraviolet spectra and chemical properties of 1,4,4-trisubstituted pyrazolidine--3,5-diones, that these are present in neutral and acidic solutions as the diketo-form (XXXI), but in alkaline solutions as the lactim (XXXII). These results were subsequently confirmed[58,82]. It was also shown that *o*-, *m*-, and *p*-chloro-1-phenyl-4-substituted pyrazolidine-3,5--diones have identical ultraviolet spectra.

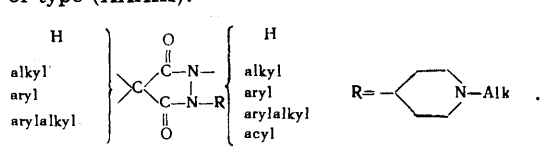
As a result of much research[96-102], begun in 1947, the relation between the position of the double bond in the tautomeric forms of 4-monosubstituted pyrazolidine-3,5-diones and the wavelengths, and also intensities, of the absorption bands was established.

The ultraviolet spectra of 1,2-diphenylpyrazolidine-3,5--diones were found to be similar to those of *N*-monosubstituted compounds[107-109].

Study of the infrared spectra of 4-mono- and 4,4-di--alkyl-1-phenylpyrazolidine-3,5-diones[82] also confirmed the existence of several tautomeric forms. A band at 7.7 μ was found[107,109-111] to be very characteristic of pyrazolidine-3,5-diones; this, together with bands close to 5.7 and 5.8 μ, which are characteristic of the carbonyl groups, is evidence of the presence of a pyrazolidine-3,5-dione ring. Similar results were obtained by Hammond *et al.*[109] for 4-alkoxy-1,2-diphenylpyrazolidine-3,5-diones; they isolated both tautomeric forms of these substances.

From a study of many 4-monosubstituted 1,2-diphenylpyrazolidine-3,5-diones, Girod[107] concluded that the majority of them exist in the diketo-form in solution and in the crystalline state. Some of these compounds are partially enolised in solution and a compound such as 1,2-diphenyl-4--(phenylthioethyl)pyrazolidine-3,5-dione exists in the enol form even in the crystalline state.

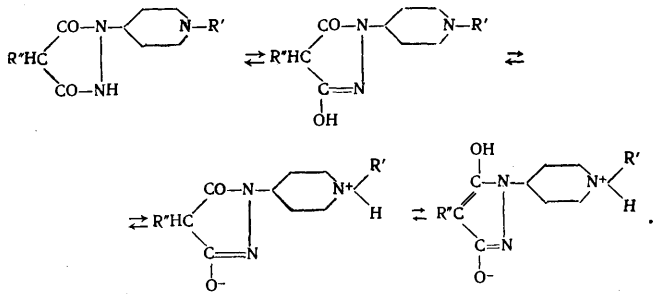
Ideas as to the tautomeric relationships in a number of pyrazolidine-3,5-diones were extended by studying compounds of type (XXXIII):[49,50,112-117]



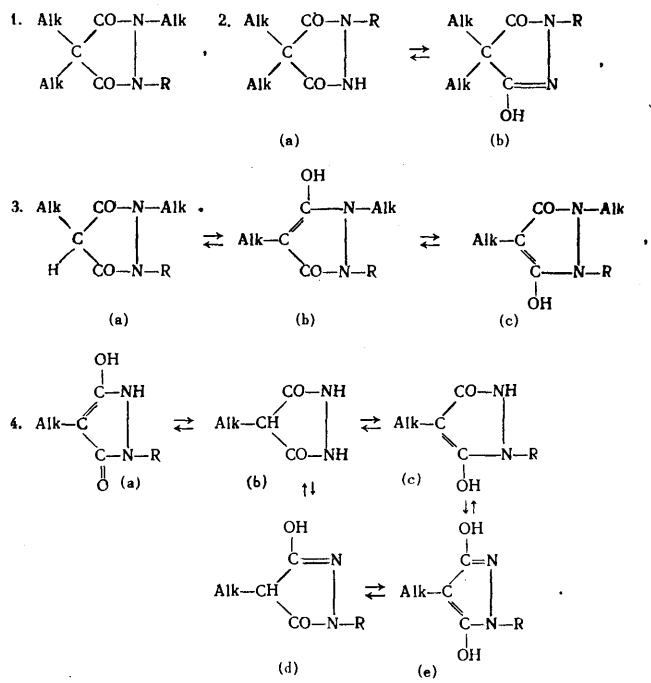
(XXXIII)

The relationships between the tautomeric forms in the series of these compounds are complicated.

Pyrazolidine-3,5-diones are acidic compounds, especially their 4-monosubstituted derivatives[106,107]. Thus, p*K* for Butadione corresponds to the acidity of aliphatic carboxylic acids. The presence in the molecule, therefore, of the basic nitrogen atom and the acidic enol or iminol hydroxyl leads to the formation of bipolar ions. For this reason the formation of iminol-enol, *i.e.* dihydroxypyrazole, tautomeric forms become possible in alkaline solutions:



Compounds of type (XXXIII) can be divided into four groups¶:

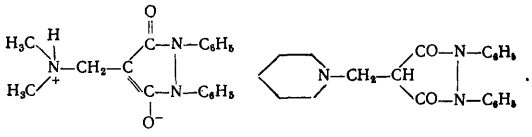


It was found that compounds of group 1 are in the diketo--form in aqueous solutions and in the solid state. Compounds of group 2 are in the iminol form (2b) in aqueous solutions. In chloroform both forms (2a) and (2b) are present, but in the solid state only the iminol form (2b). In acidic solutions and in weakly polar solvents compounds of group 3 are in the diketo-form (3a) but in neutral aqueous and in alkaline solutions they are in the enol form (3b) and (3c). In polar solvents compounds of group 4 are inclined more towards formation of the iminol (4d) and iminol-enol (4e) forms, which are stabilised by a basic substituent R, than to the enols (4a) and (4c), but in a weakly polar solvent (chloroform) two forms (4a) and (4d) are present.

Analogous tautomeric relations are characteristic of 4-amino-, 4-alkylamino-, and 4-aminoalkyl-pyrazolidine--3,5-diones[109]. Some peculiarities of their chemical properties are accounted for by this tautomerism; for example, compound (XXXIV) does not form alkaline salts although a reduction in the basicity of the nitrogen atom in

¶ The bipolar ions corresponding to these tautomeric forms are not indicated.

the side chain, for example in compound (XXXV), allows such a salt to be obtained[110]. High melting points are typical of all these compounds:

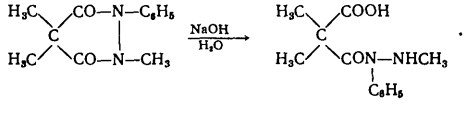


(XXXIV) (XXXV)

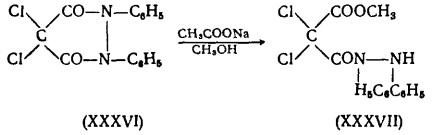
1,2,4,4-Tetrasubstituted pyrazolidine-3,5-diones with nitrogen-containing substituents no longer possess these properties because there are no hydrogen atoms attached to C_4 or N and these hydrogen atoms are required for enolisation or formation of an iminol. These compounds therefore form stable salts even with oxalic acid[118].

IV. STABILITY OF THE PYRAZOLIDINE-3,5-DIONE RING

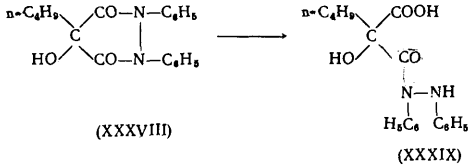
Stability towards acids and alkalis. Unsubstituted pyrazolidine-3,5-dione (III) is unstable and decomposes on boiling with strong mineral acids and alkalis, with liberation of hydrazine[7]. Substitution of the hydrogen atoms at C_4 and N stabilises the ring: mono-, di-, and tri-substituted pyrazolidine-3,5-diones are significantly more stable towards acids and alkalis[10,12,45,105], this being apparently connected with the greater stability of the enol and iminol forms. However, the C–N bond is broken on prolonged boiling of pyrazolidine-3,5-diones with anhydrous alcohols in the presence of anhydrous acids[119]. 1,2,4,4-Tetrasubstituted derivatives are less stable and decompose, with cleavage of the C–N bond, on boiling with alkalis[5,10,33]:



Tetrasubstituted pyrazolidine-3,5-diones with electronegative substituents, such as Cl or OH, at C_4 are particularly sensitive to alkaline reagents. 4,4-Dichloro-1,2-diphenylpyrazolidine-3,5-dione (XXXVI) is decomposed easily by sodium acetate at 20°:[120]

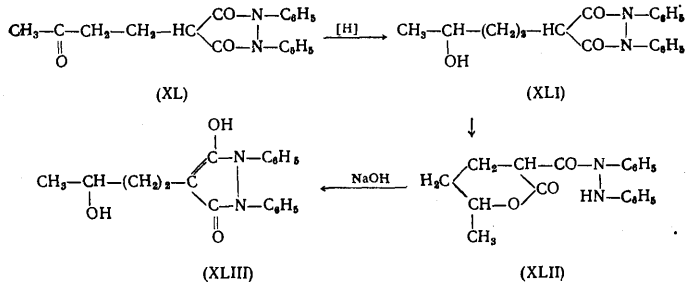


(XXXVI) (XXXVII)



(XXXVIII) (XXXIX)

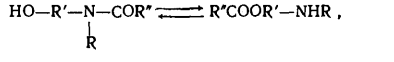
4-Hydroxybutadione (XXXVIII) is also unstable. It is decomposed by the action of dilute sodium hydroxide in the cold[121,122]. Boiling the decomposition product (XXXIX) with water leads again to ring-closure[123,124]. Recently, cleavage of the pyrazolidine-3,5-dione ring by reaction with hydrazines and amines has also been studied. Here again the C–N bond is broken[125]. Two products were isolated in the reduction of 4-(3-oxobutyl)-1,2-diphenylpyrazolidine-3,5-dione (XL); [107,126] their ultraviolet and infrared spectra and pK values showed that one of them is 4-(3-hydroxybutyl)-1,2-diphenylpyrazolidine-3,5-dione (XLI) and the other the *NN'*-diphenylhydrazide of the δ-lactone of α-carboxy-δ-hydroxyhexanoic acid (XLII):



(XL) (XLI)

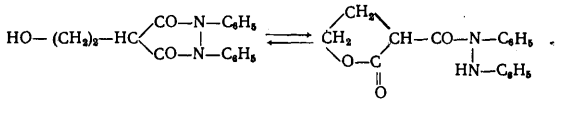
(XLIII) (XLII)

Similar conversions, which are instances of the general conversion of hydroxyalkylamides into aminoalkyl esters:



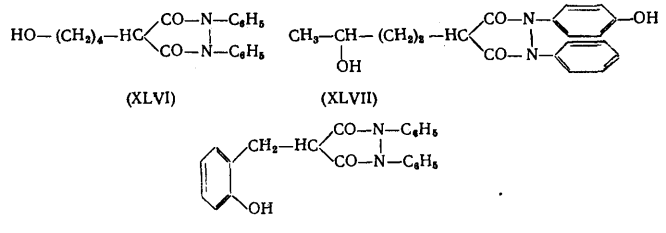
have been described previously[127].

The intermediate hydroxy-compound (XLI) is converted into the lactone (XLII) on treating it with dilute acids or on crystallisation, and (XLII) is converted into the tautomeric hydroxy-compound (XLIII) on treating the lactone with alkali. The 2-hydroxyethyl derivative (XLIV) behaves similarly, giving the γ-lactone (XLV):



(XLIV) (XLV)

Compounds with a hydroxy-group which is further away from C_4 along the side chain (XLVI), phenolic (XLVII), or an *o*-hydroxy-group in a benzyl radical (XLVIII), do not form lactones.



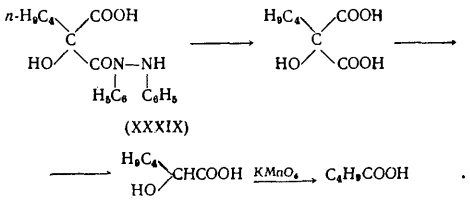
(XLVI) (XLVII)

(XLVIII)

Stability towards oxidising agents. Pyrazolidine-3,5-dione (III) is a strong reducing agent; for example, it reduces an ammoniacal solution of silver oxide even in the cold[7]. Substituents diminish the reducing power. Thus, Fehling's solution is reduced by 1-phenylpyrazolidine-3,5-dione (VI) only on heating[105] and by 1,2,4,4-tetrasubstituted derivatives only on boiling[38]. Cleavage of the ring with liberation of hydrazine evidently precedes reduction.

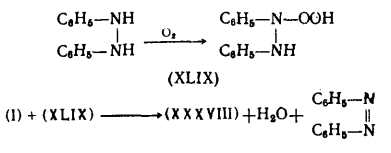
In milder oxidation the ring is not broken but is oxidised at C_4.[49,121-124,128-130].

The first careful and thorough investigation of the oxidation of 1,2-diphenylpyrazolidine-3,5-diones was carried out by Sokolova and Magidson[121,122] using Butadione (I). They showed that 4-hydroxybutadione (XXXVIII) is a by-product of the synthesis of (I). It was found that the oxygen carrier in the oxidation of Butadione is hydrazobenzene, in the presence of which Butadione is oxidised with yields up to 9%. 4-Hydroxybutadione breaks down to the mono(diphenylhydrazide) of butyltartronic acid (XXXIX), further degradation of which was also detected by the authors:



(XXXIX)

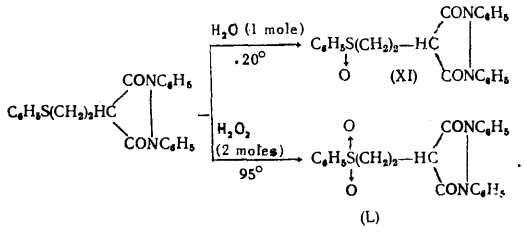
In repetitions of the experiments, Veibel *et al.*[128] could not isolate 4-hydroxybutadione but did isolate azobenzene and the hydrozide (XXXIX); they confirmed that hydrazobenzene is the oxygen carrier and that oxidation of Butadione takes place as follows:



(XLIX)

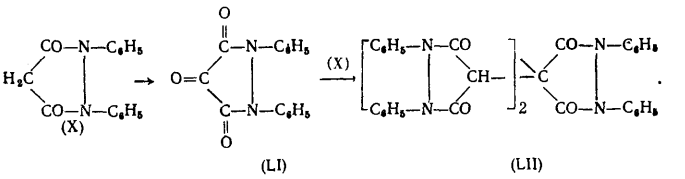
The oxidation scheme for Butadione[121,122] has been confirmed by other authors[123,124,129,130].

Extreme ease of oxidation at C_4 is characteristic also of other pyrazolidine-3,5-diones[124]; for example, 4-hydroxy--derivatives are obtained in up to 30% yield when oxygen is passed into gently boiling alcoholic solutions of these compounds. Under these conditions 1,4-diphenyl- and 1,2,4--triphenyl-pyrazolidine-3,5-dione were not oxidised. Veibel *et al.*[128] succeeded in obtaining 4-hydroxy-derivatives of 4-alkyl-1-phenyl- and 1,4-diphenyl-pyrazolidine--3,5-diones in 50–75% yields using oxidation in methanol solution in the presence of triethylamine. They found that the oxidation of pyrazolidine-3,5-diones is considerably more rapid than that of the corresponding pyrazol-5-ones. As the length of the alkyl chain attached to C_4 increases, the rate of oxidation falls, and a compound such as 1,2-diphenyl-4-tritylpyrazolidine-3,5-dione does not in general undergo oxidation; this is apparently connected with steric hindrance. It has been shown[36] that a sulphur atom in the side chain can be oxidised without oxidising C_4.



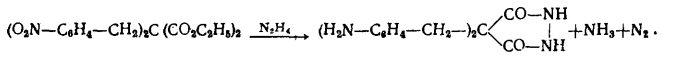
(L)

The oxidation of 1,2-diphenylpyrazolidine-3,5-dione (X) by selenium oxide in boiling dioxan has been studied recently[131]; a product of the condensation of the oxidised compound (LI) with the original substance was isolated:

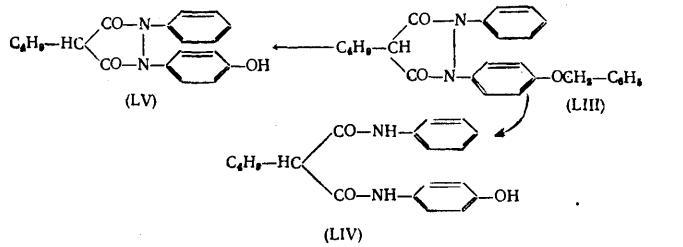


(LI) (LII)

Stability towards reducing agents. The pyrazolidine--3,5-dione ring is stable towards the usual reducing agents. It does not react with zinc dust/ammonium chloride[47] nor hydrogen/catalysts (Pd/C, Raney Ni, etc.) at ordinary or elevated temperatures (up to 80°) or at pressures up to 20 atm.[132-137] Moreover, the pyrazolidine-3,5-dione ring is formed under conditions where a nitro-group is reduced to an amino-group[138]:



However, whereas at low temperatures the benzyl group is removed from compound (LIII) without ring cleavage, at elevated temperatures the N–N bond is also broken to give the diamide (LIV):[45]



(LV) (LIII) (LIV)

Denss[139] observed a similar reaction in the reductive alkylation of pyrazolidine-3,5-diones.

V. ELECTROPHILIC AND NUCLEOPHILIC SUBSTITUTION REACTIONS

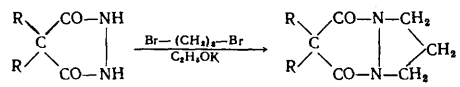
For partially substituted pyrazolidine-3,5-diones, electrophilic substitution of the hydrogen atoms at C_4, and to a lesser extent of those at the nitrogen atoms, is the most characteristic reaction. Depending on the nature of the electrophilic reagent and on the number and type of the substituents already present, substitution takes place at the C or N atoms; a completely substituted compound may be formed.

Alkylation, which is one of the most studied and frequently applied reactions, is used to obtain derivatives alkylated at C_4 and at the N atoms. When the mono- and di-substituted compounds are alkylated, depending on the conditions, both partially and completely substituted derivatives can be formed[3,5,10,17,33,134,140-142]. As Büchi and coworkers found[16], alkylation occurs first at C_4 and later at the N atoms, indicating that the hydrogen atoms at C_4 are more active than those at the N atoms. Various alkylating agents have been used: dialkyl sulphates[10], alkyl halides[3,5,16,33,143-146], substituted alkyl halides[147,148], α-halogenocarboxylic acids[149], tertiary alcohols[188], ethers[150], and diazomethane[109,151,152].

Alkylation is carried out at room temperature or slightly above[3,5,16] but sometimes by boiling with excess alkyl

halide[153]. The use of catalysts (BF_3, $AlCl_3$, $ZnCl_2$, $FeCl_3$) facilitates alkylation considerably[150,154].

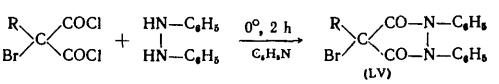
When *NN'*-unsubstituted pyrazolidine-3,5-diones are alkylated at the N atoms with 1,3-dibromopropane (or 1,4--dibromobutane) a bicyclic system which includes the pyrazolidine-3,5-dione ring is obtained[155]:

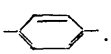


Halogenation and substitution with thiocyanate are the electrophilic substitution reactions at C_4 which occur most easily. From 4-unsubstituted pyrazolidine-3,5-diones both 4-mono- and 4,4-di-halogeno(or -thiocyanato)-derivatives can be easily obtained using the corresponding quantities of halogen or thiocyanogen[3,6,108,156].

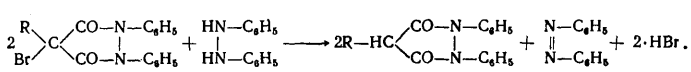
The presence of one alkyl or phenyl group at C_4 does not reduce the activity of the remaining hydrogen atom; these compounds also easily form 4-chloro- and 4-bromo-derivatives, both in the cold and on gentle heating in chlorinated hydrocarbons[3,120,157,158]. The preparations of 4-iodobutadione using iodine monochloride or iodine[159,160] and of 4-iodomethylbutadione by boiling with methylene iodide in an alkaline solution[118] have also been described.

Compounds of this same type (LV) are obtained in satisfactory yields by direct condensation of 4-alkyl-4-bromomalonyl dichloride with hydrazobenzene[44]:

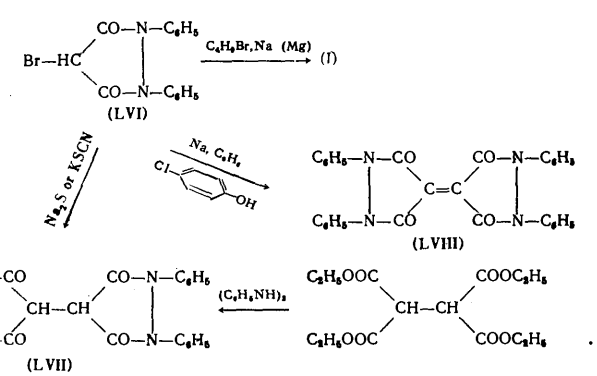


where R = C_2H_5, iso-C_3H_7, n-C_4H_9, C_6H_5, Cl-  .

Compounds of type (LV) are easily dehalogenated on heating with hydrazobenzene. Because of this Mukherjee[42] was not at first able to obtain compound (LV) using an excess of hydrazobenzene:

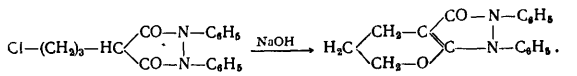


The great activity of the bromine is used to obtain various derivatives of compound (X):[44,161]



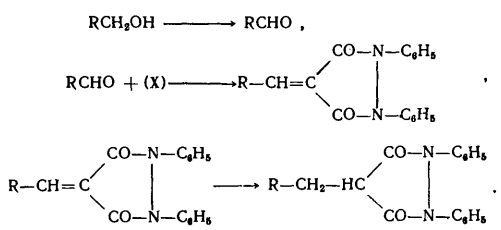
When compound (LVI) reacts with potassium thiocyanate, sodium sulphide, or triethylammonium diethylthiophosphate it does not form a substitution product but gives 1,2,1',2'--tetraphenyl-4,4'-bipyrazolidinyl-3,5,3',5'-tetraone (LVII), the structure of which has been demonstrated by synthesis[3,162]. Bromine is also removed from (LVI) by treating it with pyridine[3,162]. When (LVI) is boiled in benzene in the presence of sodium metal and *p*-chlorophenol a product which decolorises bromine and potassium permanganate solutions is obtained; structure (LVIII) is proposed for it[163].

In an alkaline medium, compounds containing a γ-halogenoalkyl chain at C_4 lose the halogen atom to form bicyclic compounds[164]:

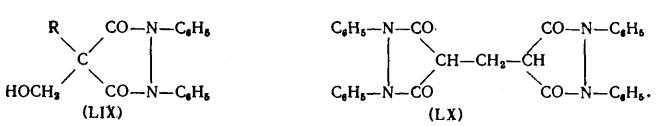


With aldehydes and ketones, 4-unsubstituted pyrazolidine-3,5-diones easily form 4-benzylidene, 4-isopropylidene , and other such derivatives[8,7,39,105,140,165], which are red substances which crystallise well. They are obtained by boiling pyrazolidine-3,5-diones with excess of the aldehyde or ketone; sometimes $ZnCl_2$ is used as catalyst[140]. Recently these unsaturated derivatives have often been used as intermediates, 4-monosubstituted pyrazolidine-3,5--diones being obtained by their reduction (generally catalytic)[140,143,166-168]. The latter compounds can also be obtained by alkylation with alcohols in the presence of catalysts, the water formed in the reaction being distilled off[169,170].

The reaction occurs in three stages[171]:

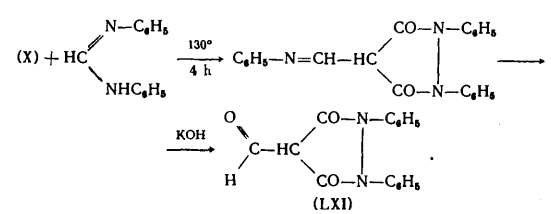


The separation of the condensation products with alkalis[39,165] and the relation between their colour and structure[172] have been studied. With formaldehyde, 4-monosubstituted 1,2-diphenylpyrazolidine-3,5-diones form 4-hydroxymethyl derivatives (LIX).[118,173,174]

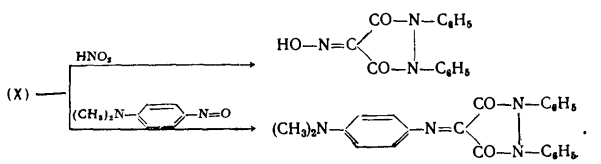


The reaction of one mole of formaldehyde with two moles of compound (X) gives unexpectedly bis-(1,2-diphenyl-3,5--dioxopyrazolidin-4-yl)methane (LX) and another substance, similar in composition but with a different melting point[3,162], which is evidently a polymer.

A pyrazolidine-3,5-dione containing an aldehyde group at C_4 (LXI) has also been described; it is obtained as follows[175]:

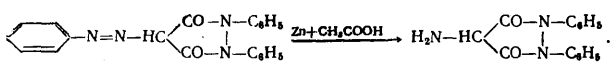


Nitroso- and isonitroso-derivatives of pyrazolidine-3,5-diones are easily formed in the reaction with nitroso(dimethylaniline)[162,176] or with sodium nitrite in acidic solution[7,13,105]. For example:



These compounds can be reduced to 4-amino-derivatives with ammonium sulphide[10,13] or zinc dust in acetic acid[108].

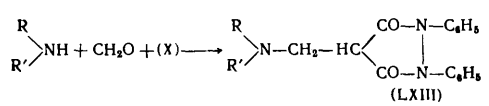
With diazonium salts, 4-unsubstituted and 4-monosubstituted derivatives give coloured azo-compounds in good yields; the products are stable to acids and alkalis under mild conditions[3,7,33,82,105,189], and they can be used for the synthesis of 4-aminopyrazolidine-3,5-diones (LXII):[109]



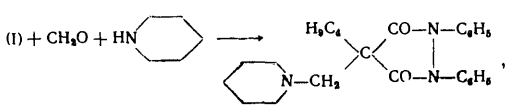
(LXII)

Compound (LXII) gives isopropylidene and acetyl derivatives[109].

In the *Mannich reaction* both 4-unsubstituted and 4-monosubstituted compounds can be used[110,118,177], giving respectively compounds of types (LXIII) and (LXIV):



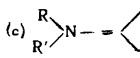
(LXIII)



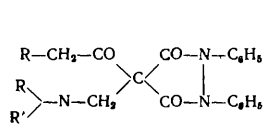
(LXIV)

where

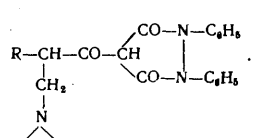
(a) $R = R' = CH_3$; (b) $R = CH_3$, $R' = H$;

(c)  (d) $R = C_4H_9$, $R' = H$.

The use of a 4-acyl derivative in the Mannich reaction does not give a 4,4-disubstituted compound (LXV) but one of type (LXVI):[177]

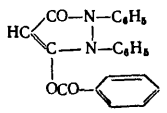


(LXV)

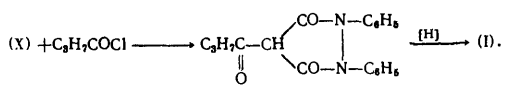


(LXVI)

Acylation of pyrazolidine-3,5-diones is one of the reactions most studied. In contrast to other electrophilic substitution reactions, acylation of 4-unsubstituted compounds gives only 4-monoacyl derivatives and no 4,4-disubstituted compounds are formed. It was originally thought[103] that these monoacyl compounds were *O*-acyl derivatives — *e.g.* (LXVII) — but it was soon shown[110,152] that when they are reduced, C_4-alkyl derivatives are formed, confirming that they have structures of type (LXVIII):



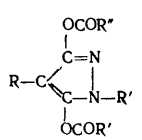
(LXVII)



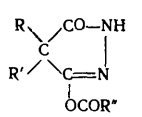
(LXVIII)

The infrared spectra of acylated compounds agree with these results[152].

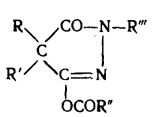
Acylation at the nitrogen atom in *N*-unsubstituted pyrazolidine-3,5-diones does not occur. When 1,4-disubstituted compounds are acylated, an *OO'*-diacyl derivative (LXIX) is obtained, and acylation of 4,4-di- and 1,4,4-tri-substituted derivatives gives compounds of types (LXX) and (LXXI):[10,12,33,49]



(LXIX)

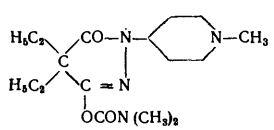


(LXX)

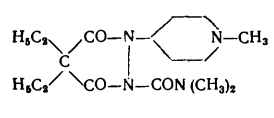


(LXXI)

These compounds were confirmed as *O*-acyl compounds from their infrared spectra and also by synthesis of alternative structures. For example, the acylation product (LXXII) differs in its properties from (LXXIII), which is obtained from an *NN'*-disubstituted hydrazine[49]:



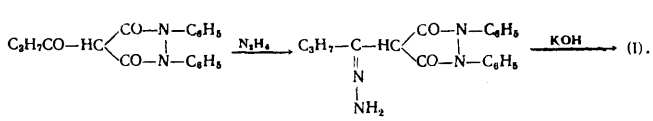
(LXXII)



(LXXIII)

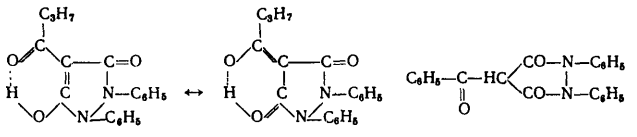
Acylation of 4-substituted 1,2-diphenyl-3,5-dioxopyrazolidines, for example (I), gives *O*-acylated derivatives, the structure of which is proved from the infrared spectra and by the ease of alkaline hydrolysis on boiling with an aqueous-alcoholic solution of potassium hydroxide[152]. Many 4-acylpyrazolidine-3,5-diones are described in a vast literature, particularly in patents[174,178-185]. Acylation is usually carried out by boiling the pyrazolidine-3,5-diones with excess acyl chloride or acid anhydride[12], sometimes in the presence of sodium acetate[10], and by the Schotten–Baumann[33] or Friedel–Crafts[177] reactions.

4-Acyl derivatives are used as intermediates for the synthesis of 4-alkyl-1,2-diphenylpyrazolidine-3,5-diones using the Kischner reaction[135,186,187]:



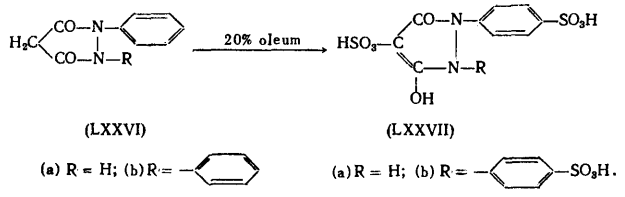
Reduction with lithium tetrahydroaluminate has also been described[177]. It was found from the infrared spectra

of 4-acyl-1,2-diphenylpyrazolidine-3,5-diones[110] that hydrogen bonding is marked in many of them (LXXIV), but the 4-benzoyl derivative is found in the trioxo-form (LXXV):[111]



(LXXIV) (LXXV)

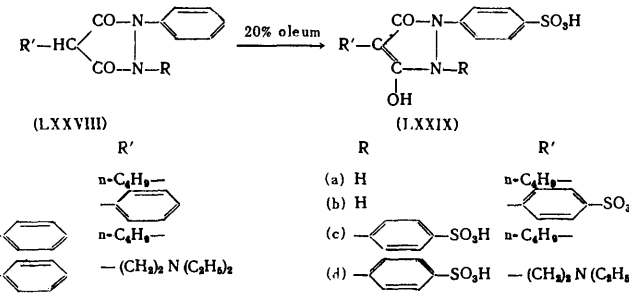
Sulphonation of pyrazolidine-3,5-diones has not been described, apart from exploratory results[3,189]. An investigation of the sulphonation of various types of pyrazolidine-3,5-dione by 20% oleum was begun only recently[190]. As with acylation, in the sulphonation of 4-unsubstituted compounds only one hydrogen atom at C_4 is replaced by the sulpho-group:



(LXXVI) (LXXVII)

(a) R = H; (b) R = (a) R = H; (b) R =

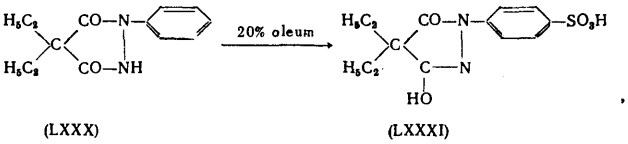
The sulpho-group at C_4 differs from the sulpho-group in aromatic sulphonic acids in that it is removed — from, for example, (LXXVIIa) and (LXXVIIb) — by the action of nitrous acid in the presence of $BaCl_2$, with formation of $BaSO_4$ quantitatively. 4-Monosubstituted pyrazolidine-3,5-diones (LXXVIIIa)-(LXXVIIId) are not sulphonated at C_4; only the hydrogen atom in the phenyl group is replaced. As shown by paper chromatography of the hydrolysates of the sulphonic acids, the sulpho-group enters only the *para*-position:



(LXXVIII) (LXXIX)

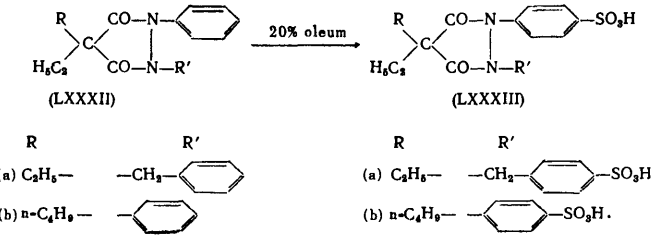
R	R′	R	R′
(a) H	n-C_6H_9—	(a) H	n-C_6H_9—
(b) H		(b) H	—SO_3H
(c) —	n-C_6H_9—	(c) —SO_3H	n-C_6H_9—
(d) —	—$(CH_2)_2N(C_2H_5)_2$	(d) —SO_3H	—$(CH_2)_2N(C_2H_5)_2$.

1,4,4-Trisubstituted compounds (LXXX) behave similarly:



(LXXX) (LXXXI)

and also 1,2,4,4-tetrasubstituted compounds (LXXXIIa) and (LXXXIIb):



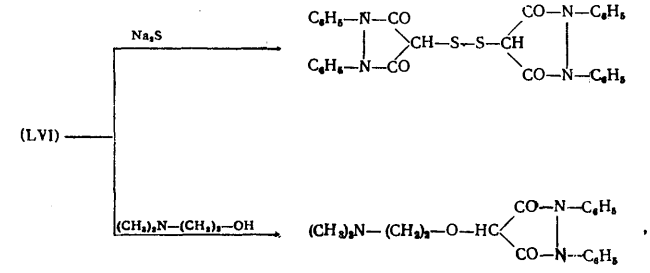
(LXXXII) (LXXXIII)

R	R′	R	R′
(a) C_6H_5—	—CH_2—	(a) C_6H_5—	—CH_2—SO_3H
(b) n-C_4H_9—	—	(b) n-C_4H_9—	—SO_3H.

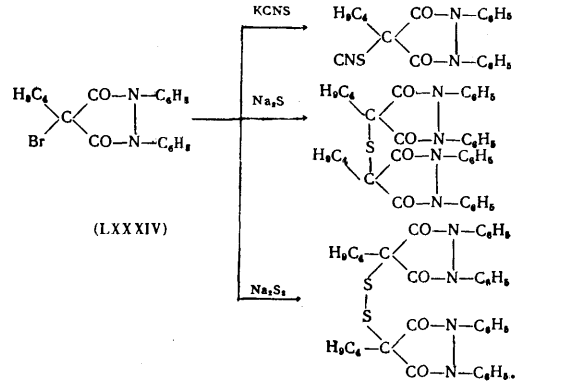
Introduction of a sulpho-group into the ring or into the phenyl group increases considerably the acidity of the enol, and also of the iminol, hydroxy-groups; they are salt-forming in all the sulphonic acids. This is especially so for a sulpho-group in a phenyl group at C_4 (LXXIXb). Whereas an alcoholic solution of the original compound (LXXVIIIb) gives only a slight green coloration with $FeCl_3$ solution, an aqueous solution of the sulphonic acid (LXXIXb) gives an intense blue colour.

Nitration of pyrazolidine-3,5-diones has hardly been studied. Nitration of compound (X) with excess of a nitrating mixture at 0° gives a tetranitro-derivative[108], but with a smaller quantity of the nitrating mixture it gives a mononitro-derivative[3,189]. Although it can be assumed in the latter case that the nitro-group is attached to C_4, this hypothesis requires proof.

Nucleophilic substitution reactions of derivatives of pyrazolidine-3,5-diones have also been little studied. Substitution of the bromine in 4-bromo-1,2-diphenylpyrazolidine-3,5-dione (LVI) has been described[108,163],



and also substitution in 4-bromo-4-n-butyl-1,2-diphenylpyrazolidine-3,5-dione (LXXXIV).[3,156,163].

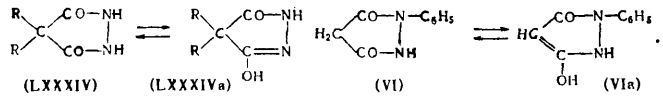


(LXXXIV)

VI. THE CHARACTER OF THE PYRAZOLIDINE-3,5--DIONE RING

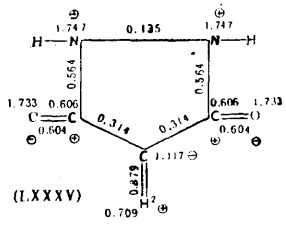
Various opinions have been expressed concerning this question. One considers that the pyrazolidine-3,5-dione ring is similar to aromatic amines[3,189]; most authors do not consider the interaction of the hydrazine part of the molecule with the β-dicarbonyl part.

Arndt[191] made a special study of the character of the pyrazolidine-3,5-dione ring. He concluded, from a comparison of the chemical properties of various hetero-rings containing two nitrogen atoms, that compounds like 4,4-diethylpyrazolidine-3,5-dione (LXXXIV) are not capable of aromaticity but compounds like 1-phenylpyrazolidine-3,5--dione (VI) are, because the enol form (VIa) possesses a sextet of π electrons:



(LXXXIV) (LXXXIVa) (VI) (VIa)

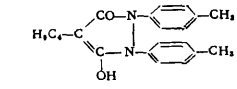
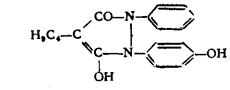
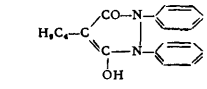
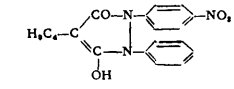
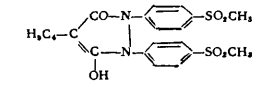
As seen from the above review of chemical properties and methods of preparation, pyrazolidine-3,5-diones in fact show a number of features characteristic of aromatic systems, namely: the system is fairly stable (particularly towards reduction), the hydrogen atom at C_4 is easily substituted in innumerable electrophilic substitution reactions, and finally 4-unsubstituted and 4-monosubstituted compounds display similarities to phenols on sulphonation. However, not one of these properties can serve as a strict criterion of aromaticity[192] because non-aromatic compounds may also possess them, as has been shown particularly clearly in a recent series of papers on cyclic β-diketones[193]. Nevertheless there are results which agree with the hypothesis of the aromatic character of the pyrazolidine-3,5--dione ring. For example, Besnainou and Chalvet[194] give a molecular diagram for pyrazolidine-3,5-dione (LXXXV) obtained by the molecular-orbital method, in which the π bond indices show that, to a considerable extent, the bonds in the ring are averaged out, there being neither "pure" double nor single bonds; this is characteristic of non-benzenoid aromatic systems[192].



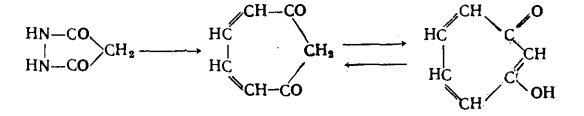
(LXXXV)

There are also other data which support the aromatic character of pyrazolidine-3,5-diones, in particular those concerning the effect of substituents in the *para*-position of the phenyl groups in 4-n-butyl-1,2-diphenylpyrazolidine--3,5-dione (I) on the pK_a values of these compounds (see Table)[195,196]. Electron-donor substituents (CH_3, OH) reduce and electron-acceptor substituents (NO_2, SO_2CH_3) increase the degree of dissociation of the enol hydroxy-group. This behaviour can be explained precisely by aromatic character of the hetero-ring, which can allow the effect of substituents in the remote *para*-position of the phenyl group to be transmitted to the enol hydroxy-group of the hetero-ring through the nitrogen and carbon atoms.

TABLE. Relation between pK_a for Butadione derivatives and the substituents in the *para*-position of the phenyl groups.

Formula	pK_a
	4.9
	4.7
	4.5
	3.2
	2.7

If the two nitrogen atoms in the pyrazolidine-3,5-dione ring are replaced by two equivalent –CH=CH– groups, we obtain system LXXXVI, the enol form of which (LXXXVII) strongly recalls tropolone:



(LXXXVI) (LXXXVII)

In this connection it is of interest that azulene, which contains a seven-membered ring and is, in our opinion, related to pyrazolidine-3,5-dione possesses, like the latter, antiphlogistic activity[197].

Thus on the basis of available data, it can be assumed that pyrazolidine-3,5-diones also belong to the class of non--benzenoid aromatic systems which possess in addition properties typical of compounds with an active methylene group.

VII. APPLICATIONS OF PYRAZOLIDINE-3,5-DIONES

Pyrazolidine-3,5-diones have had a very wide application in medicine. Besides Butadione (I), which is used extensively to treat rheumatic and inflammatory illnesses[198-200], 1,4-diphenylpyrazolidine-3,5-dione (LXXVIIIb), 4-n-butyl--2-*p*-hydroxyphenyl-1-phenylpyrazolidine-3,5-dione (LV), and 1,2-diphenyl-4-(β-phenylsulphinylethyl)pyrazolidine--3,5-dione (XI) are used clinically. Besides the large number of papers devoted to a thorough study of the biological properties of Butadione, there are a number on the pharmacological properties of other representatives of this

group[201-207]. However, the total number of pharmacological tests which have been made is comparatively small. In addition, different workers have used different methods to test for antiphlogistic activity, the most valuable property of pyrazolidine-3,5-diones. Consequently, the results produced for the same compound by different workers do not always agree. The relation between structure and physiological activity in these compounds is not known definitely although the available data permit certain conclusions to be made:

(1) The pyrazolidine-3,5-dione ring possesses specific antiphlogistic action because replacement of the nitrogen atoms in the ring by carbon produces inactive compounds[201].

(2) Substitution of the oxygen atom of a carbonyl group by sulphur does not impair the antiphlogistic and antipyretic properties of pyrazolidine-3,5-diones[204].

(3) Introduction of substituents, *e.g.* a carboxylic acid group, into the phenyl group of compounds of the Butadione type reduces their toxicity markedly[201]. A sulphonic acid group in this position reduces the toxicity even more[190,208]. Such compounds — (LXXIXa)–(LXXIXc), (LXXXI) — are practically non-toxic to animals.

(4) The most active compounds in a series of 1-phenyl- and 1,2-diphenyl-4-monoalkylpyrazolidine-3,5-diones are the 4-n-butyl derivatives.

In addition a number of compounds with other substituents at C_4 which are not worse than, and sometimes even surpass, Butadione in antiphlogistic activity and which are also less toxic have been synthesised. They are, for example, 1,2-diphenylpyrazolidine-3,5-diones containing 4-(γ-hydroxybutyl)[209], 4-(γ-oxobutyl)[210], and 4-diethylaminoethyl[206] groups.

The relation between pK_a and uricolitic activity found in a series of 4-monosubstituted 1,2-diphenylpyrazolidine-3,5-diones[195,196] is of great interest and may prove useful in the search for new uricolitics.

Methods of qualitative and quantitative analysis have been developed for pyrazolidine-3,5-diones. The available data on their characteristic colour reactions concern mainly compounds used in medicine[211-215]. Paper chromatography is often used for analysis. Originally water-saturated systems containing butanol or benzene[216,217] were used for the development but the use of water, in which the solubility of Butadione is only 1 : 11 000,[211] as the stationary phase did not give satisfactory results since the R_f values were then close to 1. Chromatographic methods were soon developed in which the paper was impregnated with a non-aqueous phase, *e.g.* a 50% solution of formamide in acetone or a 2.5% solution of petroleum jelly in ether[218], or a tartrate buffer[219]. This method was found to be useful in an industrial laboratory[220,221].

Quantitative determinations include gravimetric[220,222] volumetric[159,211,212,223,224], and spectrophotometric[188,218,225,226] methods and the microdetermination of nitrogen[211].

It was discovered recently that, apart from the range of effects valuable in the treatment of rheumatic and inflammatory illnesses, pyrazolidine-3,5-diones also possess other interesting properties, in particular selective insecticidal action[227-230]; the 4,4-dichloro-derivatives possess hypoglycemic action[120]. Pyrazolidine-3,5-diones are used as solubilising media[59,231,232] for water-insoluble medicinal preparations, and also in colour photography[233-236] and as antioxidants[237].

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INTERACTION OF DYES WITH SUBSTANCES OF HIGH MOLECULAR WEIGHT

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1. INTRODUCTION

In the technically important problem of the interaction of macromolecular substances (polymers) with complicated organic dye molecules, which underlies the dyeing of animal and vegetable fibres, we encounter combinations of various types of polymers and of dyes, both ionogenic and non-ionogenic; each individual case must be expected to have its own mechanism of interaction and its own type of bonding.

Increasing attention has recently been paid to a particular aspect of this problem — the interaction of polymer and dye *ions*, with an electrostatic type of bonding. We come up against this in practical work in various branches of chemistry, for example photographic chemistry in the optical sensitisation of photographic emulsions, histochemistry in the use of staining to differentiate tissues, and finally in the chemistry of surface-active agents in identification of the latter with dyes.

In all cases we are concerned with the same phenomenon — a change in the absorption spectrum (and also in the intensity of fluorescence) of the dye, which produces a change in colour of the material (in histochemistry this phenomenon has been termed "metachromasy" — for reviews see Refs. 1–4). This makes the application of the spectroscopic method of investigation especially fruitful.

In each of the above fields the use of this technique has led to definite advances, but nevertheless difficulties arise in practical work, indicating that insufficient study has been made of the problem. In several cases the results in different fields supplement one another; a detailed comparison of them should contribute to further progress. The purpose of the present review, which examines all the results obtained from a unified viewpoint, is to report the present position of the problem of the interaction of ionogenic high polymers and dyes in the above fields.

The fundamental condition for the formation of new absorption bands in the interaction of polymer and dye ions is that the ions should bear charges of opposite sign. Few data are available on the interaction of anionic dyes with cationic polymers; the combination of cationic dyes with anionic polymers has been studied to the greatest extent, and it is there that the main generalisations have been made.

Before passing to an account of work on the changes undergone by the spectra of dyes on interaction with polymers, we should briefly recall the properties of the most typical polymers (termed "chromotropes" in the literature on metachromasy), and also the spectral properties of the dyes employed.

2. MACROMOLECULAR SUBSTANCES PRODUCING A CHANGE IN THE COLOUR OF A DYE ("METACHROMASY")

Numerous investigations show[3] that, in addition to actual macromolecular substances of high molecular weight, substances of low molecular weight which can associate to form micelles of high molecular weight, are also effective.

Chromotropes of the first type include macromolecular electrolytes[5,6] from various sources; substances of anionic character investigated include polyelectrolytes of animal[7] (heparin†, chondroitin sulphate, hyaluronate, nucleic acids) and vegetable (agar-agar[8], alginates) origin, inorganic (silicates, polyphosphates), and finally synthetic (chitin sulphate, carboxymethylcellulose, polyacrylates). These polymeric substances contain hundreds of ionogenic groups

† Heparin is a substance, formed in the liver, which diminishes the coagulability of blood.

per molecule. The most effective are negatively charged groups: SO_4^- (agar-agar), SO_3^- (heparin), PO_3^- (nucleic acids), COO^- (chondroitin sulphate, hyaluronic acid), CH_3COO^- (carboxymethylcellulose). In most cases they have the structure of linear polyions with periodically repeating simple units. Proteins are amphoteric electrolytes[7,9,10]. Among anionic groups, carboxyls are of greatest value; the radicals of basic amino acids (arginine, lysine, and histidine[11]) act as cationic groups.

Chromotropes of the second type include anionic and cationic surface-active substances[12]: soaps and wetting agents (detergents), both natural[3] and, chiefly, synthetic, having long hydrocarbon chains (C_8–C_{20}) containing ionogenic groups at one end (in anionic substances SO_3^-, OSO_3^-, OPO_3^-, COO^-, with Na^+ ions for electrical neutrality)[13]. Surface-active substances include also the so-called colour couplers, which are necessary ingredients of each of the individual layers in multilayer materials for colour-photography[14].

3. SPECTRAL PROPERTIES OF SOME ORGANIC DYES IN THE DISSOLVED, ADSORBED, AND SOLID STATES

Dyes exhibiting metachromasy are limited to those which are water-soluble and saltlike, the dyeing ions being either positively charged (basic dyes) or negatively charged (acid dyes).

Basic dyes which have been examined in combination with substances of high molecular weight belong to various classes — thiazine, oxazine, azine, triphenylmethane, xanthen, acridine (see Table 2A), and finally polymethine, these last being used in the optical sensitisation of photographic films. Few acid dyes have been investigated (some azo dyes and xanthen dyes of the fluorescein series) (see Table 2B).

Many recent investigations have established that saltlike dyes can exist in different states in aqueous solution — as separate ions ("monomers") and in larger ionic aggregates. It is assumed to a first approximation that a solution contains a mechanical mixture of the various forms in a state of mobile equilibrium.

Each of these states of aggregation is characterised by its own absorption band in the visible region; disturbance of the equilibrium by some factor (the most important of which are temperature and concentration) produces a redistribution of the states with a corresponding change in shape of the curve[15-24] (Fig. 1). The intersection of all the curves in a single point (at 21 000 cm^{-1} in Fig. 1) indicates that only two states of the dye are present.

In some cases (Acridine Orange[21-25], polymethine dyes[26,27]) this situation is changed by an increase in concentration or a fall in temperature (Fig. 2 in Ref. 22, lower curves in Fig. 1), indicating the appearance of new states. Absorption bands corresponding to three states are shown particularly distinctly in the spectrum of several polymethine dyes (Fig. 2). In conformity with the terminology of Sheppard[28], these bands and the corresponding states of aggregation are denoted by the letters α, β, and γ; the β and γ bands are attributed to associated states of the dye.

The availability of a family of curves at different temperatures enables us to determine the heat of association[17,21,27,29-31]; from a series of curves for different dye concentrations we can determine the "order of association"

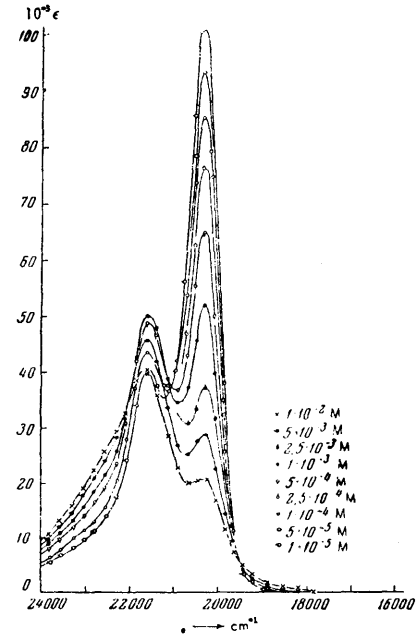


Fig. 1. Absorption curves for ether–alcohol solutions of Acridine Orange at -183° with different dye concentrations[22].

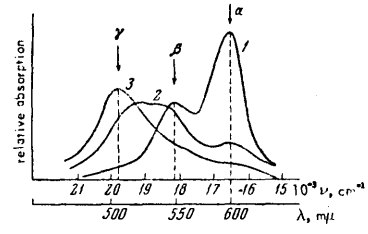


Fig. 2. Absorption curves for aqueous solutions of Pinacyanol chloride at different concentrations (M):
1) 3.2×10^{-6}; 2) 1.2×10^{-4}; 3) 1.8×10^{-3}.[26]

n by application of the law of mass action (Ostwald's dilution law). For the β centres we obtain $n \simeq 2$,[22,26,29] which indicates that they are dimeric in character; the α band corresponds to monomeric ions. The γ bands are produced by larger aggregates.

Sometimes a series of curves exhibit a second common point of intersection (at 22 000 cm^{-1} in Fig. 1), which indicates that centres of a third state are of the same kind. In conformity with Scheibe's view[26,33-40] of the dimer as the main "structural unit" in aggregates, the third state is regarded as tetrameric in these cases[21-23]. The absence of a second point of intersection (which is often observed) indicates the presence of still higher aggregates.

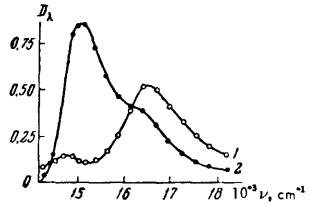


Fig. 3. Optical density curves (optical path 10 mm) for Methylene Blue in aqueous solution at 25°:
1) dimeric form; 2) monomeric form[17].

TABLE 1.

Dye	λ_{max}, mμ				Intensity ratio β_1/β_2	Remarks
	β_1	α_2	α_1	β_2		
1. Methylene Blue[17,18]	605	610	665	678	1 : 0.3	
2. Thionine[41]	545	—	596	625	1 : 0.2	
3. Acridine Orange[22,28]	465	464	495	500	1 : 0.3	at −183°C in alcohol solution[22]
4. Pyridocyanine dye[47]	457	457	495	510	1 : 0.2	at 77°K in a mixture of isopropanol and isopentane
5. Rhodamine B[43]	524	—	554	559	1 : 0.7	
6. Fluorescein						with dyes Nos. 6 and 7 dimerisation becomes appreciable only at concentrations of 0.01 M[43]
Ref. 43	472	—	496	505	1 : 1	
Ref. 42	472	—	492	512	1 : 0.	
7. Eosin[43]	495	—	517	522	1 : 0.9	
8. Chlorophyll a[49,50]	648	—	665	682	1 : 2.1	at room temperature in ethanol

From a knowledge of n we can obtain from the same set of curves values of the equilibrium constant (the weight fraction of the dye which is in the aggregated state) for each given case, and also absorption curves for the monomer, dimer, and higher aggregates in a pure form[17,25,41-43].

The absorption curves of the monomer and the dimer are each found to have two maxima (Fig. 3), while those for the tetramer have three.

The subsidiary maximum on the monomer curve, usually observed in the spectrum of a dye in organic solvents (with polymethine dyes two such maxima are observed[26]), is assigned[32] to vibrational transitions accompanying the main electronic transition $0 \rightarrow 0$ (α band). The intensification of these secondary bands ($0 \rightarrow 1$, $0 \rightarrow 2$) with dimers or higher aggregates was used to explain[21,22,25,32,33] the predominance of the corresponding maxima in the spectrum of aqueous solutions. Another view has been expressed recently, according to which[43-46] the excited state splits symmetrically into two, one of higher and one of lower energy than the original state, when two monomeric ions approach one another; the two maxima on the curve for the dimer correspond to these states.

Quantum-mechanical considerations based on crystal-field theory lead to the conclusion[47-49] that possible transitions between the ground and split excited levels are governed by the geometrical arrangement of the molecular planes with respect to the "growth axis" of the aggregate. According to this theory, the dimer will have two bands only when the molecular planes are arranged as in a "house of cards". If the planes are parallel, only one of the two possible electronic transitions is allowed in the two extreme cases (when they are perpendicular and parallel to the "growth axis"), giving a band of shorter wavelength in the first case and of longer wavelength in the second.

Table 1 gives for several dyes the positions of the maxima due to the monomer (α_1 and α_2) and to the dimer (β_1 and β_2), and also the intensity ratios for the maxima β_1 and β_2; the fact that these last are different for dyes of different groups indicates, in conformity with what has been said above, that the dimers have different geometrical structures.

With several dyes the presence of ionic association can also be demonstrated by direct[51,52] physicochemical methods‡.

Thus with polymethine dyes of the pseudocyanine series[54] values of 3–6 have been obtained for n. In such cases the γ band predominates in the spectrum of aqueous solutions of the dye, even at low concentrations; the α band appears only when the solution is heated[320].

Binary association is possible also between ions of different dyes[55,56]; spectroscopic data show[55] that the ability of two dyes to combine with one another is greater the stronger the tendency of either of them to dimerise. Examination of the influence of solvent, temperature, and time of storage of the solutions indicates that the properties of "heterogeneous" complexes are analogous to those of ordinary "homogeneous" dimers.

In addition to selective light absorption, an important optical characteristic of solutions of several dyes is their luminescence. By no means all complicated organic molecules possess this property: of the above dye groups which exhibit metachromasy, only xanthen and acridine dyes luminesce (at room temperature).

A peculiarity of the fluorescence of complicated molecules is the existence of the so-called mirror-image symmetry of the absorption and luminescence spectra (Levshin's law)[15,16] with aqueous solutions of dyes capable of association (this applies to the monomers). In most cases dimers and higher aggregates (β and γ) do not luminesce[25,57], which is the main reason for the extinction of fluorescence with rise in concentration of the dye solution[15,57-61].

At high concentrations (0.01 M) the absorption spectra of aqueous solutions of some cationic polymethine dyes contain, at the longer wavelengths (relative to the α band), yet another absorption band (Fig. 4, curve *3*), which is very narrow (one-sixth of the width of the α band). In conformity with Sheppard's terminology[28], which is adopted also in the Soviet literature, we shall speak of the J band§ and hence of "J" structures.

A characteristic feature of these structures is their ability to luminesce, the position of maximum emission in

‡ With some azo dyes (Congo Red, Benzopurpurin), whose solutions form colloidal electrolytes[13], the degree of association determined by physicochemical methods may reach several hundreds[51,53].

§ This band was observed in an aqueous solution of pseudocyanine almost simultaneously by Jelley[62,63], after whom it was named, and by Scheibe, who, with his coworkers, investigated it in detail[26,33-40].

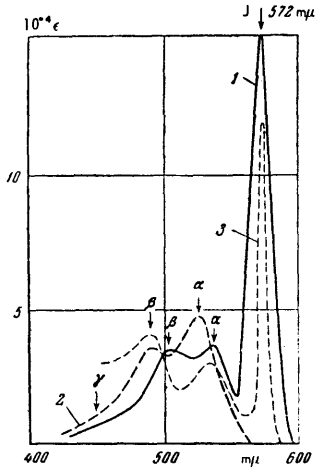


Fig. 4. Absorption curves for pseudocyanine (iodide):
1) in the presence of heparin, dye concentration $C_D = 5 \times 10^{-5}$ M, $C_{hep} = 10$ international units ml^{-1} in 0.16 M ≃ 0.95% ≃ isotonic NaCl solution[126]; 2) $C_D = 5 \times 10^{-4}$ M without heparin[126]; 3) $C_D = 1.05 \times 10^{-2}$ M, in relative units[27].

the spectrum almost coinciding with the absorption maximum¶. On the basis of the work of Scheibe and his collaborators[26,33-40] it is now accepted that these peculiar phenomena are caused by highly aggregated, polymeric threadlike structures formed by dye *ions*†, the presence of which produces a marked changed in the physicochemical properties of the solution (in particular an increase in viscosity leading to gel formation). According to Scheibe, individual ions in this aggregate are arranged in a regular order (like packs of cards); interaction between the π-electron clouds of separate ions arranged parallel to one another results in the formation of a single new cloud for the whole system. The minimum number of ions in such an "ordered aggregate" is of the order of tens and hundreds at room temperature, and about three at -183°.[40] As in the case of "heterogeneous dimerisation", here, too, the absorption resulting from the mixing of two dyes is not additive, a new J band being formed having properties intermediate between those of the bands due to the individual components of the mixture[26,34]. This shows that ions of the two dyes enter alternately into the polymeric structure, as is the case in mixed crystals.

The effect is shown best in the pseudocyanine group of dyes, in which the J bands are most narrow (4–7 mμ) and intense, their position varying from 574 to 604 mμ.[38] With polymethine dyes of other groups (carbocyanines and thiacyanines) the bands are wider (~ 15 mμ) and less intense. Among dyes of other types, only Rhodamine B in supersaturated aqueous solution has been shown to have such a band (of half-width 6 mμ)[43]. Differences in the positions of the maxima observed on passing from one dye to another are linked with the interplanar spacings along the axis of the polymer; the position of the maximum is unaffected by change in the anion of the dye[38], which supports the above view that it is the dye *ions* which polymerise. With rise in temperature the J bands are displaced towards longer wavelengths and become somewhat broader[34,40] (for the effect of low temperatures see Ref. 65). We shall return below to some other peculiarities of J bands which testify to the complexity of the J state, in connection with the properties of the adsorbed and solid states of polymethine dyes, where these characteristics are more strongly developed.

The association of dye ions to form dimers and other (including J) structures is considerably facilitated by the presence of electrolytes, as has been established by both physicochemical[51] and spectroscopic[15,21,54,57] methods. Thus the addition of salt (0.3 M NaCl) to an aqueous solution of Methylene Blue (10^{-4} g ml^{-1}) is equivalent[18] to increasing the dye concentration to 2.5 g ml^{-1}. With a still greater salt concentration (up to 1.5 M) and the same dye concentration the absorption maximum shifts to shorter wavelengths and the common point of intersection disappears, indicating formation of higher aggregates.

The introduction of organic compounds into an aqueous dye solution depresses the degree of association[18], pyridine and quinoline having the greatest effect.

The above association phenomena are most marked in aqueous solutions. It has been stated in several papers[28,38,39,65] that the presence of water is a necessary condition for association, but recent investigations have shown that the latter can be observed also in non-aqueous media[306], but at a different range of dye concentrations. Thus Rhodamine dimerises in water between about 10^{-4} M and 10^{-3} M, in glycerol at about 10^{-2} M, and in ethanol at about 10^{-1} M. At lower concentrations in alcoholic solutions this effect is observed on strong cooling (formation of J bands with pseudocyanine[40] and of dimers with Acridine Orange[22] and a pyridocyanine dye[47] at -183°).

The exceptional influence of water has been attributed to its high dielectric constant[21,22,27,40]. Recent work has shown, however, that the dielectric constant cannot be regarded as the dominant factor in the aggregation of dye ions. In fact, the ability of dyes to associate in single and mixed[19,66,67] solvents may differ greatly even when the physicochemical properties (in particular the dielectric constant) of the solvents are the same: the chemical nature of the solvent is of decisive importance. Furthermore, association, of the same type as in aqueous solutions, is observed both with similar and with different ions in some weakly polar media[41,61] (mixed solvents, for example dioxan + methanol), in spite of their low dielectric constant‡.

The above facts can be explained by intermolecular hydrogen bonding[52,67]. If OH and NH groups are present in the dye molecule, a hydrogen bond is formed[67] directly between its molecules; if such groups are absent, hydrogen bonding can occur *via* the intermediary of water molecules.

¶ Besides this "resonance" emission band, another, weaker luminescence band has been observed[27,35,57,64,65] at about 40 mμ from the first band on its long-wavelength side.

† Jelley[62,63], on the other hand, attributed them to threadlike individual undissociated molecules.

‡ A change in spectrum (redistribution of intensity at the maxima) with change in composition of the binary mixture occurs also with some non-saltlike dyes (for example with porphin colorants in aqueous acetone mixtures), and is also attributed[68] to association of their molecules.

If the structure of dye and solvent molecules is such that hydrogen bonding occurs predominantly between them, the association of dye molecules with one another is made more difficult.

From all that has been said (see also Ref.304) it is clear that the molecular structure of the dye plays an important part, both with respect to the possibility of hydrogen bonding and from the geometrical[69,70] point of view, in association phenomena of all types: indeed, it has been pointed out repeatedly[28,32,36,54,69,71-74] that a planar structure of the dye molecules is the fundamental condition for polymerisation. Quantitative support for the important role of the spatial arrangement of the parts of the molecule has been obtained[27] from a study of the tendency to association (assessed from the association constant and the binding energy of the aggregates) of a group of cyanine dyes.

When a dye capable of giving polymeric structures in aqueous solution undergoes physical adsorption[75-77], corresponding maxima appear in the spectrum of the adsorbate[78-81]. The proportions of the different structures are considerably influenced by the physicochemical properties of the adsorbent surface§ in addition to the solvent. Sometimes new maxima appear on adsorption (at 715 mμ with Methylene Blue)[83,84,305-307].

On adsorption the absorption maxima of dyes are displaced to shorter or longer wavelengths relative to their position in solution. The magnitude of the shift varies between 0 and 50 mμ. Appreciable differences in the shifts produced by adsorption on silver halides can be observed even within the same class of dyes[85,86]. (This holds also for the dyes formed when colour-photographic materials are developed[87].)

Much of the above applies also to J structures. When dyes of the polymethine type are adsorbed on mica, quartz, and other substances (silver halide microcrystals in a photographic emulsion) having negatively charged free groups on their surface, the J maxima usually appear at lower concentrations[37] than in water (10^{-4} M); they are displaced[38] compared with the position of the maxima in aqueous solution, and are also broader and weaker. Several structural details of J centres (the relative position of the ions, the slope of the planes of the ions with respect to the polymer axis, etc.) have been established by Scheibe and his coworkers[33-40] purely on the basis of adsorption experiments (and also on the orientation of the dye in a flowing concentrated aqueous solution). In particular, it has been established that the oscillations of the electric vector corresponding to the J band absorption and fluorescence take place parallel to the polymer axis. This conclusion was confirmed by other work[65], and also by more recent results[88] obtained from measurements of the polarisation spectra of stretched films of poly(vinyl alcohol) coloured with a pseudocyanine dye.

The ability of complex organic substances to luminesce is retained on adsorption. The spectra distribution of the fluorescence of dyes in the adsorbed state[89-91] indicates a shift to one side or the other relative to the luminescence spectrum in solution[89].

The absorption spectra of solid (semi-transparent) layers of dyes on different substrates depend[92-95] on the conditions of application. Their general features correspond to the spectra of concentrated solutions (this holds in particular for films which have been sublimed and examined under vacuum conditions). Sometimes the α and β bands can be traced quite clearly; in addition, bands characteristic of the crystalline state[96-98] appear, and also bands which are probably due to interaction with the substrate.

Thin films of polymethine dyes, in particular the pseudocyanines, also reveal the presence of J centres, in a series of modifications. As in the case of adsorption, the absorption bands of these centres are wider and weaker than in solution; resonance fluorescence is not observed. Depending on the experimental conditions (the presence of water), the separation of crystals of the dye can be observed in addition to the polymeric (ionic) state¶. Films obtained by the evaporation of concentrated solutions show[65,71] a new band of the J type, weaker and located near the α band; the oscillations of the electric vector are in a plane perpendicular to the polymer axis. This band is assigned[65] to fibres formed by parallel and interlinked J filaments. Another example of the complexity of the J state is the presence of a doublet structure in the absorption band observed with solid films of some pseudocyanine dyes[38] (in solution two bands, 10 mμ apart, have been observed only with one of these dyes)[38,39].

A still more complicated situation is found in the spectroscopic examination of a single film[38] of one of the above dyes: the position of the band maximum varies by 3 mμ at different points in the layer, and at the outset (as the film dries out) a band appears at shorter wavelengths, then suddenly changes its position and becomes wider. This phenomenon is influenced by the anion of the dye, indicating that the anion may be incorporated into the polymeric structure (anions must be involved in a solid film, from electrostatic considerations).

A doublet band (with the components 15 mμ apart) has been detected also[99] in the diffuse reflectance spectrum of polymethine (carbocyanine) dyes adsorbed on silver halide grains in a photographic emulsion.

Organic dyes in various states possess well defined photochemical properties[77,100-104].

The transformations of light energy occurring when adsorbed dyes are illuminated find wide application in the sensitisation and desensitisation of photographic emulsions (*e.g.* Refs.14, 77, 105–113).

The relative effectiveness of the various states of dyes in photographic films may vary within wide limits, owing to the above differences in the relative proportions of the different types of structure, depending on the physicochemical conditions at the surface of the silver halide.

A characteristic feature of solutions containing associated ions is their stability: precipitation does not occur even with a high degree of association . Such solutions

§ This gives a very delicate method for investigating the surface of absorbents; it has been used for a long time for the practical analysis and classification of clays[82-84]. On adsorbing such dyes as Methylene Blue, clays from different sources give appreciable differences in shade, caused by differences in intensity of the monomer and dimer bands in the spectrum.

¶ The appearance of a J band when an aqueous solution is "frozen out", as is observed[65] at temperatures up to -195°, should probably be attributed either to the separation of the dye in the solid state or to its adsorption on small crystals of ice.

differ in this respect from those containing aggregates of *neutral molecules*: in the latter case we are dealing with a colloidal solution of the dye, in which are suspended particles having a "phase interface"†; in time such particles separate out from the solution.

The optical properties of colloidal solutions of strongly absorbing substances (metals, dyes) are characterised by selective absorption and, when the particle size is sufficient, selective scattering. The spectral variation of the absorption and scattering can be calculated from the Rayleigh–Mee formulae for the optical properties of colloidal solutions [116-118]. Let us recall the main principles: (*a*) the intensity of both absorption and scattering depends on the particle size: in particular, with sufficiently fine particles scattering is absent, and the solution is optically clear; (*b*) the position of the absorption and scattering maxima, their half-widths, intensities, and also the type of dependence on particle size are entirely determined by the spectral variation and absolute magnitude of the optical constants‡ of the substance in the massive (solid) state. In particular, the positions of the maxima may vary to a greater or a lesser extent with the size of the particles§. When n increases on passing to longer wavelengths, which is the case with most metals, an increase in particle size is accompanied by a displacement of the maximum towards longer wavelengths. When the dispersion of the solid film changes in the opposite sense, an increase in particle size may cause the maximum to shift to shorter wavelengths.

The optical properties of dyes in the solid (massive) state are distinguished by the fact that the absolute values of the refractive index of the solid film are in the same sequence as the absorption coefficient κ_λ, and in conformity with this [116,118], according to the optical laws for colloidal solutions, the position of the bands roughly coincides with that of the maximum κ. In several cases the position of the latter approximately coincides with that of maximum absorption in a true solution; it can then be said that λ_{max} of a true (α) and a colloidal solution are close to one another. Such is the case with Fuchsine, for which the applicability of the Rayleigh–Mee formulae has been verified [118]. We can therefore speak of the similarity of the absorption maxima of colloidal (which we shall denote by the letter K) and true (α) solutions only to the extent that the latter corresponds to the maximum κ_λ. The same considerations apply also to the half-width of the absorption maximum. With polymethine dyes the maxima on the κ_λ curve and also in solution are very narrow; the maximum for the colloidal solution has a similar form.

The experimental preparation of colloidal solutions of readily soluble dyes involves several difficulties. One method [118] consists in adding a drop of a true solution of the dye (in an organic solvent) to a solvent in which this dye is insoluble; then (if the first solvent dissolves in the second) the dye separates in the form of collodial particles having a phase interface. Their size can be controlled by adjusting the proportions of dye and solvents.

There are indications that in some cases new absorption maxima (which are undoubtedly colloidal) have also been obtained directly at high (~0.1 M) dye concentrations.

Table 2, which gives the positions of the absorption maxima of dyes in the presence of macromolecular compounds, includes for some dyes the wavelengths λ_K in colloidal solutions prepared experimentally.

Colloidal solutions of Methylene Blue (Table 2A, II) have been obtained [121] by the procedure indicated above¶. With Toluidine Blue (Table 2A, V) the values of λ_K correspond to a saturated (20 M) solution of the dye in water; the data were obtained by means of a specially developed lenticular cell [122]. With Methyl Orange (Table 2B, I) the dye was added to an organic solvent in which it was almost insoluble [123].

4. SPECTRAL DATA ON THE INTERACTION OF DYES WITH MACROMOLECULAR SUBSTANCES HAVING OPPOSITELY CHARGED IONS

With cationic dyes the spectral changes produced by adding a macromolecular substance of anionic character to an aqueous solution of the dye consist mainly in the appearance of a new absorption maximum at shorter wavelengths† than the α–γ bands; when the concentration of macromolecular compounds is increased, a maximum appears on the long-wavelength side.

Fig. 5 shows a typical gradual change in spectrum of a dye (in this case a thiazine dye) produced by addition of deoxyribonucleic acid (DNA) [124]. A similar pattern is observed with other combinations of dye and high polymer [125-163].

The long-wavelength maximum is generally considerably more intense than the α maximum, and in several cases, but not always, is displaced to longer wavelengths (in the present case by ~10 mμ). Hence it must be different in nature [130-132,165,166] from the α maximum (see Section 5); we shall denote it by the symbol α' (see also Ref. 308).

Fig. 6 shows the variation in intensity of the α and short-wavelength maxima with the concentration of macromolecular substance (see also Refs. 11, 144, 151, 161, and 167–172). It is clearly seen that the range of concentrations of the latter at which the short-wavelength maximum is most strongly developed (the "optimum range") corresponds to the range of the greatest fall in the α maximum.

† Such solutions (which include also the esters of leuco vat dyes [114,115]) are quite different in nature from the above colloidal electrolytes (Congo Red, etc.) [5,13] having large charged micelles.

‡ At the present time values of the optical constants are known for only a very small number of dyes [119]. In particular, data are lacking on the oxazine and thiazine dyes, since in air solid films of these dyes are extremely rapidly converted into colloidal dispersions; the optical constants can be determined (by the method of Kravets *et al.* [120]) only for specular layers.

§ Thus with colloidal solutions of Na (in NaCl) the shift $\Delta\lambda_{max}$ is very large [116], ~20 mμ for a change in particle diameter 2ρ from "0" (the "finest" particles, when $2\rho/\lambda \to 0$) to 20 mμ; with Cu or Au, on the other hand, it is small, the adsorption curve remaining practically unchanged for a change in particle size 2ρ from the "finest" to ~60 mμ [117]. In this respect Fuchsine [118] occupies an intermediate position, λ_{max} remaining unchanged from the "finest" particles to those of ~20 mμ.

¶ When an electrolyte is added in high concentration to a dye solution, a precipitate is sometimes formed ("salting out"). In the case of Methylene Blue this deposit has a purple colour, as do colloidal solutions of this dye [121] ($\lambda_{max} \simeq 545$–560 mμ), which indicates that colloidal particles of the dye have separated out. A similar effect probably occurs in tablets of KBr + Methylene Blue [305].

† Sometimes it may arise on the long-wavelength side of the band (Rhodamine).

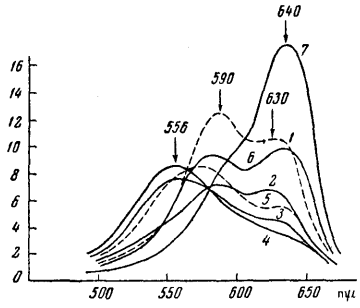


Fig. 5. Absorption curves for aqueous solutions (5×10^{-5} M) of Toluidine Blue in the presence of different concentrations (M) of deoxyribonucleic acid[124]:
1) 0; 2) 2.5×10^{-5}; 3) 4×10^{-5}; 4) 5×10^{-5}; 5) 2.5×10^{-4}; 6) 5×10^{-4}; 7) 2.5×10^{-3} M.

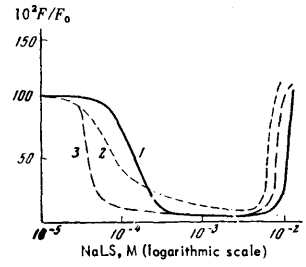


Fig. 7. Dependence of intensity of luminescence of dyes on concentration of NaLS for[150]:
1) Rhodamine 6G; 2) Trypaflavine; 3) Acridine Yellow.

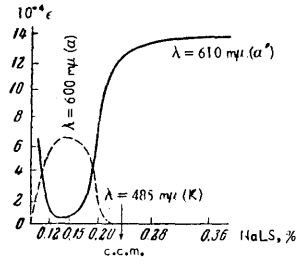


Fig. 6. Variation in intensity of α (α') and K maxima for 10^{-5} M Pinacyanol chloride with concentration of NaLS.[166]

A similar situation is found for bands arising on the short-wavelength side of the α–γ maxima in solutions of polymethine dyes with gradual change in the concentration of gelatin[173]. (In the scientific literature on photography these are termed "H bands"[14,73,173-176].)

A similar pattern is observed for the variation in intensity of the fluorescence of luminescent dyes on gradual addition of a macromolecular substance (Fig. 7)[150], this being parallel to the variation in intensity of the α band[144]. An appreciable increase in intensity of fluorescence (which is approximately doubled) compared with the region of the α band is observed also[131,132] in the region of the α' band. (For the quenching of luminescence at low polymer concentrations, see also Refs. 125 and 177–183).

Spectral data on luminescence are as yet limited to a few dye–polymer systems[184-187,309]. With increasing concentration of the latter, the luminescence band is displaced in the same direction as the absorption band: at first towards shorter, and then to longer, wavelengths compared with the luminescence band of the pure dye, in conformity with the law of mirror-image symmetry; the long-wavelength band should be attributed to luminescence of α' centres, and the short-wavelength band to that of the corresponding short-wavelength absorption centres. The intensity of emission in these bands varies: it is high for α and α' centres, and drops sharply at polymer concentrations corresponding to the formation of the short-wavelength absorption band, which makes it possible to assess the degree of interaction between polymer and dye[311]. With increase in polymer concentration, the degree of polarisation of the luminescence[184] remains low (as in an aqueous solution of the dye) up to a concentration corresponding to the minimum intensity of luminescence, after which it increases rapidly.

The extent of the "optimum" range, within which the short-wavelength maximum is most sharply defined, while the luminescence maximum is weakest, is different in the above groups of macromolecular substances. With surface-active agents combined with a polymethine dye (Pinacyanol) this range (assessed at 0.9 of the intensity of the short-wavelength maximum) is a fraction (0.3 in Fig. 6) of the polymer concentration at which the effect has its maximum development[135-139,166]; with other dyes it is rather wider (by factors of 1.5–2 in the case of a thiazine dye[146], and of 7 with Pyronine[148]). With polyelectrolytes combined with thiazine dyes and with Crystal Violet this region covers a factor of approximately one hundred in polymer concentrations[168,169]; with polymethacrylic acid and Rhodamine a fivefold difference is observed (according to luminescence data[184]). Nucleic acids, with which[124,170,171] the optimum range is very narrow, form an exception in the sequence of these substances. With gelatin and polymethine dyes[173] the width of the optimum concentration range exceeds the concentration at which the effect is a maximum by a factor of ~1.5.

Published values for the positions of the maxima with various combinations of dyes and polymers are collected together in Table 2. The most detailed data for most dyes (at different polymer concentrations) have been obtained for surface-active agents and also nucleic acids. With polymethine dyes results for polymers of the polyelectrolyte type, including gelatin, predominate; another group of polymers — the surface-active agents — is represented by the colour couplers used in colour development[212].

Table 2 includes the wavelengths of the maxima — $\alpha(\lambda_\alpha)$, $\beta(\lambda_\beta)$, $\gamma(\lambda_\gamma)$ — in aqueous (or aqueous-alcoholic) solutions of the dyes and, where available, values of λ for the J bands and of λ_K in colloidal solutions. Column 2

TABLE 2. Positions of absorption maxima of dyes in the presence of macromolecular substances*.

A. Cationic dyes + anionic polymers

Substance	λ_{max}, mμ		
	short wavelengths	long wavelengths	α′
1	2	3	4
Thiazine dyes			
I. Thionine, Lauth's Violet (C.I. 52000)**; λ_α = 596 mμ, λ_β = 545 mμ [42,188]			
Nucleic acid [158]	—	—	610
DNA [189,198]	—	—	605, 619
RNA[b] [190]	—	—	617
Mucin	535	—	—
NaLS[c] [146]	510	635—645	602
Na cellulose sulphate [193]	495	—	—
	510—535	635—645	α′—α=6—23
II. Methylene Blue (C.I. 52015); λ_α = 665 mμ, λ_β = 605 mμ [17,18], λ_K = 545—580 mμ [121]			
Nucleic acid [130]	—	—	670
$ChSO_4$[d] [162,251]	570	—	—
Agar-agar, Ref. 191	562±3	—	—
Ref. 160	560	—	—
Ref. 1	~565	—	—
Polyacrylate [192]	585	—	—
Polyacrylic acid [192]	590	—	—
NaVin[e] [192]	573	—	—
NaSPVA[f] [192]	567	—	—
KPVS[g]	550—560	—	—
NaLS [146]	(510?) 560	~750	665
Gelatin 2221 [191]	~565	—	—
Gelatin 12350 [191]	~570	—	—
Na cellulose sulphate [193]	565	—	—
	550 590	~750	α′—α=0—5
III. Azure A (C.I. 52010); λ_α = 620 mμ, λ_β = 590 mμ			
RNA [162]	—	—	640
Heparin [129,142,162]	525, 525, 530	—	—
$ChSO_4$ [129,162]	540, 550	—	—
Cartilaginous tissue[h] [127-129]	545, 550	—	—
Hyaluronic acid [129]	(510), 550	—	—
Rice starch [129]	(500)	—	—
Mucoid film[i] [127]	550	—	—
Na pectinate [162]	545	—	—
Metaphosphate [162]	530	—	—
TPBS[j] [162]	(510)	—	—
KSCN [162]	520	—	—
Na cellulose sulphate [193]	513	—	—
	510—550	—	α′—α=20
IV. Methylene Green (C.I. 52020); λ_α = 655 mμ, λ_β = 605 mμ			
KPVS [146]	~550	—	658
NaLS [146]	~530	~720	655
	530, 550	~720	α′—α=0—3

Also: thiazine and oxazine dyes + biological colloids [131,132,193] + inorganic polymers [196,198]; Azure A + KI [162].

V. Toluidine Blue (C.I. 52040); λ_α = 630 mμ, λ_β = 600 mμ [191], λ_K = 540—560 mμ [122]

Nucleic acid [158,163]	580	—	640, 648
DNA [124,164]	558, 560	—	640
RNA, Refs. 124, 196	—	—	640
Ref. 196	589	—	650
Heparin [197,198]	530, 520	—	—
$ChSO_4$ [196,199]	545, 550	—	—
Agar-agar, Ref. 191	537± 2	—	—
Ref. 1	540	—	—
Ref. 100	540	—	—
Carragheenin[k] [196]	540	—	—
Cartilaginous tissue [199]	555	—	—
Na pectinate [189]	555	—	—
Na arabate [189]	565	—	—
Na alginate [189]	555	—	—
Amyloid [199]	560	—	—
Silicate [200]	540	—	—
Na_2O, $3.3SiO_2$ [156,157]	535, 560	—	—

TABLE 2 (contd.)

1	2	3	4
Na_2O, Si_2O_5 [191]	558± 1	—	—
Na_2SiO_3 [191]	556± 1	—	—
Hexametaphosphate [130]	520	—	—
Carboxymethylcellulose, Ref. 191	550± 1	—	—
Ref. 158	550	—	—
Polyacrylate [192]	555	—	—
Polyacrylic acid [192]	570	—	—
NaVin [192]	555	—	—
SPVA [192]	540	—	—
KPVS [192]	(490) 540	660	—
Gum arabic [196]	560	—	630
Aerosil [22,188]	(500)	700	635
NaLS, Ref. 146	(490)	700	635
Ref. 163	578	670	638
Na oleate [158,163]	570	—	630
Na arginate[l] [141]	540	—	—
Gelatin 2221 [90]	560	—	—
Gelatin 12350 [90]	575	—	—
NaLS + alcohols [312]	(486—500)	676	635—640
	520—575	—	α′—α=20
Oxazine dyes			
VI. Capri Blue (C.I. 51015); λ_α = 660 mμ, λ_β = 610 mμ [160]			
Nucleic acid [160]	—	—	657
	—	—	α′—α=15
VII. Nile Blue (C.I. 51180); λ_α = 650 mμ, λ_β = 600 mμ [157]			
Na_2O, $3.33SiO_2$ [157]	570	—	—
Na cellulose sulphate [193]	560	—	—
	560—570	—	—
Azine dyes			
VIII. Phenosafranine (C.I. 50200); λ_α = 523 mμ [190]			
Nucleic acid [160]	500	—	540
DNA [190]	?	—	544
RNA [190]	?	—	542
Depolymerised DNA [190]	—	—	(523)
	—	—	α′—α=17—21
IX. Safranine (C.I. 50240); λ_α = 520 mμ [190]			
DNA [190]	?	—	541
RNA [190]	?	—	543
Na_2O, $3.3SiO_2$ [156]	510	—	—
	~510	—	α′—α=21—23
Triphenylmethane dyes			
X. Fuchsine base (C.I. 42510); λ_α = 543 mμ, λ_β = 480 mμ [160], $\lambda_K \simeq$ 500 mμ [118]			
Nucleic acid [160]	—	—	560
Agar-agar [160]	485	—	—
	—	—	α′—α=17
XI. Rosaniline hydrochloride (C.I. 42500, 42510); λ_α = 545 mμ, λ_β = 475 mμ [152]			
DNA [182]	470	590	560
	470	—	α′—α=15
XII. Crystal Violet (C.I. 42555); λ_α = 590 mμ, λ_β = 540 mμ [160]			
Nucleic acid [160]	—	—	600
Heparin [169]	510	—	—
$ChSO_4$ [201,251]	510	—	—
Agar-agar [160]	510	—	—
Cartaginous tissue [199]	512	—	—
Bovine serum albumin [134]	—	—	610
Denatured	—	—	600
Natural			
Na_2O, $3.33SiO_2$ [157]	510	—	—
	510—512	—	α′—α=10—20
Xanthen dyes			
XIII. Pyronine G (C.I. 45005); λ_α = 545 mμ, λ_β = 510 mμ			
KPVS [130,143,181]	465	600	545
NaLS [146]	450	—	550
NaLS	—	—	560
	450—465	600	α′—α=0—15

Also: triphenylmethane dyes + surface-active agents [202] + nucleic acids [203] pyronine + nucleic acids [204,205].

TABLE 2 (contd.)

1	2	3	4
XIV. Rhodamine 6G (C.I. 45170***); λ_α = 527 mμ, λ_β = 500 mμ [87]			
DNA [190]	—	—	533
RNA [190]	—	—	536
Na alginate [161]	485	—	—
KPVS [150]	490	560	527
NaLS [149]	~504	565	535
K octyl sulphate [149]	—	570	532
Polymethacrylic acid [144]	510	—	527
	495—510	560—570	α′—α=0—10
Acridine dyes			
XV. Acridine Yellow (C.I. 46025); λ_α = 440—445 mμ [188]			
NaLS [149]	<350	490	455
DNA [188]	325—330	—	455—460
	350	490	α′—α=20
XVI. Acridine Orange (C.I. 46005); λ_α = 495 mμ, λ_β = 465 mμ [125], $\lambda_\gamma \simeq$ 445 mμ [26]			
DNA, Refs. 166, 205, 206, 309	—	—	507
Refs. 185, 207	465	—	502
Ref. 310	—	—	504
Refs. 308, 313	464	—	504
Ref. 314	464	—	—
RNA, Ref. 318	464	—	504
Refs. 166, 207	—	—	506
Heparin, Refs. 166, 207	450	—	502
Ref. 125	452	—	—
Poly-C^{m} [133]	435	—	—
Poly-U^{R} [166]	440, 450	—	498
Poly-P^{O} [166]	455	—	492
Poly-A [113]****	464	—	—
	435—465	—	α′—α=3—11
XVII. Trypaflavine (C.I. 46000); λ_α = 450 mμ, λ_β = 432 mμ			
KPVS [146,147]	432?	~500	—
NaLS [144,146]	440	~500	460
Silica gel [186]	—	—	460
	440	500	α′—α=10
XVIII. 3,6-Diamino-10-methylacridine Cl; λ_α = 450 mμ [188]			
DNA, Ref. 190	—	—	470
Ref. 185	430	—	465—470
RNA [190]	—	—	468
	430	—	α′—α=15—20
XIX. 3-Amino-7-dimethylaminoacridine; λ_α = 500 mμ			
DNA [190]	—	—	550
RNA [190]	—	—	550
	—	—	α′—α=50
XX. 2,8-Diaminoacridine sulphate (Proflavine); λ_α = 445 mμ [188]			
DNA, Ref. 208	—	—	462
Ref. 185	425	—	460
RNA [208]	—	—	462
	425	—	α′—α=15—77

1	2	3	4	5	6
Polymethine dyes					
XXI. 3,1′-Diethyl-5,6-dimethyl-8′-chlorothia-4′-quinocarbocyanine iodide; λ_α = 645 mμ, λ_β = 580 mμ, λ_γ = 550—560 mμ [191] (alcoholic—aqueous solution)					
Agar-agar [191]	540	—	—	—	—
Gelatin 2221 [191]	542	~700	—	—	—
XXII. 1,1′-Diethyl-2,2′-quinocyanine chloride (iodide); λ_α = 524 mμ, λ_β = 490 mμ, λ_γ = 454 mμ, λ_J = 572 [126] (574 [26]) mμ, λ_K = 400 mμ [27]					
Heparin [126]	400	566—572	538	508	—
$ChSO_4$ [126]	?	572	524	488	—
Hyaluronic acid	400?	575	524	490	454
NaPES^{P}	—	572	538	508	—
	400?	566—572	α′—α 0—14	β′—β 0—18	γ′—γ 0

TABLE 2 (contd.)

1	2	3	4	5	6
XXIII. 3-H-3′-Ethyl-4-oxo-5-[(3″-ethylbenzothiazolin-2″-ylidene)isopropylidene]-thiazolinothiacyanine iodide; λ_α = 600 mμ [173], λ_β = 550 mμ [173], J = 650 mμ [173]					
Gelatin 2221 [173]	470?	~650	600	~560	—
Gelatin 12350 [173]	500	~650	?	~550	—
	470—500	650	α′—α 0	β′—β 0—10	
XXIV. Pinacyanol chloride (1,1′-diethyl-2,2′-carbocyanine chloride); λ_α = 600 [26] (610 [136]) mμ, λ_β = 545 [26] (550 [209], 552 [138]) mμ, λ_γ = 510 [26] (522 [209], ≃530) mμ, $\lambda_K \simeq$ 480 mμ [29], λ_J = 635 mμ [27]					
Nucleic acid [189]	—	—	610	—	—
Heparin [160]	~490	640	—	—	—
Agar-agar [189]	480	~640	—	—	—
Silicates [154,155]	478—498	~640—640	—	—	—
TPBS [162]	~490	~650	—	—	~519
NaLS [154,158,167]	480, 185	—	615	570	—
			610	562	
KLS^{C} [136]	480	—	615	570	—
K oleate [136]	467	—	620	575	~537
K myristate [136]	480	—	613	570	—
K octanoate [210]	489	—	607	563	—
K nonanoate [210]	490	—	604	561	—
Gelatin, Ref. 209	~480	~630	(590)	(545)	—
Refs. 40, 211	~490	—	?	~575	—
	467—498	630—650	α′—α 4—15	β′—β 15—30	γ′—γ 9
XXV. 3,3′-Diethyl-4,5:4′5′-dibenzoxacarbocyanine p-toluenesulphonate; λ_α = 545 mμ [191], λ_β = 500 mμ [191], $\lambda_\gamma \simeq$ 480 mμ (aqueous—acetonitrile solution)					
Agar-agar [191]	455	—	—	—	—
Carboxymethylcellulose [191]	450	—	—	—	—
Gelatin 2221 [191]	455	—	~550	~510	—
Gelatin 12350 [191]	460	—	545	500	—
	450—460	—	0—5	0—10	—
XXVI. Pinachrome Blue (6,6′-diethoxy-1,1′-diethyl-2,2′-carbocyanine bromide); λ_α = 615 mμ [191], λ_β = 560 mμ [191], λ_γ = 525 mμ [191] (aqueous—alcoholic solution)					
Agar-agar [191]	503±0.5	—	—	—	—
$Na_2Si_2O_5$ [191]	508±0.5	~650	—	—	—
Na_2SiO_3 [191]	513±0.5	~650	—	—	—
Carboxymethylcellulose [191]	498±0.5	660—670 700	~610—615	—	—
Gelatin 2221 [191]	513±0.5	670—680	~635	~560	~540
Gelatin 12350 [191]	507±0.5	670—680	~635—640	~560	~535—540
	498—513	650—680	α′—α —5±25	β′—β=0	γ′—γ= =10—15
XXVII. 3,3′-Diethylthiacarbocyanine chloride; λ_α = 550 [209] (548 [212]) mμ, λ_β = 505 [209] (515 [212]) mμ, λ_γ = 475 mμ [211] (?)					
Gelatin [209]	?	~580	~560	505	?
Agar-agar [209]	?	~580	?	?	?
Colour coupler^{q} [212,246]	?	?	570	?	?
	58	580	α′—α 10—20		

Also: azo dye + mucopolysaccharides [171].

(Absorption curves for other polymethine dyes in the presence of coloured colour couplers are given in Ref. 212.)

E. Anionic dyes + cationic polymers

Substance	Short wavelength λ_{max}, mμ
Azo dyes	
I. Methyl Orange (C.I. 13025); λ_α = 507 mμ (acid form), λ_β = 463 mμ (alkaline form) [213], λ_K = 415—420 mμ	
β-Lactoglobulin [123]	412
Human blood serum albumin (cryst.) [123]	433
Octadecyltrimethylammonium chloride [213]	426
	412—433
II. Azo dye^{r}; λ_α = 472 mμ	
Bovine blood serum albumin (cryst.) [214]	440
Xanthen dyes	
III. Fluorescein (Uranine) (C.I. 45350); λ_α = 490 mμ	
Chitosan chloride [151]	445
Glucosamine chloride [151]	~436
	435—445

TABLE 2 (contd.)

Substance	Short wavelength λ_{max}, mμ	
IV. Resorcinol–benzoin; λ_α = 488 mμ		
N-Methylquinolinium perchlorate [215]	495	
V. Eosin (C.I. 45380); λ_α = 515 mμ		
Chitosan chloride [151]	~480	~533
Glucosamine chloride [151]	~480	~520
N-Methylquinolinium perchlorate [215]	—	~530
Serum albumin	—	530, 539
	~480	displaced by 5–25 mμ

Also: xanthen (phthalein) dyes + proteins; azo dyes + proteins [216-220], + surface-active agents [136,221], + inorganic colloids [222]; xanthen dyes + surface-active agents [136,177,178,223-226], + polyelectrolytes [194,196-200,227-232]. Indigoid dyes + polyelectrolyte [233]; anionic dyes + cationic inorganic complexes and biological materials [234].

* The superscript letters refer to notes below.

** The "Farbstofftabellen" numbers cited in the Russian paper have been replaced by "Colour Index" numbers (Ed. of Translation).

*** This C.I. number and the corresponding Schultz number given in the Russian paper actually represent Rhodamine B; Rhodamine 6G is C.I. 45160 (Ed. of Translation).

**** Ref. 113 seems to provide no clue to the nature of "Poly-A" (Ed. of Translation).

Key to superscript letters in Table 2.

a DNA = deoxyribonucleic acid.
b RNA = ribonucleic acid.
c NaLS (KLS) = Na (K) dodecyl (lauryl) sulphate (surface-active agents).
d $ChSO_4$ = chondrotin sulphate (polyelectrolyte).
e NaVin = Na salt of vinyl acetate–maleic acid copolymer.
f NaSPVA = Na salt of sulphonated poly(vinyl alcohol).
g KPVS = K poly(vinyl sulphate).
h Cartilaginous tissue contains mainly $ChSO_4$ [f] and hexauronic acid.
i Mucoid is an animal tissue containing up to 95% of hyaluronic acid.
j TPBS = triisopropylbenzenesulphonate.
k Carragheenin is a substance resembling agar-agar [8].
l Sodium arginate (sodium 2-amino-5-guanidinovalerate).
m Poly-C = polyribocytidylic acid.
n Poly-U = polyuridylic acid.
o Poly-P = sodium polyphosphate glass
p NaPES = sodium polyethylsulphonate.
q Sodium 1-hydroxy-2-(*N*-1-naphthyl-*N*-octadecylcarbamoyl)naphthalene-4-sulphonate (surface-active agent).
r *p*-(*p*-Phenylazo)phenylazophenyldimethylammonium acetate.

contains values of λ_{max}‡ for the short-wavelength maximum, and columns 4–6 for the α', β', and γ' maxima. Nucleic acids are no exception in the sense of yielding a short-wavelength maximum; with Acridine Orange the coincidence of its position with that of the dimeric maximum may give rise to doubt as to its nature§, but its presence in other cases, for example with Toluidine Blue in solution and also on paper chromatograms [235], leaves no doubt as to the theoretical possibility of its existence.

Values obtained by different workers for λ_{max} are identical within the limits of accuracy of the determination (2–3 mμ). More detailed data [191], where each value is based on a series of up to ten independent experiments, show a reproducibility of 1–3 mμ for Methylene Blue and Toluidine Blue, and of 0.5 mμ for Pinacyanol, which possesses a narrower maximum. These results suggest that the different positions of the maxima for a given dye in the presence of different polymers are to a considerable extent real.

It is significant that gelatin is no exception to the sequence of polymers; with solutions of dyes in the presence of gelatin, values of λ_{max} for the short-wavelength band (H band) lie within the limits of scatter of these values for other polymers. This applies not only to polymethine dyes but also to dyes of other classes. With the similarity mentioned above between the concentration dependence for the two systems — polymethine dyes + gelatin (H band) and other dye–polymer combinations — it compels us to acknowledge their identity and to speak of their common nature.

In several cases interaction of basic dyes with high polymers is accompanied by the appearance of a new absorption band in the long-wavelength part of the spectrum beyond the α band¶. As an example, Fig. 8 shows a series of absorption curves for Thionine in the presence of the

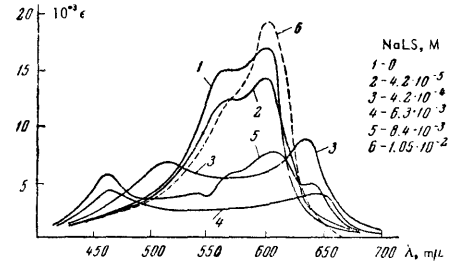


Fig. 8. Absorption curves for aqueous solutions (5×10^{-5} M) of Thionine in the presence of different concentrations (M) of sodium dodecyl sulphate at 17° [146]:
1) 0; 2) 4.2×10^{-6}; 3) 4.2×10^{-4}; 4) 6.3×10^{-3}; 5) 8.4×10^{-3}; 6) 1.05×10^{-2} M.

‡ Values are given for λ_{max} corresponding to the optimum polymer concentration, *i.e.* the shortest wavelengths. As can be seen from Fig. 7, at other concentrations an apparent shift in the maximum to longer wavelengths is sometimes observed owing to superposition of the dimer maximum; if this phenomenon has, nevertheless, occurred, the values of λ_{max} are indicated by the symbol ~.

§ Indeed it has been assumed [314], on the basis of adsorption and luminescent data, to be dimeric in nature.

¶ The colour caused by the long-wavelength bands (greenish in the case of dark blue dyes) is attributed in the literature to "negative metachromasy" [1,189], in contrast to "positive" metachromasy, which is associated with the short-wavelength maximum. The spots on paper chromatograms of DNA stained with Toluidine Blue and Azure A [235] have a reddish violet tinge at the periphery, and are greenish in the centre, which indicates a spatial separation of the substances responsible for the corresponding absorption bands in the case of DNA (with RNA only a greenish tinge is observed).

surface-active agent sodium dodecyl sulphate. Here the long-wavelength maximum ($\lambda \simeq 640$–650 mμ) arises together with the short-wavelength maximum (curves *3* and *4*) at some intermediate ("optimum") concentration; at higher concentrations both maxima give way to the α′ maximum (curve *6*). Positions of the long-wavelength band for several other cases are given in column 3 of Table 2A; with thiazine, xanthen, and acridine dyes it is observed only in the presence of surface-active agents and nucleic acids. The maximum is not usually sharp, appearing in several cases merely as a shoulder on the absorption curve. With polymethine dyes the long-wavelength maximum is observed also in the presence of polymers of other types, including gelatin. In some cases (the pseudocyanine XXII in Table 2A) a narrow band is present, coinciding in position and character with the J band (Fig. 5, curve *2*). (We may compare also the long-wavelength bands for carbocyanine dyes arising in the presence of surface-active colour couplers[212].) With other polymethine dyes (Table 2A), especially in the presence of gelatin, this band, coinciding in position with the J band in aqueous solution, has the same diffuse character that other dyes show in the presence of surface-active agents and nucleic acids.

The complexity of the J state, exhibited in the variety of spectral curves, has been mentioned above; there is every reason to suppose that the same state is involved in all the cases of the appearance of a long-wavelength band which have been examined†. In conformity with this, the long-wavelength bands occurring in the presence of polymers will be denoted by the symbol J′, in contrast to such J bands in solution and on adsorption on a silver halide. The J′ bands are narrow and intense only with dyes of one type, the isocyanines and carbocyanines; with all other dyes they are more or less diffuse.

Extending the analogy with the absorption bands observed in photographic emulsions, we must identify the α′ bands with the B bands[209].

5. NATURE OF ABSORBING CENTRES FORMED IN THE INTERACTION OF DYES WITH MACROMOLECULAR SUBSTANCES HAVING OPPOSITELY CHARGED IONS

All investigators (*e.g.* Refs. 2, 3, 162, 173–175) agree that the short-wavelength maximum is due to aggregated dye structures produced in combinations of a cationic dye with an anionic polymer as a result[125,126,152,162,164,166,195,239,308] of adsorption of positively charged dye ions on negatively charged terminal groups of the polymer. The distance between neighbouring groups is usually of the order of 3–5 Å, and since no electrostatic repulsion is present, owing to the mutual neutralisation of charges, the electron levels of dye molecules situated side by side and held together by the polymer substrate coalesce. Compact neutral dye particles are obtained, which are the same as the colloidal particles (with a "phase interface") discussed above.

Comparison of the short-wavelength absorption maxima of Methylene Blue and Crystal Violet in the presence of polymers with the spectra of colloidal solutions of these dyes has shown their similarity[121]. The coincidence of λ_{max} for the short-wavelength absorption band with λ_K is found also with some other dyes (Table 2A, dyes V, X, and XXII)‡.

All these results support the above attribution to the colloidal nature[240] of these absorption bands, which we shall therefore term K bands. This is also supported by direct observations. Thus a strong yellowish green luminescence is observed[200] when dye solutions containing polymers are examined in the ultramicroscope; this luminescence may change shade in various ways, as with colloidal solutions of gold, for example.

Some spectral phenomena accompanying the interaction of polymers and metal ions must also be discussed in terms of the formation of colloidal particles. Thus the spectrum of the complex formed by copper ions with imidazole[241] (λ_{max} 278 and 580 mμ) agrees with that of colloidal solutions of metallic copper[117] and differs sharply from the spectrum of copper ions (λ_{max} 700 mμ); all these phenomena are characteristic of poly-*N*-vinylimidazole[242] ($\lambda_{max} \sim 630$ mμ) and of bovine serum albumin[243].

A similar phenomenon to the possibility of aggregation of ions of different kinds, both with dimers and with J centres (Section 3), is observed also in the interaction of dyes with polymers: a mixture of two dyes in the presence of a polymer gives not two but one K maximum, with properties intermediate between those of this maximum for each dye separately[196]. This fact completely fits the above hypothesis of the formation of K particles.

Complete coverage of all the end-groups of the polymer molecules takes place at a definite ratio of polymer and dye concentrations. Several investigations show[124–129,132,152,164,168,169,176,221,235,244] that the maximum effect occurs at the stoichiometric (1 : 1) ratio of numbers of charged groups in dye and polymer; thus for one molecule of heparin[125,126], containing about 50 SO_3H end-groups, there are, under optimum conditions, on the average 50 (between 35 and 75) dye molecules (Acridine Orange, diethylpseudocyanine). Taking the distance between the end-groups as 4 Å, we obtain a value of ~20 mμ for the size of the colloidal dye particle.

The polymer concentration corresponding to the above stoichiometric ratio is in fact the above-mentioned optimum concentration for the formation of K particles; its value should obviously depend on the dye concentration[167]. This is shown very clearly by results[184] obtained on the quenching of the luminescence of a dye at different concentrations: the values of the above optimum concentration for a polymethacrylate are 10^{-2}, 10^{-3}, and 5×10^{-4} M at Rhodamine 6G concentrations of 10^{-4}, 10^{-5}, and 10^{-6} M respectively.

At a given dye concentration the values of the above optimum concentration (in practice we shall always be dealing with a more or less wide range of optimum concentrations) are different for different polymers. This forms the basis of a method for differentiating histological tissues. A

† In the scientific literature on photography, the long-wavelength bands observed with polymethine dyes in the presence of gelatin have long been assigned to the J state[73,74,176,209,236].

‡ Conversely, in cases where the aggregates causing a given band in the dye spectrum are unknown, their colloidal nature can be assessed from the coincidence of λ_K with λ_{max} for the short-wavelength band in the presence of polymers. Such is the case with the weak band at ~480 mμ in an aqueous solution of dye XXIV[103], which is revealed when the solution is illuminated (these structures being significantly more stable to light than the structures α–γ).

necessary condition for the application of this method, which is not always observed, is to vary the dye concentration [245] between wide limits, so that it is possible to cover both the optimum and adjacent ranges§.

Further increase in the polymer concentration diminishes the probability of covering all possible adsorption centres, and polymer molecules may be present on which are adsorbed dye particles containing smaller numbers of molecules, right down to three, two, and finally one. The spectrum of these dye structures adsorbed on polymers should differ from the spectrum of the dye ions in the absence of polymer (see above, Section 4). In fact, we have seen above (Table 2A, columns 4–6) that at high polymer concentrations the α' bands differ from the α bands¶. By analogy we shall speak also of β' and γ' bands. They can readily be identified for polymethine dyes (see Fig. 4). Thus the α', β', and γ' centres should be attributed to monomeric, dimeric, and polymeric structures linked with the macromolecular substance (the type of bonding in the β' and γ' centres is still not clear).

We should take the same view of the nature of the absorption bands in the case of the interaction of anionic dyes with cationic polymers. Here, too, the short-wavelength maximum coincides with the colloidal maximum (Table 2B, dye I); the long-wavelength maximum should probably be attributed to an α' band†.

Interaction of thiazine dyes and anionic polymers results in the appearance of further bands — in addition to K and α' (β', γ') bands — having $\lambda_{max} < \lambda_K$ and $\lambda_{max} > \lambda_{\alpha'}$. The nature of the former must be linked with that of the so-called "red form" of Methylene Blue ($\lambda_{max} \sim 506–523$ mμ), which has been detected in several systems [78,79,237,238,315,316]. It has been ascribed [315] to an isomer of the dye. The latter bands, which we have denoted by the symbol J', should be assigned to ordered aggregates of *ions* of the dye combined with the macromolecule. This is an important difference between these bands and the K bands, which are caused by the aggregation of neutral dye molecules. The difference in character is illustrated by a difference in the photochemical activity of these structures: in the sensitisation spectra of photographic emulsions, H(K) bands are often hardly in evidence [86,111–113,305]‡, whereas J(J') structures are most effective.

§ Actually, differences in the shade or colour of the luminescence between different regions of a preparation can be expected only if the relative dye and polymer concentrations correspond to the optimum concentration in one region and to either the α or the α' range [205,206,245] in the other region; if conditions correspond to the same condition in both regions, the change in colour is insignificant, which may lead to incorrect conclusions.

¶ With several polymethine dyes, interaction with colour couplers is accompanied [212,246] by the appearance (sometimes together with a long-wavelength band of the J type) of a band which has been displaced by 10–15 mμ to longer wavelengths compared with the α band (for example, dye XXVII in Table 2A). In the original papers this band is denoted by the letter *k* and is attributed to the adsorption of dye on "colloidal particles" (*i.e.* micelles) of the component, which is fully consistent with the above views. On this basis we shall include these bands in the α' type.

† The coincidence of its position with that of the long-wavelength maximum of the dimer (Table 1) is probably fortuitous.

‡ The spectral contiguity of the H (K) and γ (γ') bands may lead to their being confused. This is probably the case in Refs. 72, 85, and 113: feebly active states denoted as H II are obviously K states, while the more active are γ states.

In all the cases examined above we are dealing with polymer–dye complexes. The mutual saturation of the hydrophilic groups of the two components of the complex markedly reduces the solubility, with separation of a precipitate§ in the case of both K and J' structures. With K structures the deposit comes down in the form of films (agar-agar [121], gelatin [191], chondroitin sulphate [251]) [317], filaments (carboxymethylcellulose [191], carragheenin [252], nucleic acids [217,253]), and granules [253], which are more or less deeply stained the colour of the K structures.

The complex will not pass through a regenerated cellulose membrane [167]; it has been isolated by centrifuging, dissolving the precipitate in alcohol, and recrystallising. With Pinacyanol + sodium dodecyl sulphate, large needle-shaped monoclinic crystals were obtained; chemical analysis showed that, as with other dye–polymer systems, their composition did not entirely agree with calculation. With K particles separation of a coloured precipitate is observed at some intermediate relative concentrations of polymer and dye [1,3,125,169,173,198,200,239,251] (there are indications [2,11,127,171,183] that this takes place at the stoichiometric ratio of charged groups in dye and polymer mentioned above). The formation of a precipitate (sometimes immediately the solutions of polymer and dye are mixed, sometimes over a period of time [318–320]) occurs as a result of the molecules, deprived of their charge, combining with the dye adsorbed on them (perhaps by hydrogen bonding [254]); individual coloured polymer molecules may remain suspended in the solution for a long time, revealing themselves optically by an absorption spectrum with a K maximum and also by a Tyndall cone [200,239,318].

6. CONDITIONS FOR COMPLEX FORMATION BETWEEN MACROMOLECULAR SUBSTANCES AND DYES HAVING OPPOSITELY CHARGED IONS

The primary condition for the formation of polymer–dye complexes with aggregated dye particles (K or J' structures) is the presence of polymer molecules having a sufficiently large number of charged groups.

At low concentrations surface-active agents exist as individual ions [12,255]. With rise in concentration the physicochemical properties of the solution (electrical conductivity, surface tension, viscosity, specific volume) undergo sudden changes [255] within definite intervals of concentration, outside which these properties remain constant. Thus with sodium dodecyl sulphate changes have been noted [255] at the concentrations 0.005–0.007, 0.019–0.021, 0.028–0.030, and 0.05–0.07 M. A similar pattern is observed with other wetting agents which have been investigated [255,256]. Among these intervals, one (in the case of sodium dodecyl sulphate 0.028–0.030 M) is outstanding, the changes in physical properties being most marked in this range. The existence of such a concentration range was noted long ago as a characteristic feature of solutions of surface-active agents; it is attributed to the formation of micelles [255,257], which are in thermodynamic equilibrium with the molecules or ions forming them. The comparative narrowness of this

§ The fact that a water-insoluble precipitate comes down when oppositely charged ions interact is widely known; in particular, it occurs when solutions of anionic and cationic dyes are mixed [247], and also with macromolecular substances having oppositely charged groups (heparin + albumin at pH < 4.5 [248], polyelectrolyte + + surface-active agent [249], see also Ref. 250).

range enabled it to be regarded as practically a single concentration, the so-called critical micelle concentration (c.c.m.), the values of which for a series of surface-active agents[13] lie within the limits 10^{-4}–10^{-1} N. Recent investigations indicate[255], however, that the process of association in solutions of surface-active agents begins at considerably lower concentrations. The subsequent ranges are linked either with further development of this process (stepwise association) or with a change in the character of the micelles resulting from their rearrangement.

It follows from the above that the picture of micelle formation in such a solution is still far from clear; this also makes it difficult to examine conditions for the formation of a complex between surface-active agent and dye. It was at first suggested that, since the change in colour of a solution or the extinction of its fluorescence (caused by separation of K complexes) takes place in the region of the critical micelle concentration, these optical phenomena were caused by micelle formation.

This view forms the basis of a spectroscopic method for determining c.c.m. which has found widespread use[135-139,210,258]. The concentration of surface-active agent which corresponds to the maximum change in the optical characteristics of the dye is determined. As noted above, this corresponds to the formation of polymer–dye complexes; thus in essence the spectroscopic method records[167] the separation not of pure micelles but of their complexes with an aggregated dye.

To what extent these two processes coincide is still obscure. Values of c.c.m. determined by physicochemical methods prove[225] to be smaller in the presence of a dye: *i.e.* a dye facilitates micelle formation. Values of c.c.m. obtained by the spectroscopic method are usually also somewhat smaller[139,167,259,260] than when physicochemical methods are used. Probably, however, the separation of surfactant–dye complexes, if it does precede the separation of pure micelles, is not very intense¶, so that, for a rough estimate of the concentration of micelle formation, the optical method, which is experimentally considerably simpler than most physicochemical methods, is nevertheless worthy of attention.

The separation of dye–surface-active agent complexes in other regions of stepwise association is also not understood (results[167] show that this can occur: the optimum region for the separation of K complexes corresponds to the second of the critical concentration ranges for sodium dodecyl sulphate).

A detailed study of the absorption spectra of surface-active agent plus dye solutions in all the regions of stepwise association should provide important help in clarifying these matters; it might give information on the nature and the structure of the aggregates in each concentration range.

In solutions of polymers of the polyelectrolyte type and at low concentrations, macromolecules having a large number of charged groups are formed; it is to be expected that polymer–dye complexes will be precipitated also on great dilution of the polymer solutions. Since these are masked spectroscopically by the predominant free dye molecules, the lower limit of the optimum concentration range should be indefinite, as is in fact observed. The structure of the macromolecules (in the sense of the type of link between the monomeric units) should be of considerable importance. This structure may change in the presence of a dye, since the electrostatically neutralised macromolecules will be coagulated, which is a general characteristic of neutral polymer molecules[192,231,232]. Structural rearrangements may well be possible with this type of polymer too (this is indicated by the presence of a second region of separation of K particles[168]). Thus stretched molecules of polymethacrylic acid[184] are able to react with one another to form characteristic aggregates comprising "packs" of molecules. Further increase in the concentration results in the production of "globules".

The degree of homogeneity of the polymer solution should play an important part. Actually, we are always concerned in practice with a mixture of macromolecules having different degrees of polymerisation[6], and there are indications that the active centres in a polymer molecule are heterogeneous: nucleic acids[208] and serum albumin[262] each show two groups of such centres, each of which is characterised by its own bonding constant.

Examination of the picture sketched above for the formation of polymer–dye complexes shows that the structure of the monomeric units in both polymer[6] and dye is very important. In fact, if dye ions are to combine into a single whole, they must be arranged sufficiently close together. (For the J structure this minimum distance has been determined as 3–5 Å.[63,73,263].) The three-dimensional structure of the dye molecule therefore has a similarly important role in the separation of aggregates in the presence of a polymer[171,190,193,208,264] to that in polymerisation in solution, which has been discussed above.

Replacement of methyl by ethyl groups at nitrogen atoms in a dye is known to prevent the formation of H(K) centres[173]; not only the nature of the substituents but also their position is of substantial importance[86].

In the polymers it is necessary that the distance between neighbouring charged groups should correspond to the minimum† mentioned above (in other words, there should be a minimum density of charge on the surface of the polymer molecules)[2,73,162]. The flexibility of the polymer molecules would have some influence, by allowing the distance between the charged groups to fit the required distance between the planes of the dye molecules[165,166]. A quantitative indication of aggregating power is given by the intensity ratio of the α' and K bands[165,166,304,313]; this "packing factor" depends appreciably on the molecular structure of the polyanion.

The intensity of the effect (with the same dye at a constant concentration) is proportional to the total quantity of complexes which separate in unit volume[171]: *i.e.* it is determined by the total number of charged groups per unit volume[2,162,194,214] of the polymer solution. This number

¶ A further cause of uncertainty in the optical determination of c.c.m. is that, as mentioned above, the separation of K centres takes place at stoichiometric proportions of dye and polymer, and consequently depends on the dye concentration[167,184]. (More definite results are to be expected from a direct optical method — from the ultraviolet absorption spectra of solutions of surface-active agents[261].)

† Metachromasy, *i.e.* the separation of K particles, is absent in dilute solutions of hyaluronic acid, in which the distance between the COO groups is 10.3 Å; it appears only in gels or films of this substance[162]. The effect is less marked in synthetic polynucleotides than in the natural derivatives, where the distance between the phosphate groups is less[265].

depends on the degree of dissociation of the ionised groups in the polymer, which is determined mainly by the pH of the solution, being low at low pH and high at high values. This explains why metachromasy is not usually observed at pH < 3–4 [1,2,164,192,194,208,266] (it becomes more intense with increase in pH [261]). In solutions of polymers containing strongly ionised groups (sulpho, quaternary nitrogen), on the other hand, pH has practically no effect [227] (with heparin the effect is observed also at pH ~2 [198])‡.

The total number of groups is affected by the configuration of the polymer molecules; thus the separation of H(K) centres is more intense and starts at lower concentrations in a more hydrolysed gelatin [173].

The degree of polymerisation of the polymer has no influence on the intensity of the effect [164,194,268] above some minimum degree of polymerisation (in the case of polymetaphosphates, eight PO_3 groups [206] or $M > 3000$ [268]). The effect remains unchanged also during the aging of polymers [268] (polymetaphosphate), when some of the side chains split off, and under the action of ultrasonic waves [268]. It is not entirely clear how the intensity of this effect depends on the nature of the groups.

The number of charged groups (charge density) in the polymer molecule (or group of molecules forming a single common substrate for the dye particle) determines the size of the particle and hence (see Section 3) the position of the maximum λ_K. We have seen above (Table 2) that values of λ_K for the same dye in the presence of different polymers may vary by 15–30 mμ. Calculation (largely tentative) shows that such differences correspond to changes in diameter of the dye particle from 20 to ~80–120 mμ, and hence to changes in the number of charged groups from ≃50 to 200–300. The charge density for several polymers of the polyelectrolyte type changes [230] within similar limits (by factors of 3–5). However, in order to assess the possibility of such differences in any actual case, a more detailed idea of the structure and shape of the micelles of the given substance is needed (some information is given in Refs. 184, 269–271, and 321).

Examination of the degree of polarisation of luminescent dyes in the presence of polymers should have an important role in this connection. Study of the interaction of dyes with native and denatured polymers is promising [308,309,313,314]. In the case of nucleic acids there is some suggestion of the formation of complexes (intercalation [322]) of inclusion compounds. The different cases of the interaction of dyes with proteins have indicated [272–276] that denatured proteins, whose molecules are uncoiled, are far more active [277] than the native proteins, which have coiled molecules (see also Refs. 180–182), while fibrillar proteins are more active than globular proteins.

The structure of polymers should influence also the shape of the colloidal particles.

7. PHYSICOCHEMICAL PROPERTIES OF COMPLEXES OF MACROMOLECULAR SUBSTANCES AND DYES HAVING OPPOSITELY CHARGED IONS

The stability of a polymer–dye complex can be influenced by all the factors which weaken or strengthen the bonds in the complex.

Numerous experiments show that, when a polymer solution containing K complexes is heated to 60°–70°, [2,132,149,152,159,164,171,192,198,199,230,266,278,279,319] and also when alcohols and other organic substances are added to it, [2,3,125,126,162,164,199,230,240,278,280] the K maximum disappears from the spectrum of the solution, the α and β maxima becoming stronger. Corresponding to this, the fluorescence also changes. The effect of heating is reversible: on cooling, the absorption in the region of the K maximum is more or less reestablished [319]. This effect indicates rupture of the bonds holding ions of the dye and the polymer, a colloidal dye particle being being split off. The thermal stability of the complexes depends on the nature of the polymer [319].

The mechanism by which organic compounds of low molecular weight act on the polymer–dye complex is not yet clear; it is obvious that, as with the action of heat, the primary effect consists in fission of the polymer–dye bond. Different polymers require different quantities of alcohol to break down the colour centres [280]; the effect is stronger in alcohol–water mixtures [278].

Compared with the solutions, the precipitates are very stable towards both heat and organic solvents. The solubility of the precipitated complexes§ is of importance in the study of the metachromasy of biological materials, but the literature contains only isolated data of a qualitative character. Thus the water-insoluble complexes of cationic dyes and anionic polymers are soluble in alcohol–pyridine [121] and alcohol–water mixtures [73], chloroform [3,142], ether [142], alcohols [167], and benzene [225]; a good solvent for a cationic surface-active agent is also a good solvent for the complexes which it forms with anionic dyes [220].

The polymer–dye complexes are considerably affected by salts¶. In the interaction of a cationic dye with an anionic polymer, small concentrations (up to 0.1 M) of salts [168] break down existing complexes [2,125–127,137,154,155,162,177,192,195,208,230,231,279,283]; the effect increases with increase in valency [154,195] of the inorganic cation, but the anion is of no significance [230]. The stability of the complex is governed to a large extent by the above-mentioned surface charge density of the polymer; it falls in the sequence of groups: sulphate, phosphate, carboxyl [230]. A similar phenomenon has been noted for complexes of an anionic dye with a cationic polymer when organic acids are added to a protein–dye mixture.

‡ Ionisation also governs [184] the shape of the macromolecules in solution: at low pH they are coiled up, and with increasing degree of ionisation become extremely unsymmetrical. A decrease in pH in breakdown of the packs with the formation of globules. The possibility of the structure of a protein changing with pH has also been pointed out [10,217].

§ A method for the analytical determination both of the combined dye and of the polymer is based on precipitation of the complexes. When a solution of the polymer and the dye is shaken with petroleum ether, the complex separates at the interface between the solution and the solvent; absorptiometric measurements on the solution before and after this operation give the quantity of combined dye [281]. The polymer concentration can be obtained by extracting the complex, dissolving it in a suitable solvent, and making absorptiometric measurements on the solution [220,282].

¶ Simple ionic salts are implied; inorganic and organic polymers behave similarly in the presence of dyes (see Table 2, A and B).

In both cases we are dealing with competition, which is very general in physical chemistry[284], between ions of the dye and of the salt (or aromatic acid)[216]. A similar phenomenon is observed when to a polymer–dye solution is added a second polymer having similar ions to the first (silicate + + surface-active agent[155], polyelectrolyte + surface-active agent[177], nucleic acid + inorganic colloid[285]), where the ions of the two polymers compete for the dye ions. This effect occurs also when proteins are added to solutions of anionic polymers[2,3,126,197,228,286], especially if the protein is strongly basic (protamine). The polymer–protein complex is obviously less stable than the polymer–dye complex, and therefore certain agents (ascorbic acid, heating to 90°)[286] reestablish the K band†

The dispersing action of proteins on salt solutions of several dyes[276] should also be regarded as competition (between ions of the dye and of the protein) for the other ion of the dye.

At low pH the formation of K complexes is difficult (Section 6); but once precipitated, the complexes prove to be very stable[220] with respect to pH, since owing to loss of water they are unable to interact with hydrogen ions in the environment.

Complex formation has a considerable influence on the reactivity of dyes. Thus with indicators of the phthalein series, addition of a protein to an acid solution of the dye restores the primary form of the latter[183]. The time required for reduction of dyes by various reducing systems is appreciably increased in the presence of polymers[233]; this is possible when the ions of dye and polymer are of different kinds, but is not observed when they are similar.

Dyes are considerably more stable to light in the presence of polymers than in pure solution[163,171,182,214]; the photochemical stability of the complexes depends on the nature of the polymer[319].

The depressant action of colour couplers on the degree of optical sensitisation[212,246,324] with some dye–coupler combinations should probably[14,287] also be explained by bonding of the dye.

Great resistance is observed also towards "alkaline" fading; the bleaching of triphenylmethane dyes at pH ~ ~10–12 is markedly diminished in the presence of anionic surface-active agents, and is intensified on addition of cationic surface-active agents[202].

8. OTHER CASES OF INTERACTION BETWEEN MACROMOLECULAR SUBSTANCES AND ORGANIC MOLECULES

(*a*) Interaction between Ionogenic Polymers and Organic Substances Having Oppositely Charged Ions

This covers the interaction of cationic surface-active agents (pyridinium salts) with the dye Congo Red[288,289], an aqueous solution of which contains large micelles and is a colloidal electrolyte. In neutral solution the dye has an absorption band at ~500 mμ; on addition of a surface-active agent a new band appears at 460–470 mμ, and at high concentrations of the agent (0.25 M) a maximum becomes visible at 530 mμ. A water-insoluble precipitate separates over a definite range of concentrations of the surface-active agent (0.5–5 M depending on the dye concentration). The same final effect is observed also in an acid solution of the dye: addition of the surface-active agent changes the colour of the solution from blue to orange red (λ_{max} = 470 mμ); at a definite (optimum) concentration a precipitate is formed. The general picture of the phenomenon fully corresponds to that described above; it is assumed that the ions of the surface-active agent interact with a sulpho-group in the dye. However, the nature of the complex formed when both components are micellar in character is obscure[290].

Another example from this field is the interaction of serum albumin[291] with dinitrobenzene derivatives (of anionic type). Combination of the albumin with a dinitroaniline derivative displaces the absorption maximum of the latter (350–370 mμ).

In the manufacture of photographic colour films we encounter[87] the interaction of gelatin with indoaniline and azomethine dyes formed in the colour development of these materials. The absorption maxima of these dyes are displaced in the presence of gelatin (compared with an alcoholic solution) by up to 30 mμ on either side; these shifts cannot be explained as resulting from a change in polarity of the medium and in the polarisability of the dye molecules. In some cases the addition of gelatin produces a new maximum on the short-wavelength side, which can reasonably be assigned to an aggregated state of the dye. All these facts indicate that these dyes interact with the gelatin; a knowledge of the nature of the resulting complexes is of fundamental importance for a rational development of colour-sensitive photographic materials.

The same type of interaction occurs also between molecules of two polymers having oppositely charged ions. An example is the formation of mucoproteins, which are complexes of the positive groups of a protein and, for example, heparin or chondroitin sulphate[248]; the physicochemical properties of these complexes (in particular the stoichiometric proportions 1 : 1) are the same as in the above cases of the interaction of polymers and dyes. The absence of spectroscopic data prevents us, however, from assessing the nature of these complexes (isolated α′ or aggregated K).

(*b*) Interaction between Non-Ionic Polymers and Dyes

This question is of practical importance in connection with surface-active agents, in view of the possible application of the spectroscopic method to the determination of critical micelle concentrations.

Experiments with several dyes in the presence of polyethylene glycol and laurylethyl alcohol[292,293] show the absence of precipitation and, in the case of fluorescent dyes, extinction of the luminescence; no new maximum can be observed on the absorption curves. With Pinacyanol the spectral changes produced by increasing the concentration of surface-active agent consist in an increase in intensity of the monomeric maximum (α) at the expense of the dimeric (β), with a shift in these maxima to longer wavelengths. With Erythrosine (C.I. 45430) there is only a displacement of the maximum.

It can be concluded from all these results that, in contrast to the above cases of interaction between dyes and

† There may be other explanations of the action of proteins (steric masking of anionic groups, formation of a covalent bond between hydroxyl groups of the protein and anionic groups of the polymer)[3].

oppositely charged polymers, no polymer–dye complexes are formed in the present case; the shift in the maxima is to be attributed to a " solvent effect".

Other workers[289,294], who have investigated the interaction of polyethylene glycol and of several other neutral substances (polyvinyl alcohol, several surface-active agents) with an azo dye, speak of the formation of complexes: $mD + nS = D_mS_n$,[294] where D is a dye molecule, S a polymer molecule, and D_mS_n a molecule of the complex; with polymers n/m tends to $\frac{1}{2}$.

In several cases polyvinylpyrrolidone can also be regarded[182,215,263,295,296] as a non-ionic polymer, its solutions being used as an artificial substitute for blood plasma; other data[7,250], however, indicate that this substance possesses feebly basic properties, and hence should interact with anionic dyes. This has received experimental confirmation: physicochemical[263,295,296] and optical (luminescence[215]) methods have established the formation of complexes between this polymer and these dyes.

(*c*) Interaction between Dyes and Complexes of Two Macromolecular Substances

Ternary systems of this type are met in investigating the properties of complexes of surface-active agents with polymers[297-300], in particular the solubilising power of surface-active agents[12], which is changed by this interaction. For this purpose fat-soluble dyes are employed; quantitative data on their solubilisation are obtained spectroscopically. Changes have been noted in the absorption spectrum of the dye, which indicates that its molecules are incorporated into the complex.

(*d*) Interaction of Dyes with Macromolecular Substances by Formation of a Covalent Bond

Dyes of a new type (the so-called reactive dyes[301]) form covalent bonds with polymers; their use is continually extending for various kinds of colouring, in particular in histochemistry[302].

A covalent bond has also been detected between proteins and triphenylmethane dyes[275,276,303]; here the dye adds on to thiol or amino-groups in the proteins, with the result that a new absorption band appears in the ultraviolet region of the spectrum, close to the band due to the carbinol base. Proteins prove to be more reactive when denatured than in the native state.

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RECENT PROGRESS IN THE SYNTHESIS OF MONOCYCLIC AND POLYCYCLIC AROMATIC HYDROCARBONS

V. R. Skvarchenko

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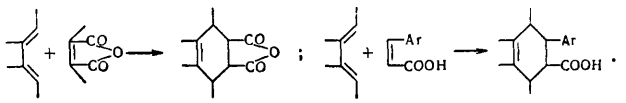
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1. INTRODUCTION

Tetrahydrophthalic acids and their anhydrides, as well as tetrahydrobenzoic acids, are readily accessible compounds, being obtained by diene synthesis from conjugated diene hydrocarbons with maleic anhydride, its homologues and cyclic analogues, and hence with cinnamic acids:

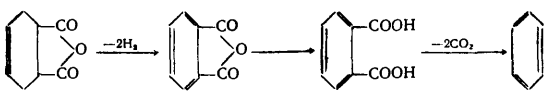


The chemical and physical properties of tetrahydrophthalic acids of various structures have been reviewed by Buckles[1], who examined methods for their preparation, reactions involving addition at the double bond, reactions of the carboxyl groups, oxidative reactions, and also reactions involving isomerisation and dehydrogenation.

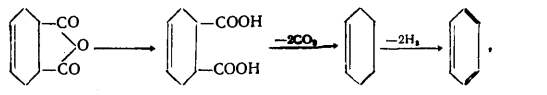
The present review surveys the conversion of 1,2,3,6-tetrahydrophthalic (cyclohex-4-ene-1,2-dicarboxylic) acids and their anhydrides and also of 1,2,5,6-tetrahydrobenzoic (cyclohex-3-enecarboxylic) acids into aromatic hydrocarbons.

2. AROMATISATION OF ADDUCTS OF DIENE SYNTHESIS — TETRAHYDROPHTHALIC ACIDS AND THEIR ANHYDRIDES — BY DECARBOXYLATION AND DEHYDROGENATION

Aromatisation of the adducts from diene synthesis is usually accomplished in three successive stages: (I) tetrahydrophthalic anhydride is dehydrogenated, the resulting aromatic anhydride is converted into the acid or a salt, and the product then subjected to decarboxylation; alternatively (II) the initial tetrahydrophthalic anhydride is first converted into tetrahydrophthalic acid or a salt thereof, a hydroaromatic hydrocarbon (or a mixture of isomeric hydrocarbons) is obtained by decarboxylation, and then the hydrocarbon is dehydrogenated to an aromatic hydrocarbon; or finally (III) the adducts undergo simultaneous decarboxylation and dehydrogenation:



(I)

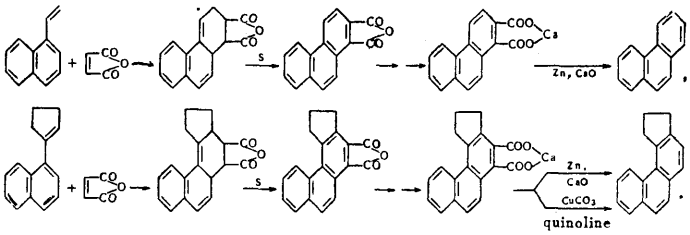


(II)



(III)

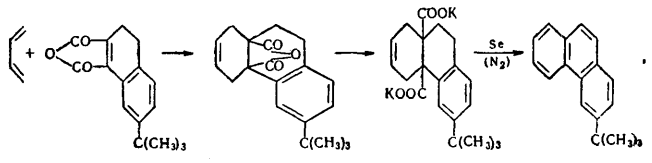
Thus the first reaction sequence (I) has been used for the synthesis of phenanthrene and 3,4-cyclopentenophenanthrene[2]:



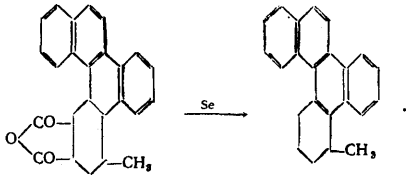
Decarboxylation of calcium phenanthrene-1,2-dicarboxylate by heating with copper carbonate in quinoline gave, instead of phenanthrene, a substance of undetermined structure.

Dehydrogenation of Adduct from Diene Synthesis

Dehydrogenation of adducts by heating with sulphur has been described by other workers too[3-5]. Some adducts are resistant to heating with sulphur (for example 1,2,3,4-tetrahydro-1,2-dimethylphenanthrene-3,4-dicarboxylic anhydride), but are readily dehydrogenated by selenium[4]. When adducts are heated with selenium, however, dehydrogenation may be accompanied, depending on their structure, by decarboxylation, for example[6]:

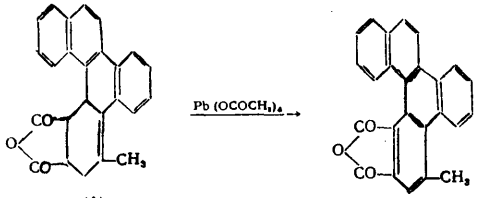


or else decarboxylation alone may take place[7]:



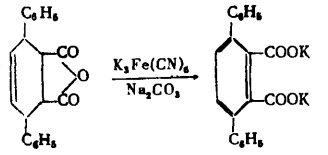
(A)

Tetrahydrophthalic acids and their anhydrides can be dehydrogenated in other ways. Thus the anhydride (A), which on being heated with selenium was decarboxylated and converted into methylcyclohexenochrysene, was not decarboxylated but dehydrogenated on being heated with lead tetraacetate[7]:



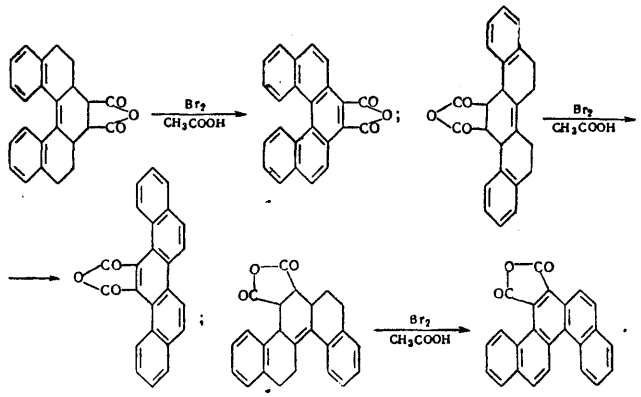
(A)

1',2',3',4'-Tetrahydro-*p*-terphenyl-2',3'-dicarboxylic anhydride was converted into a salt of 3,6-diphenylphthalic (*p*-terphenyl-2',3'-dicarboxylic) acid by heating with potassium ferricyanide† (in sodium carbonate solution)[8]:

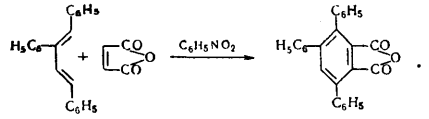


This same anhydride was dehydrogenated by heating in nitrobenzene[10].

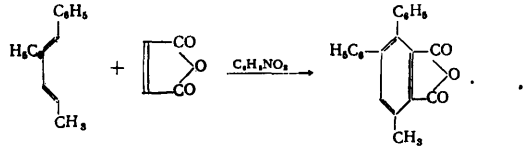
The partial dehydrogenation of fused hydroaromatic anhydrides by heating them with bromine in acetic acid has been described[11]:



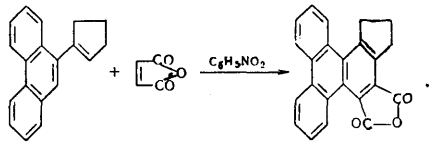
Diene synthesis in nitrobenzene yields aromatic anhydrides directly. Thus when 1,2,4-triphenylbuta-1,3-diene was heated with maleic anhydride in nitrobenzene, only 3,4,6-triphenylphthalic anhydride was isolated[12]:



1,2-Diphenylpenta-1,3-diene and maleic anhydride under these conditions yielded 3-methyl-5,6-diphenylphthalic anhydride[12]:

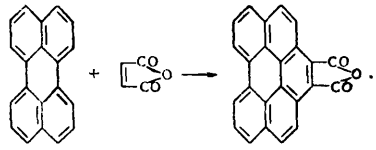


Diene synthesis with 9-cyclopentenylphenanthrene and maleic anhydride in nitrobenzene took place in an analogous manner[12]:

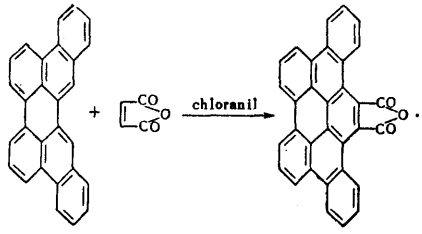


† The action of this reagent on tetrahydrofluoranthenedicarboxylic acid produced decarboxylation as well as dehydrogenation, with the formation of fluoranthene[9] (see p. 577).

Many multifused aromatic hydrocarbons (perylene[13], ovalene[14], 2,3:4,5-dibenzocoronene[15]), which do not give adducts with maleic anhydride when heated in inert solvents, form adducts of aromatic structure on being heated in nitrobenzene, for example:



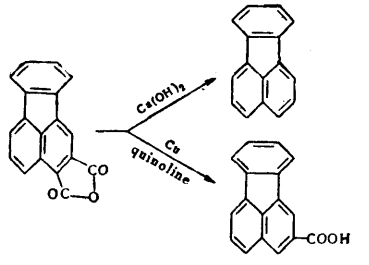
Anhydrides of aromatic structure can be obtained also by heating the components of diene synthesis in the presence of chloranil[16-20]:



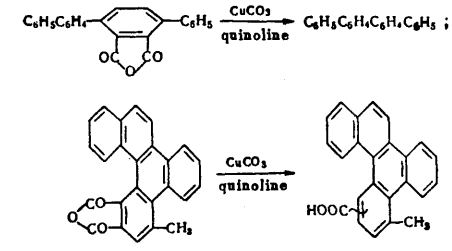
Decarboxylation of Aromatic Dicarboxylic Acids, Salts, and Anhydrides Obtained by Dehydrogenation of Adducts of Diene Synthesis

Such decarboxylation has been carried out in various ways — by dry distillation with zinc dust in the presence of calcium oxide[2], by heating with copper powder in the presence of sodium carbonate and calcium oxide[21] or barium oxide[4,11] or hydroxide[5], by heating with calcium hydroxide[22,23], or by prolonged heating with caustic potash in an autoclave[20], dry distillation with soda lime[8,13-15,17-19], or boiling in quinoline with copper[11,15-18,21] or copper carbonate[3,7].

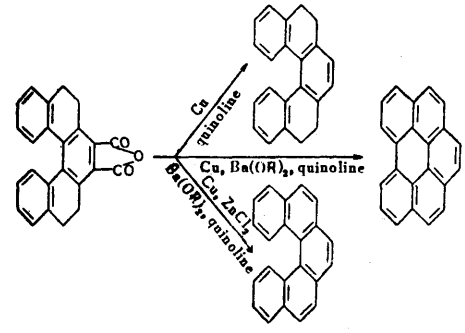
Decarboxylation is most often effected by dry distillation with soda lime and boiling with copper powder in quinoline. The reaction can go in different ways depending on the structure of the initial compound and on the reagent employed. Heating fluoranthene-3,4-dicarboxylic anhydride with calcium hydroxide at red heat, for example, gives a 50% yield of fluoranthene; when the same anhydride is boiled with copper bronze in quinoline, only partial decarboxylation occurs, the reaction product being fluoranthene-3-carboxylic acid[22]:



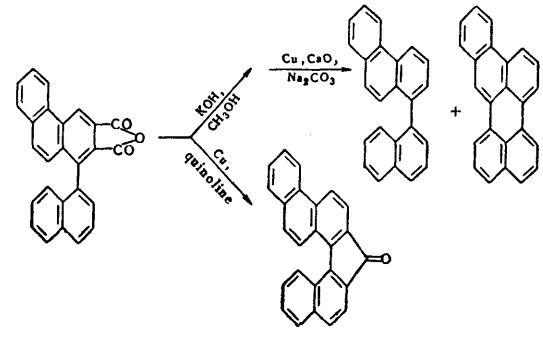
3-*p*-Biphenylyl-6-phenylphthalic anhydride on being heated with copper carbonate in quinoline was converted into a 31% yield of quaterphenyl[3]; whereas when an aromatic anhydride having a fused polycyclic system was heated under these conditions, only partial decarboxylation took place, the product of the reaction being the corresponding monocarboxylic acid[7]:



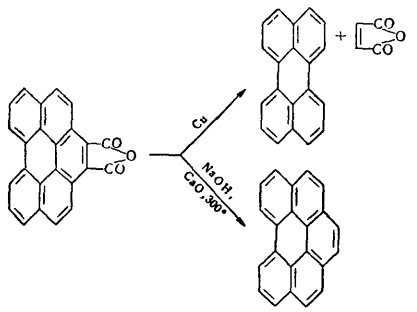
1,2,7,8-Tetrahydro-3,4:5,6-dibenzophenanthrene-9,10-dicarboxylic anhydride on decarboxylation by heating with copper in quinoline gave the tetrahydro-3,4:5,6-dibenzophenanthrene; when this anydride was heated under the same conditions but with the addition of barium hydroxide, decarboxylation was accompanied by dehydrogenation and pyrocondensation with the formation of 1,12-benzoperylene; when barium hydroxide and zinc chloride were added to the reaction mixture, the anhydride underwent decarboxylation and dehydrogenation, but in this case 3,4:5,6-dibenzophenanthrene was isolated as the final product of the reaction[11]:



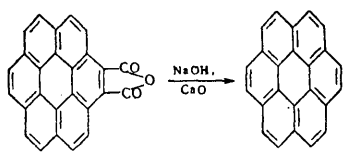
The anhydride of 1-1′-naphthylphenanthrene-2,3-dicarboxylic acid can also undergo decarboxylation in various ways[21] depending on the conditions and the reagents used:



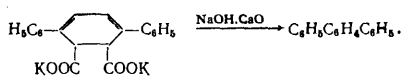
The adduct of perylene and maleic anhydride on being heated with copper powder in a vacuum underwent breakdown, the original perylene being re-formed[13]:



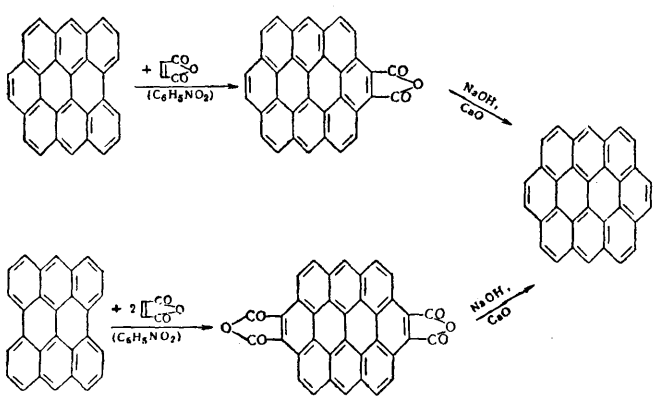
Coronene-1,2-dicarboxylic anhydride was decarboxylated to only an insignificant extent on being heated with copper in quinoline; successful decarboxylation of this anhydride to coronene (as also of the maleic anhydride adduct of perylene to benzoperylene[13]) was accomplished by heating with soda lime (in a current of nitrogen at 400°)[18]:



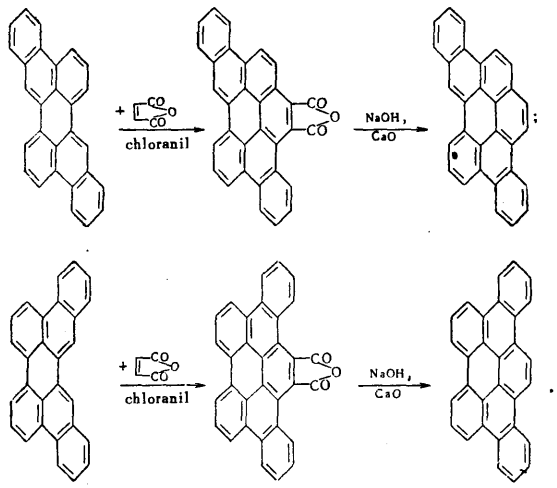
When soda lime is used as decarboxylating agent, reaction usually occurs in only one way, with formation of the corresponding aromatic hydrocarbons (in higher yields than when copper in quinoline is used). Thus a good yield of *p*-terphenyl has been obtained by distilling potassium 3,6-diphenylphthalate with soda lime[8]:



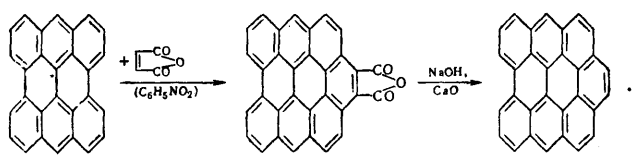
Decarboxylation with soda lime of dehydrogenated adducts of diene synthesis has been used to obtain many fused polycyclic aromatic hydrocarbons. Clar synthesised ovalene by distilling with soda lime (at atmospheric pressure and 400°) the adduct of 1,14-benzobisanthene and maleic anhydride or the adduct of bisanthene with two molecules of maleic anhydride[14]:



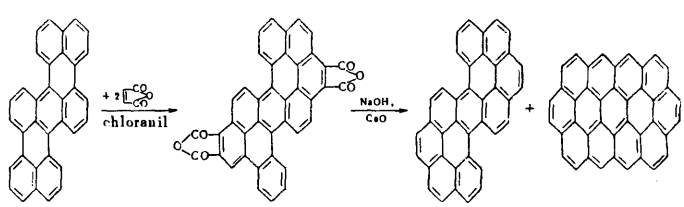
Analogous reactions have been used to convert 2,3:8,9-dibenzoperylene into 1,12:2,3:8,9-tribenzoperylene[14], and 2,3:10,11-dibenzoperylene into 1,12:2,3:10,11-tribenzoperylene[19]:



2,3:4,5-Dibenzocoronene has been obtained by heating 2,3:4,5-dibenzocoronene-9,10-dicarboxylic anhydride with soda lime at 500° (in a vacuum) in a current of hydrogen[15]:



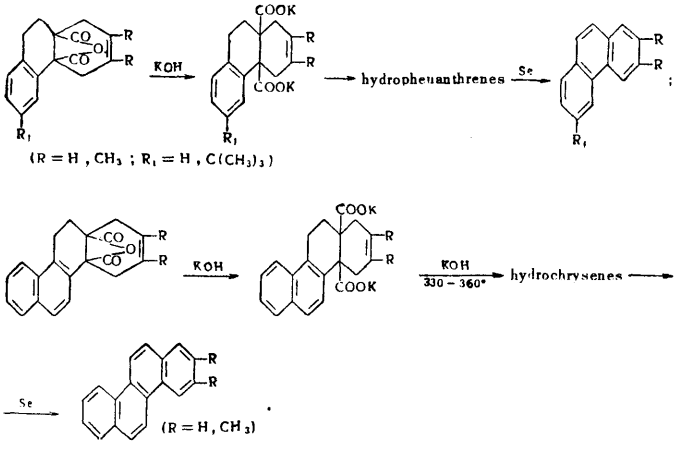
When the dianhydride resulting from the interaction of di-1,8-naphthyleneanthracene (tetrabenzopentacene) and maleic anhydride in the presence of chloranil is heated with soda lime (under the conditions described for the preparation of coronene[18]), formation of the normal reaction product, dinaphthoperopyrene, is accompanied by that of yet another polycyclic aromatic hydrocarbon ["circumanthracene" (Ed. of Translation)][17]:



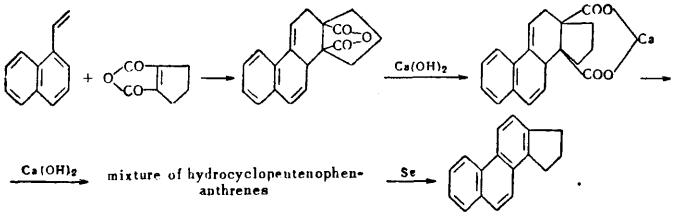
From the published results above it can be concluded that the conversion of adducts of diene synthesis into aromatic hydrocarbons by dehydrogenation followed by decarboxylation has been accomplished by many workers using various techniques and various dehydrogenating and decarboxylating agents. But methods which have been used successfully for the aromatisation of some adducts prove unsuitable for other adducts, sometimes of similar structure, and therefore the reactions which have been described (and the reagents employed in them) are not of general validity.

In the work of Fieser[6,24-26], Sen-Gupta[27-29], and their coworkers, and also in the work of other investigators[30], conversion of adducts of diene synthesis into aromatic hydrocarbons has been achieved by dehydrogenation and

decarboxylation in a different sequence: the initial adducts (or acids and salts obtained from them) were subjected first to decarboxylation and then to a subsequent dehydrogenation. This route (II) (p. 571) would have advantages over the first series of reactions (I), as it might be employed for the synthesis of hydroaromatic hydrocarbons. However, dibasic hydroaromatic acids or their anhydrides on decarboxylation usually yield a mixture of isomeric hydroaromatic hydrocarbons. Thus decarboxylation‡ of the potassium salts of dibasic acids of the hexahydrochrysene or hexahydrophenanthrene series (by heating them with excess of caustic potash) yields a mixture of hydrochrysenes or of tetra- and hexa-hydrophenanthrenes respectively[6,24-26].



When the calcium salts of dibasic acids obtained from adducts of various diene hydrocarbons with cyclopent-1--ene-1,2-dicarboxylic anhydride were distilled with calcium hydroxide, a mixture of hydroaromatic hydrocarbons was also formed, dehydrogenation of which gave the corresponding individual fused aromatic hydrocarbons containing the indane system, for example[27-29]:

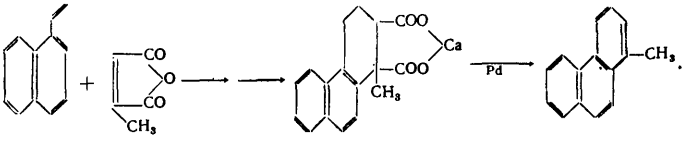


Thus the method is not suitable for the synthesis of individual hydroaromatic hydrocarbons of this structure: furthermore, subsequent dehydrogenation of hydroaromatic hydrocarbons is sometimes accompanied by cyclisation, aromatisation, or dealkylation. Hence the aromatisation of diene adducts by decarboxylation followed by dehydrogenation is of only limited application.

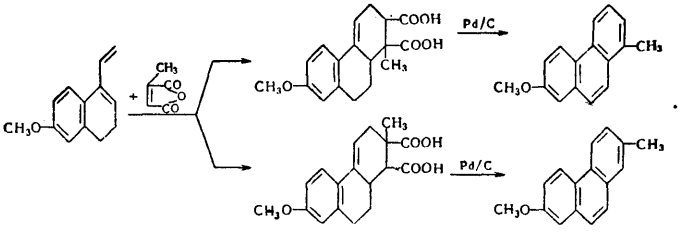
Depending on their structure, some diene adducts can be converted into aromatic hydrocarbons by simultaneous decarboxylation and dehydrogenation (III) (p. 571). Such a reaction is effected by the action of catalysts, such as platinum and palladium blacks[31], palladium on carbon[32-42], and others[30,43-48].

‡ Decarboxylation was accompanied by partial dehydrogenation and decarbonylation, and also elimination of potassium formate and oxalate[25].

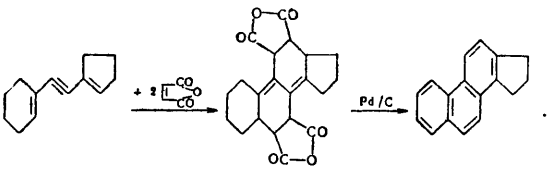
Thus the calcium salt of the dicarboxylic acid obtained by hydrolysis of the adduct of 1-vinylnaphthalene and methylmaleic (citraconoyl) anhydride has been converted into 1-methylphenanthrene by heating with palladium black in a current of nitrogen at 310°:[31]



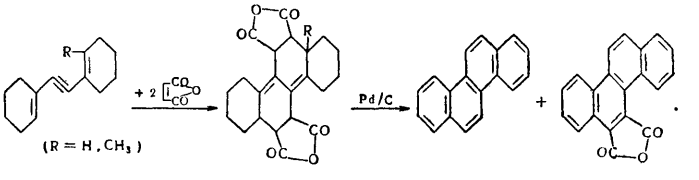
3,4-Dihydro-6-methoxy-1-vinylnaphthalene on reaction with methylmaleic anhydride forms a mixture of isomeric (*"ortho"* and *"meta"*) adducts, the structures of which were proved by heating them each with palladium on charcoal (in a current of nitrogen at 300°–315° or 320°), when they were converted respectively into 7-methoxy-1(and 2)-methylphenanthrene[32,37]:



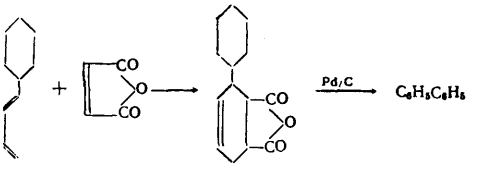
Butz and his coworkers subjected to aromatisation the dianhydride of steradiene-6,7,11,12-tetracarboxylic acid — the adduct of cyclohexenylcyclopentenylacetylene with two molecules of maleic anhydride — by heating it to 340°–390° with palladium on carbon (in the presence or absence of calcium hydroxide), with the aim of preparing 1,2-cyclopentenophenanthrene[33,34]:



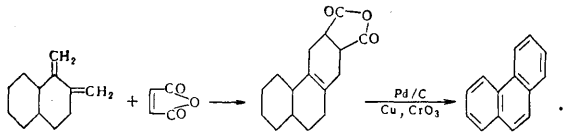
The structurally analogous dianhydride of tetradecahydrochrysene-5,6,11,12-tetracarboxylic acid on being heated under the same conditions was converted only into an insignificant yield of chrysene[35]:



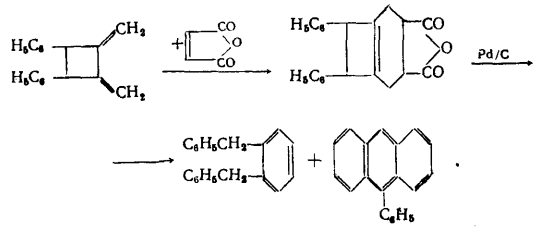
The adduct of cyclohexylbuta-1,3-diene and maleic anhydride has been converted into biphenyl by heating its benzene solution in the presence of 10% palladium on carbon in an atmosphere of nitrogen at 300° for 7 h:[36]



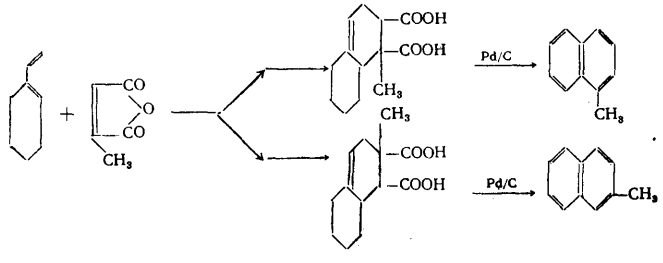
The structure of 1,2-dimethylenedecalin has been proved by converting its adduct with maleic anhydride into phenanthrene (in 67% yield) by heating it in the presence of 10% palladium on carbon and a copper–chromium oxide catalyst at 275° for $3\frac{1}{2}$ h:[45]



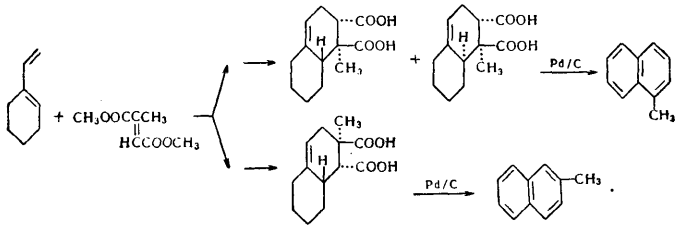
It is interesting that the vacuum distillation of the adduct of 1,2-dimethylene-3,4-diphenylcyclobutane with maleic anhydride in the presence of a mixed catalyst (10% palladium on carbon together with barium oxide) gives a mixture of two hydrocarbons, *o*-dibenzylbenzene and its dehydrogenation product, 9-phenylanthracene[49]:



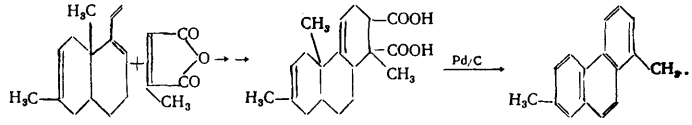
In a study of the condensation products formed by 1-vinylcyclohexene with methylmaleic anhydride, Nazarov converted the isomeric acids obtained by hydrolysis of the *"ortho"* and *"meta"* adducts into methylnaphthalenes. Aromatisation was effected by heating benzene solutions of the acids in the presence of 10% palladium on carbon in an autoclave at 360°–370° for 18 h:[39]



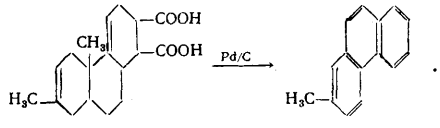
Under the same conditions isomeric methylnaphthalenes were obtained from acids, themselves obtained by hydrolysing diene adducts of 1-vinylcyclohexene with dimethyl mesaconate[40]:



When the dicarboxylic acid obtained by hydrolysis of the adduct of *cis*-3,4,5,8,9,10-hexahydro-6,9-dimethyl-1-vinylnaphthalene with methylmaleic anhydride is heated over 5% palladium on carbon in an autoclave (1 h at 140°–150° and 2 h at 340°–350°), decarboxylation and dehydrogenation are accompanied by partial demethylation, the methyl group in the ring-fusion position being split off with the formation of 1,7-dimethylphenanthrene[41]:

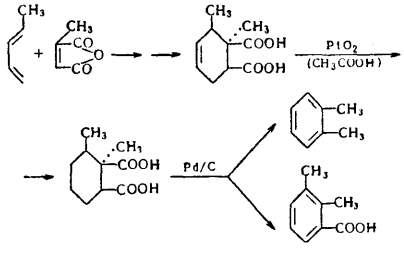


Similar demethylation took place in the aromatisation of 7,13-dimethyl-$\Delta^{4,6}$-decahydrophenanthrene-1,2-dicarboxylic acid. This acid, which has a similar structure to the above, was converted into 2-methylphenanthrene on heating over 10% palladium on carbon under more severe conditions (370° for 11 h), but the yield was only 4%[38]:

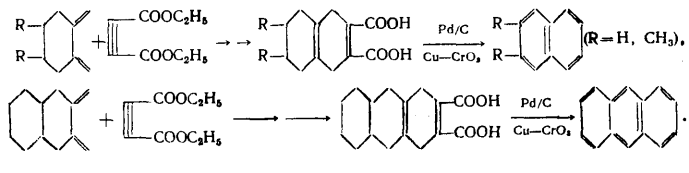


Thus this method for the aromatisation of the adducts of diene synthesis in the presence of catalysts also is not of general application, often giving low yields of aromatic hydrocarbons and being accompanied by side-reactions, including dealkylation.

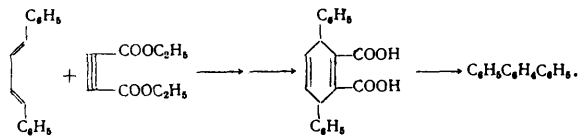
Aromatisation with decarboxylation over palladium on carbon is characteristic not only of tetrahydrophthalic acids (or their anhydrides), several hexa- and di-hydrophthalic acids undergoing a similar reaction. For example, hexahydro-2,3-dimethylphthalic acid, obtained by hydrogenation of the adduct of *trans*-pentadiene with methylmaleic anhydride, was converted into *o*-xylene by heating with 10% palladium on carbon in a sealed tube at 320° for 24 h; heating under the same conditions for 16 h produced only partial decarboxylation with the formation of 2,3-dimethylbenzoic acid[42]:



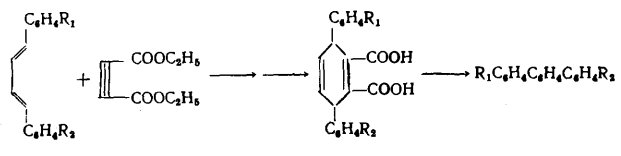
Several substituted dihydrophthalic acids (obtained by hydrolysis of the adducts of dienes with acetylenedicarboxylic ester) have been converted by heating them with palladium on carbon in the presence of a copper–chromium oxide catalyst[43,44,50]:



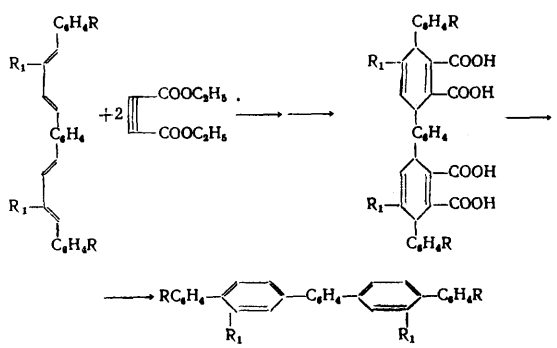
An interesting reaction is the oxidative decarboxylation of dihydrophthalic acids. Lohaus converted 3,6-dihydro--3,6-diphenylphthalic acid (from the adduct of 1,4-diphenylbutadiene with acetylenedicarboxylic ester) into the theoretical yield of *p*-terphenyl by heating it with $K_3Fe(CN)_6$ in alkaline solution[48]:



McDonald and Campbell used the Lohaus method (without isolating the products of diene synthesis from the reaction mixture) to obtain high yields of polyphenyls: *p*-terphenyl (in 60% yield), 4-methyl-*p*-terphenyl (70%), 4,4″-dimethyl-*p*-terphenyl (42%), quinquephenyl (52%), and 4,4‴- and 2′, 3‴′-dimethylquinquephenyl[47]:

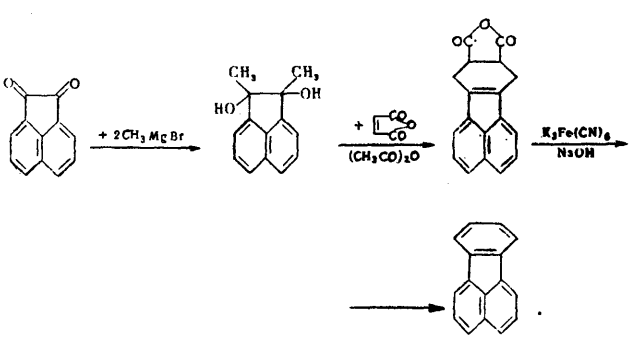


($R_1=R_2=H$, CH_3; $R_1=H$, $R_2=CH_3$).

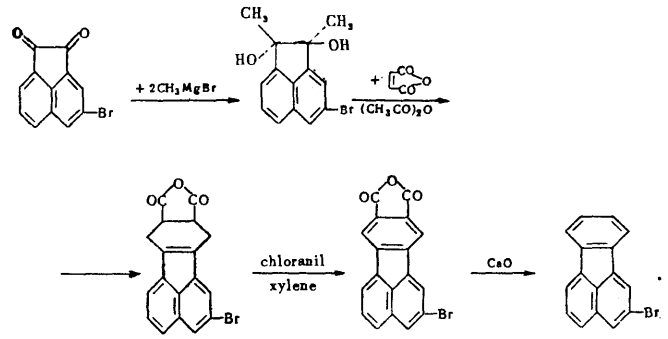


($R=R_1=H$; $R_1=H$, $R=CH_3$; $R=H$; $R_1=CH_3$).

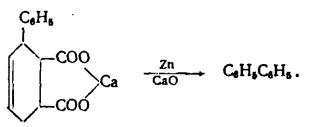
The substituted 1,2,3,6-tetrahydrophthalic anhydride formed by reaction of maleic anhydride with the *trans*-diol, itself obtained from acenaphthenequinone and methylmagnesium iodide, also underwent oxidative decarboxylation on being heated with alkaline $K_3Fe(CN)_6$ solution, and was converted into fluoranthene (in 50% yield)[9]:



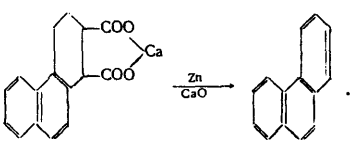
This reaction probably represents only a particular case, since the same workers employed a different scheme to prepare substituted fluoranthenes (7,10-dimethylfluoranthene, 1-bromofluoranthene, 7,8-benzofluoranthene, and 2,5-di-*p*-tolyl-8,9-benzofluoranthene), although these compounds were obtained by them in considerably smaller yields (12–25%[9,23]), for example:



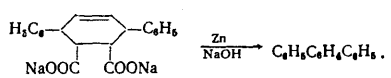
Several cases have been reported of the simultaneous decarboxylation and dehydrogenation of tetrahydrophthalate salts in the presence of zinc dust. Dry distillation of calcium 3-phenyltetrahydrophthalate with zinc dust and calcium oxide gave biphenyl[46]:



The same reaction has been used to convert calcium tetrahydrophenanthrene-1,2-dicarboxylate into phenanthrene[2]:

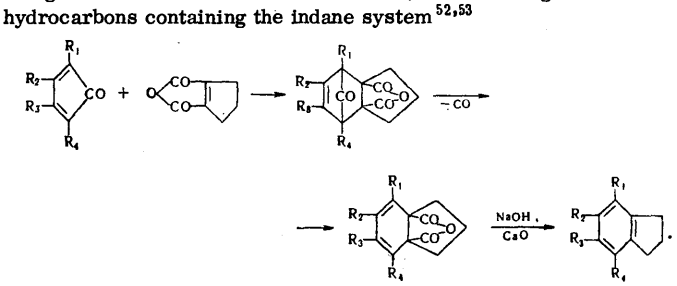


Distillation of sodium 3,6-diphenylhexahydrophthalate with zinc dust and caustic soda gave *p*-terphenyl[46]:

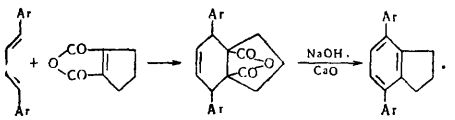


Diene adducts in which the anhydride group is combined with tertiary carbon atoms are also able to undergo simultaneous decarboxylation and dehydrogenation on being heated with soda lime in a vacuum. Thus the adducts of dienes with cyclopent-1-ene-1,2-dicarboxylic anhydride§

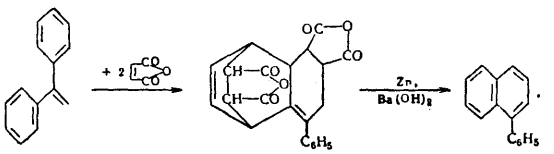
§ Cyclopent-1-ene-1,2-dicarboxylic anhydride gives with tetrasubstituted cyclopentadienones adducts which, on being heated in tetralin, readily split off the *endo*-carbonyl group, being converted into dihydroindanedicarboxylic anhydrides; these last compounds are in turn decarboxylated and simultaneously dehydrogenated on being heated with soda lime in a vacuum, also forming aromatic hydrocarbons containing the indane system[52,53]



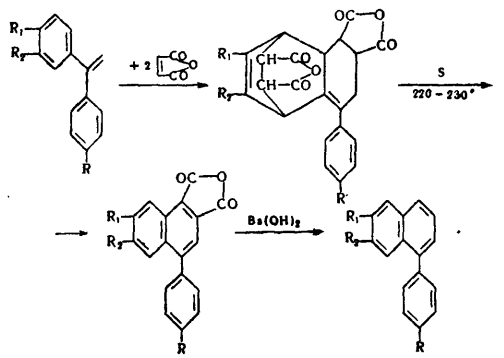
have been converted into aromatic hydrocarbons containing an indane group[51]:



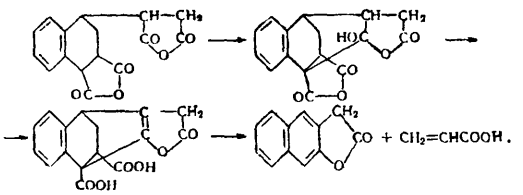
Apart from the usual products of diene synthesis — 1,2,3,6-tetrahydrophthalic anhydrides — the products obtained by reaction of dienes with two molecules of maleic anhydride can also be converted into aromatic hydrocarbons. Thus Wagner-Jauregg obtained 1-phenylnaphthalene by distilling with zinc dust or barium hydroxide the adduct of 1,1-diphenylethylene with two molecules of maleic anhydride[54]:



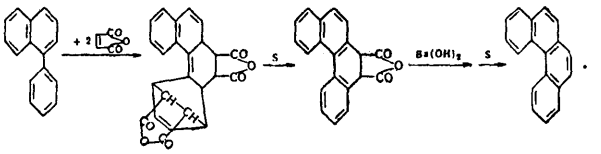
When these "double" adducts¶ are heated with sulphur, they split off one of the maleic anhydride molecules and, being dehydrogenated, are converted into anhydrides of arylnaphthalenedicarboxylic acids; the latter have in turn been converted into their barium salts, which on decarboxylation by heating with copper bronze are converted into 1-arylnaphthalenes (in yields of 22–90%)[55,56]:



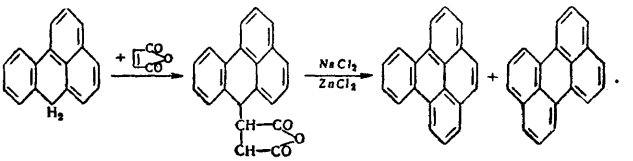
¶ Aromatic and hydroaromatic hydrocarbons of the "styrene" type on reaction with maleic anhydride may form "double" adducts of different structure (of the Schmitz–Josten type), which on dry distillation split off acrylic acid and are converted into lactones of hydroxynaphthylacetic acid[57,58]



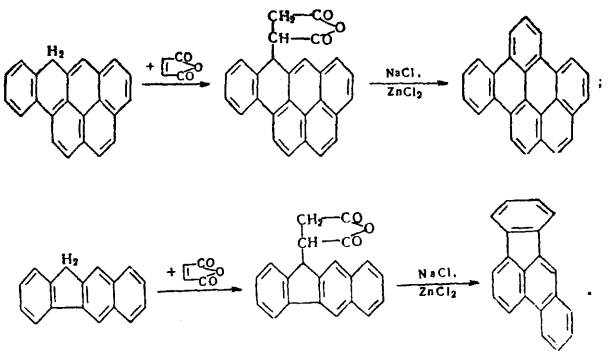
3,4-Benzophenanthrene has been obtained by a similar series of reactions[59]:



To obtain fused aromatic hydrocarbons of complicated structure, Clar used addition products of non-benzenoid fused polycyclic hydrocarbons with maleic anhydride. These compounds, which are substituted succinic anhydrides, undergo aromatisation on being melted with sodium chloride and zinc chloride, with the elimination of carbon dioxide and water. Mesobenzanthrene has been converted by this method into 1,2-benzopyrene (contaminated with perylene)[60]:

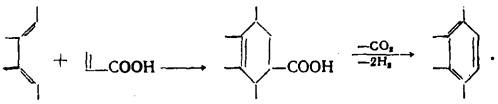


Similar schemes have been used to obtain 1,2:4,5-dibenzopyrene[60], 1,12:10,11-dibenzoperylene[61], and 2,3-benzofluoranthene[61], for example:

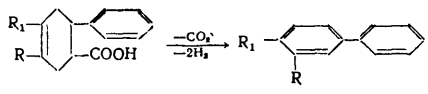


It is evident from the published results which have been quoted that only tetra(and hexa- and di)-hydrogenated *phthalic acids* and their anhydrides — the adducts of dienes with maleic anhydride, its homologues and cyclic analogues — have been converted into polycyclic aromatic hydrocarbons by successive or simultaneous decarboxylation and dehydrogenation.

The present reviewer has shown that *tetrahydrobenzoic acids* — the adducts of dienes with acrylic, cinnamic, and *p*-phenylcinnamic acids — can also be converted into aromatic hydrocarbons by simultaneous decarboxylation and dehydrogenation without the use of any chemical reagents or catalysts. This thermal aromatisation of tetrahydrobenzoic acids is achieved simply by heating in an autoclave; adducts with acrylic acid (at 500°) have given benzene and alkylbenzenes[62]:

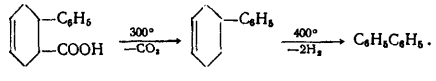


Adducts of dienes with cinnamic acid have been decarboxylated and dehydrogenated by heating them in an autoclave to 400°, hydrocarbons of the biphenyl series being formed[63]:

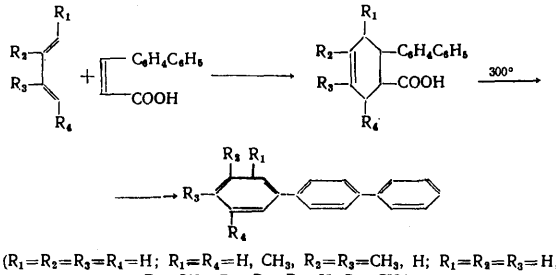


(R=R$_1$=H, CH$_3$; R=H, R$_1$=CH$_3$).

Separate experiments established that the first stage in the reaction is decarboxylation with the formation of cyclohexenes, which are then dehydrogenated. Thus when 1,2,3,6-tetrahydro-2-phenylbenzoic acid (the adduct of butadiene and cinnamic acid) was heated in an autoclave at 300°, it was merely decarboxylated with the formation of cyclohex-3-enylbenzene; when the latter was heated in an autoclave to 400° (*i.e.* under conditions for the aromatisation of 2-phenyltetrahydrobenzoic acids), it was readily dehydrogenated to biphenyl[63]:



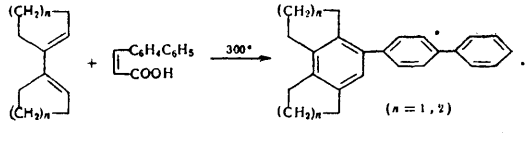
Adducts of *p*-phenylcinnamic acid already split off hydrogen and carbon dioxide at 300°, being converted into *p*-terphenyl and its homologues[64]:



(R$_1$=R$_2$=R$_3$=R$_4$=H; R$_1$=R$_4$=H, CH$_3$, R$_2$=R$_3$=CH$_3$, H; R$_1$=R$_2$=R$_3$=H, R$_4$=CH$_3$; R$_1$=R$_2$=R$_4$=H, R$_3$=CH$_3$).

Hydrocarbons of the benzene, biphenyl, and *p*-terphenyl series can also be obtained in a single stage, by directly heating under the above conditions the original components of the diene synthesis (diene hydrocarbons with acrylic, cinnamic, and *p*-phenylcinnamic acids respectively); yields of the hydrocarbons are increased if the initial reaction mixture is first heated in an autoclave under the optimum conditions for obtaining the given adduct, and then at 500°, 400°, or 300° respectively[62-64].

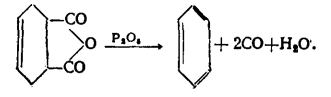
Dicyclic hydrocarbon ring assemblies — 1,1′-bi(cyclohexenyl) and 1,1′-bi(cyclopentenyl) — yielded by the same reaction *polycyclic hydrocarbons containing the* p-*terphenyl system* (2,3 : 4,5-dicyclohexeno-*p*-terphenyl and 2,3 : 4,5-dicyclopenteno-*p*-terphenyl)[65]:



3. AROMATISATION OF ADDUCTS OF DIENE SYNTHESIS — TETRAHYDROPHTHALIC ACIDS, THEIR ANHYDRIDES, AND TETRAHYDROBENZOIC ACIDS — BY DECARBONYLATION AND DEHYDRATION

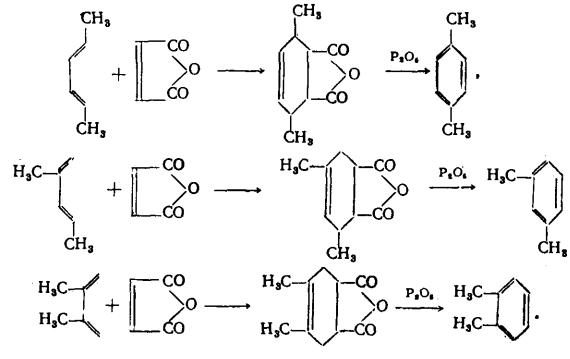
In all the methods described above, the conversion of 1,2,3,6-tetrahydrophthalic anhydrides (or acids) into aromatic hydrocarbons has been accomplished by successive or simultaneous decarboxylation and dehydrogenation.

A fundamentally different route for the aromatisation of such anhydrides is reaction with phosphorus pentoxide, involving the simultaneous elimination of carbon monoxide and water:

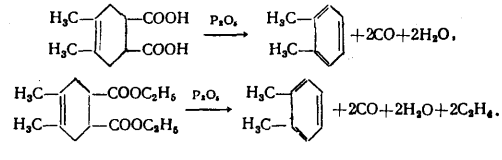


This reaction, discovered in 1953[66], is now a general method for preparing aromatic hydrocarbons of various classes — alkylbenzenes, biphenyls, polyphenyls, and fused aromatic and hydroaromatic hydrocarbons (tetralins, indanes, fluorenes, phenanthrenes, octahydrophenanthrenes, and chrysenes).

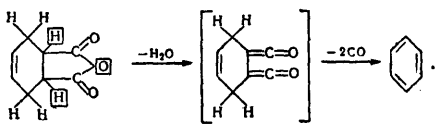
The aromatisation of 1,2,3,6-tetrahydrophthalic anhydrides by means of phosphorus pentoxide is distinguished by its experimental simplicity (a mixture of the anhydride and the pentoxide is heated in a Wurtz flask, and the resulting hydrocarbon is distilled off), it gives high yields (40–90%), and permits the preparation of aromatic hydrocarbons having substituents in definite positions, uncontaminated by isomeric hydrocarbons. Thus the maleic anhydride adducts of the isomeric alkadienes C_6H_{10} (hexa-2,4-diene, 2-methylpenta-1,3-diene, and 2,3-dimethylbuta-1,3-diene) gave on aromatisation over phosphorus pentoxide the *isomeric xylenes*[66]:



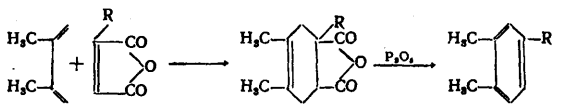
Not only the anhydrides but the tetrahydrophthalic acids themselves and their esters undergo similar cleavage under the influence of phosphorus pentoxide, losing water and carbon monoxide (and in the case of esters also eliminating ethylene) and being converted into aromatic hydrocarbons. Thus *o*-xylene has been obtained from 4,5-dimethyltetrahydrophthalic acid and its ethyl ester[67]:



It might be supposed that the first stage in the reaction between phosphorus pentoxide and tetrahydrophthalic anhydrides is dehydration with the intermediate formation of the corresponding diketens, which then undergo decarbonylation with simultaneous intracyclic redistribution of hydrogen and formation of a stable aromatic ring:

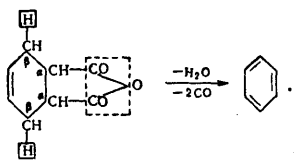


For aromatisation to take place via the intermediate formation of diketens, it is necessary that hydrogen atoms should be present in position 1, *i.e.* in the α position with respect to the carboxyl groups; reaction should not have taken place with tetrahydrophthalic anhydrides having an alkyl group in one of these positions. It was found, however, that in this case the reaction took place normally, with the formation of aromatic hydrocarbons: adducts of 2,3-dimethylbuta-1,3-diene with alkylmaleic anhydrides gave 1,2,4-trialkylbenzenes (1,2,4-trimethylbenzene, ethyldimethylbenzene, and butyldimethylbenzene)[67,68]:

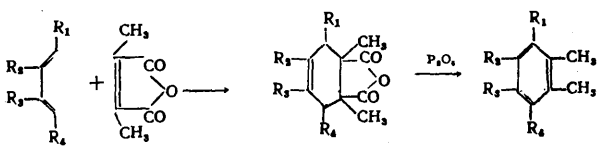


(R=CH_3, C_2H_5, C_4H_9).

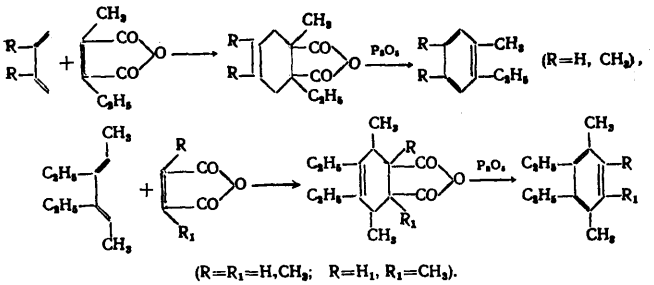
From this it was concluded that the formation of aromatic hydrocarbons by the reaction of tetrahydrophthalic anhydrides with phosphorus pentoxide is due to simultaneous dehydration (involving hydrogen atoms in the β positions with respect to the carboxyl groups) and decarbonylation, and does not involve the intermediate formation of diketens[67]:



Adducts of dienes with dialkylmaleic anhydrides can also undergo aromatisation in the presence of phosphorus pentoxide. This method has been used to synthesise tetramethylbenzenes (using dimethylmaleic anhydride as the initial dienophil)[69], ethyltoluene and ethyltrimethylbenzene (using ethylmethylmaleic anhydride as dienophil)[70], and also diethylpolymethylbenzenes (using 3,4-diethylhexa-2,4-diene as a suitable diene, and maleic anhydride and its homologues as dienophils)[71,72]:

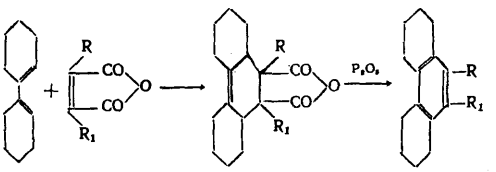


(R_1=R_4=H, CH_3; R_2=R_3=CH_3, H; R_1=R_2=H, R_3=R_4=CH_3).



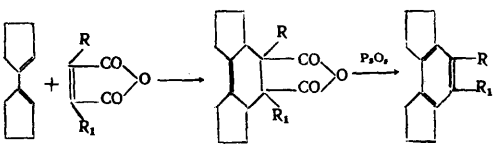
(R=R_1=H,CH_3; R=H_1, R_1=CH_3).

The aromatisation of tetrahydrophthalic anhydrides in the presence of phosphorus pentoxide has also been used to obtain tricyclic hydroaromatic hydrocarbons of fused structure. The initial diene hydrocarbons were the bi(cycloalkenyls): 1,1′-bi(cyclohexenyl), 1,1′-bi(cyclopentenyl), and 1-(cyclopent-1-enyl)cyclohexene[73,74]. With 1,1′-bi(cyclohexenyl) as initial diene hydrocarbon, and maleic and alkylmaleic anhydrides as dienophils, octahydrophenanthrene and its homologues have been prepared[73]:



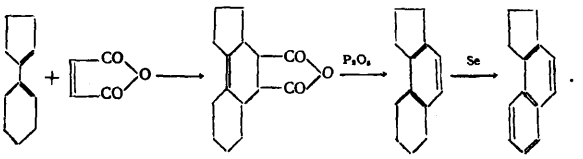
(R=R_1=H, CH_3; R=H, R_1=CH_3).

1,2,3,6,7,8-Hexahydro-as-*indacene* and its homologues have been obtained from adducts of 1,1′-bi(cyclopentenyl) with maleic, methylmaleic, and dimethylmaleic anhydrides[73]:

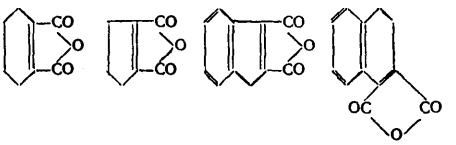


(R=R_1=H, CH_3; R=H, R_1=CH_3).

The adduct of 1-(cyclopent-1-enyl)cyclohexene with maleic anhydride has been converted by reaction with phosphorus pentoxide into 4,5-cyclohexenoindane, which was then dehydrogenated to 1,2-cyclopentenonaphthalene by heating with selenium[74]:

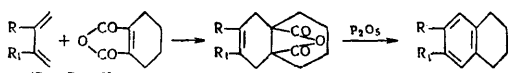


In the synthesis of *hydroaromatic polycyclic hydrocarbons* the dienophils used were cyclic analogues of maleic anhydride — the 1,2-dicarboxylic anhydrides of cyclohexene, cyclopentene, indene, and 3,4-dihydronaphthalene:

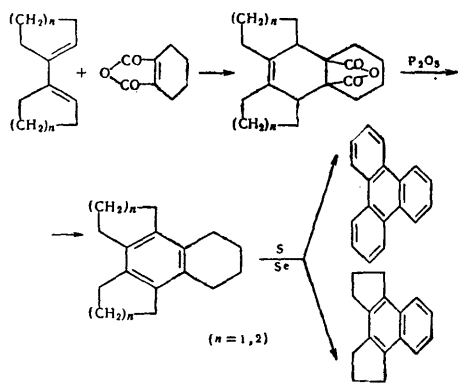


The products resulting from reaction of adducts of these dienophils with phosphorus pentoxide were polycyclic aromatic hydrocarbons — tetralins, indanes, fluorenes, and 9,10-dihydrophenanthrenes. Their formation also involved elimination of carbon monoxide and water, and in all cases it was only the six-membered ring containing a double bond which became aromatic.

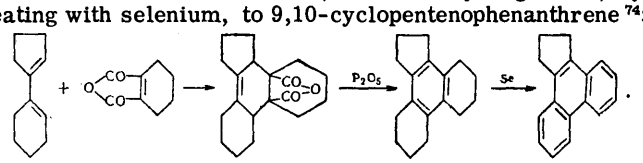
The adducts of butadiene and its homologues (isoprene and 2,3-dimethylbuta-1,3-diene) with *cyclohex*-1-*ene*-1,2-*dicarboxylic anhydride* on being heated with phosphorus pentoxide gave tetralin[75] and alkyltetralins[76]:



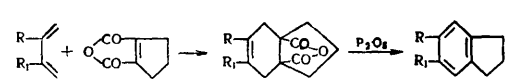
Aromatisation by means of phosphorus pentoxide of adducts of cyclohex-1-ene-1,2-dicarboxylic anhydride with dicyclic diene hydrocarbons — 1,1′-bi(cyclohexenyl) and 1,1′-bi(cyclopentenyl) — yielded *hydroaromatic fused polycyclic hydrocarbons containing a tetralin ring system* (1–12-dodecahydrotriphenylene and dicyclopentenocyclohexenobenzene), which were then dehydrogenated (by heating with sulphur or selenium) to triphenylene and 1,2:3,4-dicyclopentenonaphthalene[75]:



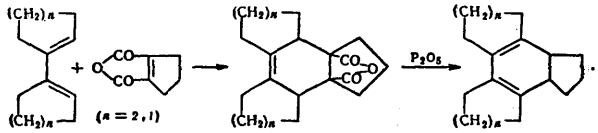
The use of 1-(cyclopent-1-enyl)cyclohexene as initial diene component enabled a polycyclic aromatic hydrocarbon containing the indane ring system (dicyclohexenocyclopentenobenzene) to be obtained; it was dehydrogenated, by heating with selenium, to 9,10-cyclopentenophenanthrene[74]:



Adducts of another cyclic analogue of maleic anhydride — *cyclopent*-1-*ene*-1,2-*dicarboxylic anhydride* — have been converted, by heating with phosphorus pentoxide, into *indane* and *its homologues*, as well as into *polycyclic hydrocarbons containing the indane system* — 4,5:6,7-dicyclohexenoindane† and 4,5:6,7-dicyclopentenoindane (tricyclopentenobenzene)[77]:

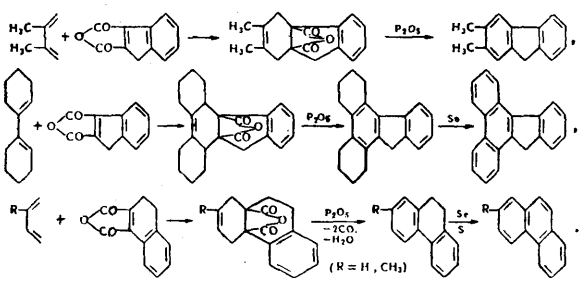


† As mentioned in the previous paragraph, this hydrocarbon has also been obtained by using phosphorus pentoxide in a different way[74].

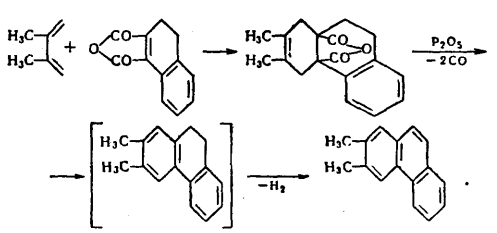


Thus aromatisation in the presence of phosphorus pentoxide can be used to convert adducts of diene hydrocarbons with cyclic analogues of maleic anhydride into high yields (44–84%) of dicyclic and also — with bi(cycloalkenyls) as dienes — polycyclic hydroaromatic hydrocarbons, which can then be dehydrogenated in the usual way to the corresponding aromatic hydrocarbons.

A study has been made of the reaction with phosphorus pentoxide of adducts of diene hydrocarbons with dienophils of more complicated structure (*indene*-1,2-*dicarboxylic* and 3,4-*dihydronaphthalene*-1,2-*dicarboxylic anhydrides*). Under the influence of phosphorus pentoxide (at 160°–300°) these adducts, like those of cyclohex-1-ene-1,2-dicarboxylic and cyclopent-1-ene-1,2-dicarboxylic anhydrides, underwent aromatisation, eliminating carbon monoxide and water and being converted into fluorenes[78] and 9,10-dihydrophenanthrene[79] respectively:

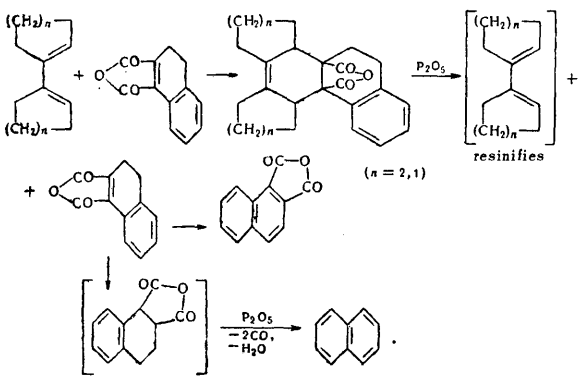


In the case of one of the adducts of 3,4-dihydronaphthalene-1,2-dicarboxylic anhydride, it was shown that heating the reaction mixture with phosphorus pentoxide to 350° for several hours resulted in the appearance of a secondary reaction, dehydrogenation of the normal reaction product (a homologue of dihydrophenanthrene). Thus when the adduct from 2,3-dimethylbuta-1,3-diene was heated with phosphorus pentoxide at 320°–350° for 6 h, instead of the expected 9,10-dihydro-2,3-dimethylphenanthrene, only its dehydrogenation product, 2,3-dimethylphenanthrene, was isolated[79]:



Adducts of the same dienophil with dicyclic diene hydrocarbons proved most resistant to the action of phosphorus pentoxide: their decomposition was carried out at 300°–400° for 10 h, but neither 1,2:3,4-bi(cyclohexeno)- nor 1,2:3,4-bi(cyclopenteno)-9,10-dihydrophenanthrene (nor the corresponding phenanthrenes) were found among the reaction products, both adducts giving only naphthalene-1,2-dicarboxylic anhydride and naphthalene. The formation of these substances can be explained by decomposition of the

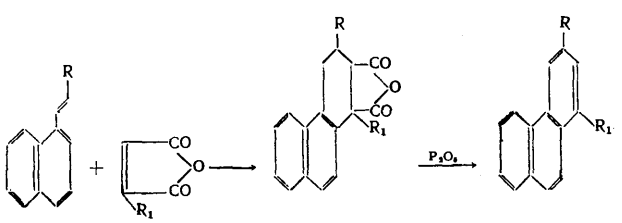
adducts at the high temperatures (300°–400°) into the original diene (which resinifies under the influence of the phosphorus pentoxide) and the dienophil, 3,4-dihydronaphthalene-1,2-dicarboxylic anhydride; the latter is converted (by a type of irreversible catalysis) into a mixture of naphthalene-1,2-dicarboxylic anhydride, which does not change further and is among the final products of the reaction, and 1,2,3,4-tetrahydronaphthalene-1,2-dicarboxylic anhydride, which in the presence of the phosphorus pentoxide undergoes the usual aromatisation, splitting off carbon monoxide and water and being converted into naphthalene (second reaction product)[79]:



Thus adducts of dicyclic diene hydrocarbons with 3,4-dihydronaphthalene-1,2-dicarboxylic anhydride, in contrast to adducts of these dienes with the other cyclic dienophils studied, undergo breakdown on being heated with phosphorus pentoxide.

Depending on the structure of the diene adducts, their reaction with phosphorus pentoxide may not yield dihydrogenated derivatives of aromatic hydrocarbons but the fused aromatic hydrocarbons — phenanthrenes and chrysenes — directly (in one stage).

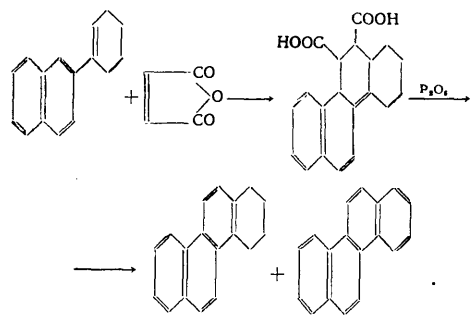
The initial diene components used in the preparation of hydrocarbons of the *phenanthrene* series were 1-vinylnaphthalene and 1-propenylnaphthalene, the adducts‡ of which with the simplest dienophils — maleic and methylmaleic anhydrides — were made to react with phosphorus pentoxide[80]:



(R=R$_1$=H, CH$_3$; R=H, CH$_3$, R$_1$=CH$_3$, H).

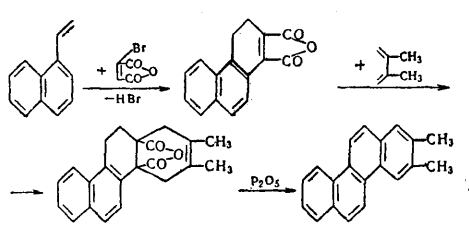
The formation only of 1-methylphenanthrene (from the adduct of 1-vinylnaphthalene) and 1,3-dimethylphenanthrene (from the 1-propenylnaphthalene adduct), not mixed with isomeric hydrocarbons having a different orientation of the methyl groups, provides in addition a proof of the *"ortho"* structure of the adducts of these dienes with such unsymmetrical dienophils as methylmaleic anhydride.

The synthesis of *chrysene* from 2-cyclohexenylnaphthalene was accomplished in a similar manner to that of phenanthrenes from adducts of 1-vinyl- and 1-propenyl--naphthalene. 4b,5,6,6a,7,8,9,10-Octahydrochrysene-5,6--dicarboxylic acid, obtained by hydrolysing the adduct of 2-cyclohexenylnaphthalene with maleic anhydride, was heated with phosphorus pentoxide. Decarbonylation and dehydration of the acid by the phosphorus pentoxide took place only on gradual and prolonged heating (from 210° to 350° during 6–7 h), 1,2,3,4-tetrahydrochrysene being formed; a small amount of chrysene was also isolated from the reaction products, its formation being due to simultaneous dehydrogenation[81]:



The synthesis of *homologues of chrysene* by the same method necessitated the use either of homologues of 2-cyclohexenylnaphthalene as the initial diene component, or of homologues of maleic anhydride as the dienophil. However, these last homologues do not react even with 2-cyclohexenylnaphthalene itself, and therefore chrysene homologues were obtained by a synthesis involving a larger number of stages but from more readily available components.

2,3-Dimethylchrysene was synthesised by the reaction of phosphorus pentoxide with 1,4,4a,11,12,12a-hexahydro--2,3-dimethylchrysene-4a,12a-dicarboxylic anhydride, which was obtained by a two-stage diene synthesis: reaction of 1-vinylnaphthalene with bromomaleic anhydride gave 3,4-dihydrophenanthrene-1,2-dicarboxylic anhydride, and the latter then entered into a diene synthesis with 2,3-dimethylbuta-1,3-diene in the presence of picric acid and phenothiazine[81]:

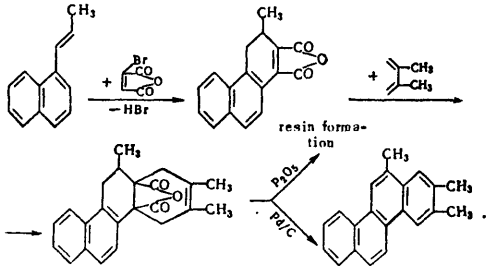


The tetrahydro-2,3-dimethylchrysene formed as an intermediate was immediately and completely dehydrogenated

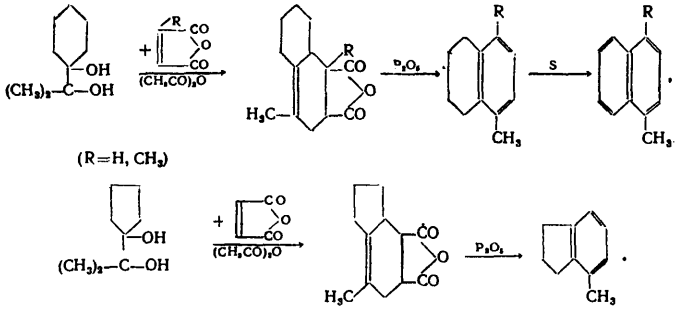
‡ Adducts of 1-vinylnaphthalene and its homologues with some dienophils are unstable: in acid medium or on prolonged heating they isomerise readily into a more stable isomer, with migration of the double bond into the naphthalene ring. Under the conditions of diene synthesis employed[80] all the adducts obtained were anhydrides of 1,2,3,4-tetrahydrophenanthrene-1,2-decarboxylic acid.

under the conditions of the reaction (whereas tetrahydrochrysene was only partly dehydrogenated).

2,3,12-Trimethylchrysene could not be synthesised in a similar manner using 1-propenylnaphthalene as the initial diene: when the 1,4,4a,11,12,12a-hexahydro-2,3,12-trimethylchrysene-4a,12a-dicarboxylic anhydride obtained by a similar two-stage diene synthesis was heated with phosphorus pentoxide, it resinified, and only on being heated with palladium on carbon to 330°–340° could it be converted into 2,3,12-trimethylchrysene[81]:



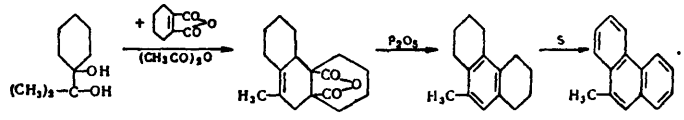
It is evident from the above that the initial dienes used in the synthesis of dicyclic and polycyclic aromatic hydrocarbons have included alkadienes, bi(cycloalkenyls), alkenylnaphthalenes, and alkenylcycloalkenes. Alkadienes and alkenylcycloalkenes are in many cases obtained by dehydration of the corresponding pinacols. In the synthesis of several *tetralin and indane hydrocarbons*, the adducts for aromatisation with phosphorus pentoxide have been obtained in a single stage, by heating unsymmetrical pinacols with maleic or methylmaleic anhydride in acetic anhydride[82]:



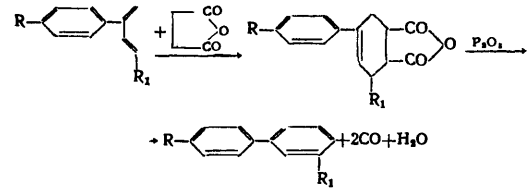
The 5,8-dimethyltetralin and the 1,4-dimethylnaphthalene obtained from it were uncontaminated with the isomeric hydrocarbons 5,7-dimethyltetralin and 1,3-dimethylnaphthalene respectively, which could have been formed if the initial anhydride had been contaminated with a small quantity of the isomeric *"meta"* adduct, the anhydride of Δ^4-octahydro-2,4-dimethylnaphthalene-1,2-dicarboxylic acid.

The use of pinacols enables the stage of preparing the diene hydrocarbons to be avoided, the latter often being unstable and polymerising readily under the conditions of diene synthesis; the above method for obtaining several homologues of tetralin and indane is simpler than the method described earlier (p. 581).

The preparation of aromatic hydrocarbons from adducts in which the diene component is a pinacol has been applied also to the synthesis of methylphenanthrenes. Thus 9-methylphenanthrene has been obtained from the adduct of the mixed pinacol of acetone and cyclohexanone with 3,4,5,6-tetrahydrophthalic anhydride[80]:

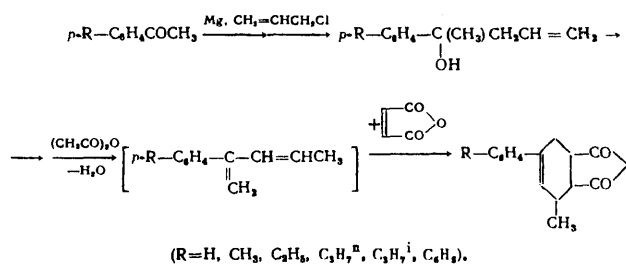


The aromatisation of diene adducts in the presence of phosphorus pentoxide can be employed for the synthesis not only of fused dicyclic and polycyclic aromatic-hydrocarbons but also of non-fused hydrocarbons — *biphenyls* and p-*terphenyls*. Thus 4-aryltetrahydrophthalic anhydrides, in which the aryl substituent is remote from the anhydride group (the behaviour of the 2- and 3-aryl anhydrides, in which the aryl substituent is located closer to the anhydride group, will be considered below), behave in a similar manner to alkyltetrahydrophthalic anhydrides on being heated with phosphorus pentoxide, simultaneous decarbonylation and dehydration yielding aromatic hydrocarbons of these series[83,84]:



R=R₁=H; R₁=CH₃; R=H, CH₃, C_2H_5, $C_3H_7^n$, $C_3H_7^i$, C_6H_5).

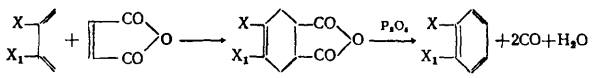
A general method for synthesising alkylbiphenyls having the unsymmetrical structure of 4′-alkyl-3-methylbiphenyls (R = Alk, $R_1 = CH_3$) involves the reaction of phosphorus pentoxide with adducts of 2-arylpenta-1,3-dienes and maleic anhydride. Here, too, there is no need to isolate the 2-arylpentadienes on formation from the corresponding unsaturated alcohols: it has proved possible to make maleic anhydride react (in the presence of acetic anhydride and potassium hydrogen sulphate) with unsaturated aromatic alcohols — allylarylmethylmethanols — which are readily obtained from *p*-alkylacetophenones, magnesium, and allyl chloride, and are dehydrated (with simultaneous migration of the double bond) in the process of diene synthesis itself[84]:



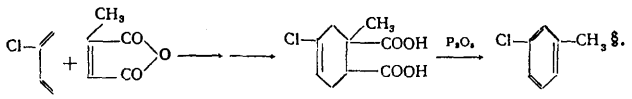
(R=H, CH_3, C_2H_5, $C_3H_7^n$, $C_3H_7^i$, C_6H_5).

Halogenated tetrahydrophthalic acids and their anhydrides — the adducts of halogenated dienes with maleic and

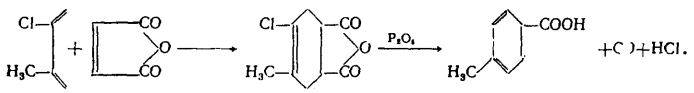
methylmaleic anhydrides — can also undergo decarbonylation and dehydration in the presence of phosphorus pentoxide[85]:



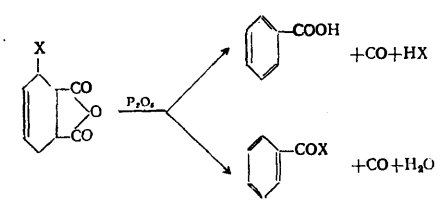
(X=Cl, Br, X_1=H; X=X_1=Cl).



Further study of the reaction of halogenated tetrahydrophthalic acids with phosphorus pentoxide gave unexpected results: 4-chloro-1,2,3,6-tetrahydro-5-methylphthalic anhydride (the adduct of methylchloroprene and maleic anhydride) yielded, instead of the expected *o*-chlorotoluene, *p*-toluic acid (with the elimination of hydrogen chloride and one molecule of carbon monoxide):



This type of anomalous reaction was found to be characteristic of other halogenated tetrahydrophthalic acids. For example, 3-chloro-1,2,3,6-tetrahydrophthalic anhydride (the adduct of butadiene and chloromaleic anhydride) and the corresponding 3-bromo derivative are converted into benzoic acid on reaction with phosphorus pentoxide; but in these two cases, in contrast to the preceding case, the corresponding benzoyl halides were also isolated from the reaction products:

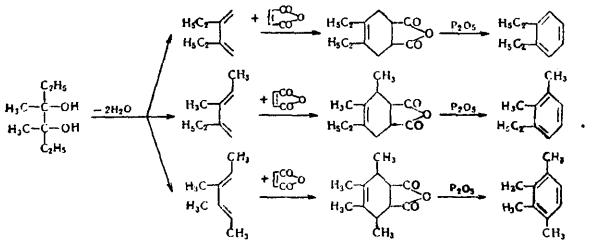


Thus if halogenated tetrahydrophthalic acids and their anhydrides readily split off hydrogen halide, their aromatisation under the influence of phosphorus pentoxide does not result in the formation of aryl halides.

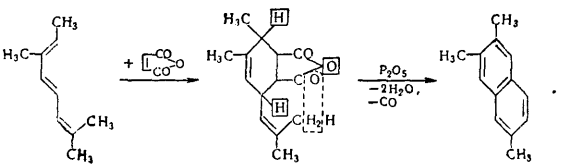
Thus the two consecutive reactions — diene synthesis using maleic anhydride, its homologues, and cyclic analogues as dienophils followed by aromatisation of the adducts by the action of phosphorus pentoxide — represent a convenient and fairly general route for the synthesis of mono-, di-, and poly-cyclic aromatic and hydroaromatic hydrocarbons of fused and non-fused structure, such as alkylbenzenes and their halogenated derivatives, tetralins, indanes, fluorenes, including polycyclic hydrocarbons containing the tetralin, indane, and fluorene systems, and also phenanthrenes and hydrophenanthrenes, chrysenes, biphenyls, and *p*-terphenyls.

The above survey shows that all the reactions undergone by adducts of diene synthesis (alkyl-, cycloalkenyl-, and some aryl-tetrahydrophthalic anhydrides) under the influence of phosphorus pentoxide consist in simultaneous decarbonylation and dehydration. This represents the *first type of aromatisation reaction* of adducts of diene synthesis[83].

Apart from preparative purposes, the aromatisation of diene adducts by means of phosphorus pentoxide can also be used to establish the structure of the original diene system. Thus this reaction has been employed by Kazanskii and his coworkers[91] to identify the individual components in the mixture of diene hydrocarbons obtained by the dehydration of 3,4-dimethylhexane-3,4-diol (the pinacol from ethyl methyl ketone):



In order to establish the structure of alloocimene, its maleic anhydride adduct was also subjected to aromatisation with phosphorus pentoxide: the product of the reaction was 2,3,6-trimethylnaphthalene, the formation of which was represented as follows[92]:

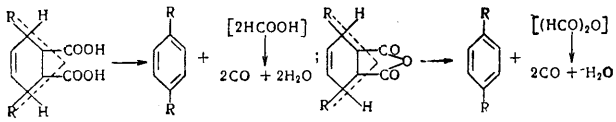


The reaction of diene adducts with phosphorus pentoxide — their conversion into easily identifiable aromatic hydrocarbons — is of value also for elucidating the spatial direction of diene synthesis with dienophils of unsymmetrical structure. This method has been used, for example, to demonstrate the *"ortho"* structure of the adducts of 1-vinyl- and 1-propenyl-naphthalene with methylmaleic anhydride[80], the preferential formation of the *"para"* adduct of this same dienophil with the mixed pinacol of cyclohexanone and acetone[82], and finally the preferential formation of the *"meta"* adduct in the reaction of chloroprene with methylmaleic anhydride in propionic acid[85].

Since the aromatisation of tetrahydrophthalic anhydrides under the influence of phosphorus pentoxide consists in decarbonylation accompanied by dehydration involving β-hydrogen atoms[67] (see p. 580), a formal analogy can probably be drawn between this reaction and the pyrolysis of xanthates, esters, and acetyl derivatives of amines, which also results in the formation of a double bond as a result of β-elimination[93,94]. In the last three reactions, however, a C–O or a C–N bond undergoes cleavage, whereas in the

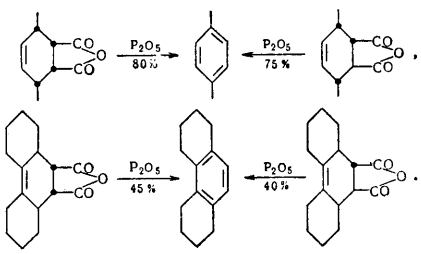
§ The infrared absorption spectrum showed that the resulting *m*-chlorotoluene was contaminated with the *para* isomer, but insufficient of the latter was present to be detected by chemical methods (for example, by oxidation). The preferential formation of the *"meta"* adduct in the reaction of chloroprene with methylmaleic anhydride is perhaps due to the fact that it was prepared by heating in propionic acid, whereas the *"para"* adducts of chloroprene described by other workers[86–90] were obtained by heating in non-polar solvents (benzene, toluene) or else in the absence of solvent.

aromatisation of tetrahydrophthalic anhydrides in the presence of phosphorus pentoxide it is a C–C bond which is broken, formic acid or its anhydride is split off, and decomposes into carbon monoxide and water:



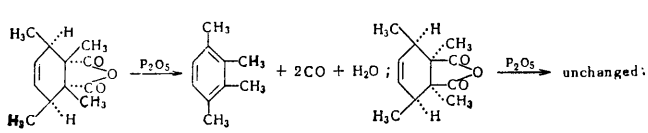
The above scheme gives grounds for assuming that the course of this reaction may depend on certain spatial factors — the mutual disposition of the β-hydrogen atoms which are to be eliminated and the anhydride grouping in the reactant tetrahydrophthalic anhydride molecule, or of the carboxyl groups in tetrahydrophthalic acids. Thus the reaction with phosphorus pentoxide, like several pyrolytic reactions[93,94], might prove stereospecific in the case of 3-alkyl- or 3,6-dialkyl-tetrahydrophthalic anhydrides, which can exist in different spatial conformations.

However, the stereoisomeric 1,2,3,6-tetrahydro-3,6-dimethylphthalic (*cis* and *trans*) anhydrides, and also the stereoisomeric (*cis* and *trans*) 3,4:5,6-dicyclohexeno--1,2,3,6-tetrahydrophthalic anhydrides, show identical behaviour with phosphorus pentoxide: on being heated to 150°–160° they are converted into the corresponding hydrocarbons (*p*-xylene and octahydrophenanthrene) in practically the same yield[95]:



The fact that in these cases the reaction with phosphorus pentoxide is unaffected by the spatial configuration of the adducts can, however, be explained by the possibility of interconversion of these stereoisomeric anhydrides, reaction with phosphorus pentoxide being preceded by isomerisation with preferential formation of the reactive configuration.

The stereoisomeric 1,2,3,6-tetrahydro-1,2,3,6-tetramethylphthalic anhydrides obtained by diene synthesis from hexa-2,4-diene and dimethylmaleic anhydride[95] and having *trans-cis-trans* and *cis-cis-cis* configurations (the "*exo*" and "*endo*" configurations respectively) react differently with phosphorus pentoxide: only one of these anhydrides, that possessing the "*exo*" configuration, undergoes aromatisation readily with conversion into 1,2,3,4-tetramethylbenzene[95], since in this particular case *cis*-elimination takes place (of β-hydrogen atoms and the anhydride group), which is the preferential direction in many pyrolytic processes[93,94]:

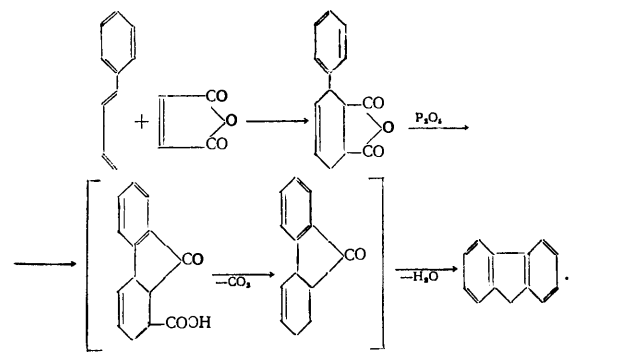


Thus the first type of reaction involving aromatisation of adducts of diene synthesis under the influence of phosphorus pentoxide can be employed not only for the purposes mentioned above (to synthesise aromatic hydrocarbons of various classes, establish the structure of the original dienes, and establish the structural direction of the diene synthesis), but in certain cases also to establish the spatial configuration of the diene adducts[95].

As has been reported above (see p. 583) aryltetrahydrophthalic anhydrides in which the aryl substituent is remote from the anhydride group undergo the first type of aromatisation in the presence of phosphorus pentoxide, carbon monoxide and water being split off with the formation of polyphenyls.

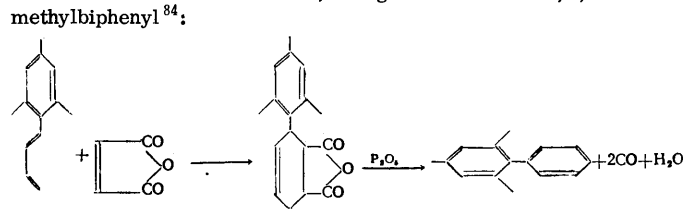
Aryltetrahydrophthalic anhydrides in which the aryl group occupies a different position can undergo aromatisation in a different way (without elimination of carbon monoxide) under the influence of phosphorus pentoxide, with the formation of hydrocarbons of the *fluorene series*.

Thus 1,2,3,6-tetrahydro-3-phenylphthalic anhydride (the adduct of 1-phenylbuta-1,3-diene and maleic anhydride), in which the phenyl substituent is next to the anhydride group¶, gave fluorene (in 21% yield) on reaction with phosphorus pentoxide. The reaction probably passes through intermediate stages involving intramolecular acylation of the benzene ring, resulting in formation of tetrahydrooxofluorenecarboxylic acid, which is then decarboxylated to tetrahydrofluorenone[96], the latter being converted into fluorene under the influence of the phosphorus pentoxide†:



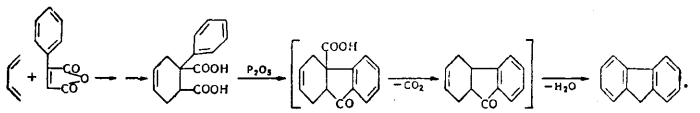
An analogous transformation is undergone by 1,2,3,6--tetrahydro-1-phenylphthalic acid, obtained from the

¶ It must be noted that 1,2,3,6-tetrahydro-3-mesitylphthalic anhydride — the adduct of 1-mesitylbuta-1,3-diene and maleic anhydride — in which the phenyl ring at the side of the anhydride group contains *ortho* substituents, underwent aromatisation under the conditions of reaction with phosphorus pentoxide by splitting off carbon monoxide and water, being converted into 2,4,6-trimethylbiphenyl[84]:



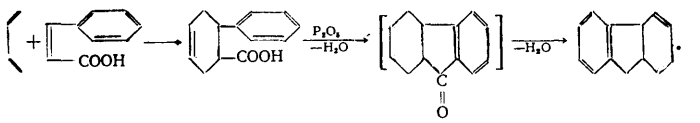
† Many published data support the possibility of each of the above reactions taking place in the presence of phosphorus pentoxide. Hydroaromatic ketones of different structures — with the ketone group inside or outside the ring and with the double bond in the γδ or the αβ position relative to the ketone group — are converted into aromatic hydrocarbons on being heated with phosphorus pentoxide, the yield depending on the structure of the original ketone[97,98].

adduct of butadiene and phenylmaleic anhydride (yield of biphenyl 50%)[83]:

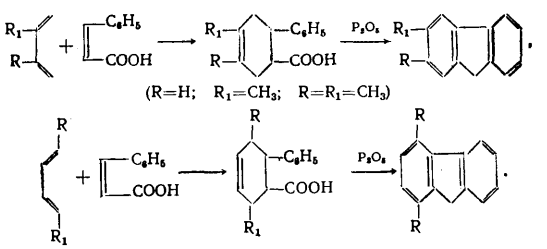


The conversion of aryltetrahydrophthalic acids and their anhydrides into fluorenes under the influence of phosphorus pentoxide has been termed the *second type of aromatisation reaction* of adducts of diene synthesis[83].

Since an intermediate stage in the above synthesis of fluorene from the adduct of butadiene and phenylmaleic anhydride is the splitting off of a carboxyl group from the adduct, this reaction was subsequently simplified by replacing the 2-phenyltetrahydrophthalic anhydride with 1,2,3,6-tetrahydro-2-phenylbenzoic acid, the adduct of butadiene and cinnamic acid. When this adduct was heated with phosphorus pentoxide, fluorene was obtained in higher yield (63%)[95,96]:

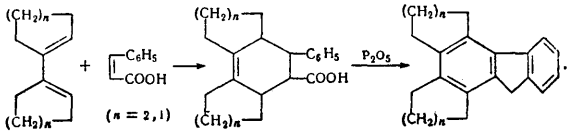


The adducts of cinnamic acid with isoprene, penta-1,3-diene, 2,3-dimethylbuta-1,3-diene, and hexa-2,4-diene yielded respectively 3-methylfluorene, 1-methylfluorene, 2,3-dimethylfluorene, and 1,4-dimethylfluorene[96,99]:



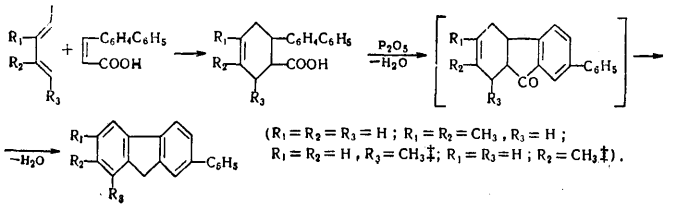
The preparation of 3-methylfluorene instead of the isomeric 2-methylfluorene from the adduct of isoprene and cinnamic acid, and also of 1-methylfluorene (not 4-methylfluorene) from the adduct of penta-1,3-diene and cinnamic acid, confirms the structure of these adducts as respectively 1,2,3,6-tetrahydro-4- and -6-methyl-2-phenylbenzoic acids.

The adducts of cinnamic acid with 1,1′-bi(cyclohexenyl) and 1,1′-bi(cyclopentyl) gave 1,2:3,4-dicyclohexenofluorene and 1,2:3,4-dicyclopentenofluorene[96]:

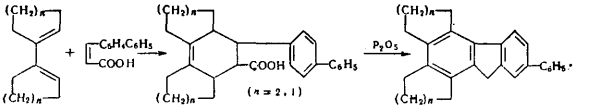


An advantage of this reaction for the preparation of fluorenes compared with those mentioned previously (see p. 581 and this page above) is that it makes use of more readily available dienes (alkylbutadienes instead of arylbutadienes) and a more accessible dienophil (cinnamic acid instead of indene-1,2-dicarboxylic or phenylmaleic anhydride).

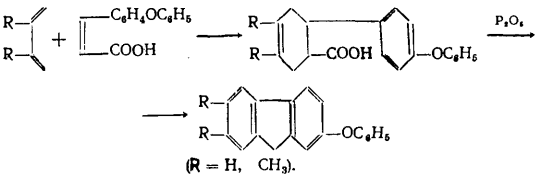
The reaction with phosphorus pentoxide has been carried out also with 2-aryltetrahydrobenzoic acids of more complicated structure, with *p*-biphenylyl as the aryl substituent (acids of this type have been obtained by diene synthesis using *p*-phenylcinnamic acid, which has proved an active dienophil)[100]:



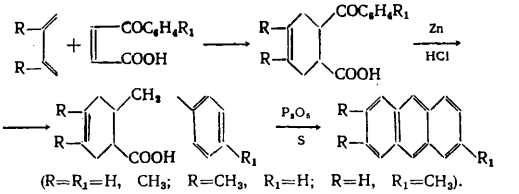
With *p*-phenylcinnamic acid as the initial dienophil, and the dicyclic diene hydrocarbons 1,1′-bi(cyclohexenyl) and 1,1′-bi(cyclopentenyl) as dienes, polycyclic aromatic hydrocarbons can be obtained containing the 2-phenylfluorene system — 2-phenyl-5,6:7,8-dicyclohexenofluorene and 2-phenyl-5,6:7,8-dicyclopentenofluorene respectively[65]:



Tetrahydro-2-phenoxybenzoic acids, the adducts of dienes with *p*-phenoxycinnamic acid, react in a similar manner with phosphorus pentoxide, being converted into 2-phenoxyfluorenes[101]:



The second type of aromatisation is undergone also by 2-benzyl-1,2,3,6-tetrahydrobenzoic acids (obtained by reducing aroyltetrahydrobenzoic acids — the adducts of diene hydrocarbons and aroylacrylic acids — with amalgamated zinc in hydrochloric acid), which are converted into dihydroanthracenes, subsequent dehydrogenation of which (by heating with sulphur) yields anthracenes[102]. This synthesis of anthracenes could be simplified by carrying out the aromatisation of the benzyltetrahydrobenzoic acids by heating them with phosphorus pentoxide in the presence of sulphur, the dihydroanthracenes formed under these conditions being completely dehydrogenated to the corresponding anthracene hydrocarbons[102]:



‡ The structure of these adducts (as "*ortho*" and "*meta*" adducts), obtained from unsymmetrical dienes and dienophil, was proved by converting them (by decarboxylation followed by dehydrogenation in the presence of platinum) into 3- and 4-methyl-*p*-terphenyls respectively.

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EFFECT OF IRRADIATION ON THE ADSORPTION AND CATALYTIC PROPERTIES OF SEMICONDUCTORS AND DIELECTRICS

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I. INTRODUCTION

There have been many recent publications on the effect of various types of radiation on the adsorption and catalytic properties of semiconductors and dielectrics. Increases in adsorption capacity and catalytic activity of up to 3–4 orders of magnitude have been reported. These effects combine obvious scientific interest with great technological potentialities, yet their mechanism is still obscure, and a theoretical interpretation and a unified description of the observed phenomena are still awaited.

The present review aims to give a systematic survey of existing factual material in the hope that it may prove generally informative and that it may stimulate new experimental and theoretical work†.

II. RADIATION EFFECTS ON SEMICONDUCTORS AND DIELECTRICS (GENERAL FORMULATION, INFLUENCE ON ELECTRONIC PROPERTIES)

Energetic electromagnetic radiations and fast particles interact with matter by a complicated cascade process involving, as a rule, ionisation effects and structural changes in the crystal lattice of solids[1]. The primary reaction with the bombarding stream causes many secondary changes in the material. The most important disturbances produced include: (a) non-equilibrium free and localised charge carriers (electrons and holes); (b) lattice defects of the "vacancy" and "interstitial" type, singly or in clusters; (c) chemical impurities produced by nuclear reactions within the solid. The observed radiation effects follow, as a rule, from changes of these types.

Any of the above defects can be induced by various kinds of radiation, but with different efficiencies.

† Experimental and theoretical papers dealing with the effect of light on the adsorption and catalytic properties of semiconductors and dielectrics are excluded.

The most characteristic effect of γ-irradiation is excitation of electrons and ionisation. The resulting non-equilibrium Compton electrons and photoelectrons give rise to phenomena analogous to photoconductivity.

Vavilov and coworkers[2,3] have reported some interesting results of their work on γ-conductivity in silicon and germanium. The mean energy required to generate a hole-electron pair by γ-irradiation was shown to be independent of the quantum energy of the γ-rays, thus establishing a proportionality between the quantum yield and the γ-quantum energy. The γ-conductivity of semiconductors of the CdS group was investigated by Konozenko *et al.*[4] As in the case of photoconductivity the excess concentration of free carriers of a given sign is given by the expression $\Delta n = g\tau$, where g is the rate of generation of carriers (proportional to the intensity of the γ-irradiation) and τ is the average lifetime of non-equilibrium carriers. Since semiconductors have very low τ values, the effect decays very rapidly when irradiation ceases. More lasting effects of ionisation processes are possible only if hole or electron trapping can occur. Particularly effective trapping centres have been shown (in the case of germanium) to be associated with surface states, which can gradually release charge carriers over a period of hours after irradiation has ceased[5].

Direct ionisation processes produce larger effects in insulators than in semiconductors because longer carrier trapping times are possible in these materials. Typical ionisation phenomena in these materials include[1,6,7] the formation of colour centres, luminescence, paramagnetic resonance absorption, etc. Several features of γ-conductivity in various dielectrics (quartz, polyethylene, sulphur, mullite) have been studied experimentally and fully discussed by Vul[8].

Besides ionisation processes, γ-irradiation of semiconductors and dielectrics produces significant structural changes. These defects produce localised energy levels within the forbidden energy band of the crystals which can be detected by measurements of the temperature coefficients of the resistivity and of the Hall effect, and by the spectral characteristics of the photoconductivity and of the recombination processes[9-11].

Defects of this type arise when atoms (or ions) are displaced from their normal sites. In semiconductors, this occurs mainly through the secondary, internal irradiation of the material by fast Compton electrons and photoelectrons produced by the primary γ-irradiation[1]. The number of resulting displacements, N_γ, can be estimated from the formula $N_\gamma = \varphi_\gamma N_0 \sigma_\gamma$, where φ_γ is the intensity of γ-irradiation, N_0 is the number of atoms per unit volume of sample, and σ_γ is the effective displacement cross-section under γ-irradiation. Displacement cross-sections for semiconductors subjected to γ-quanta of normal energies (γ-rays from ^{60}Co, reactor γ-quanta) are not large, as a rule. The measured value for germanium is[12] $\sigma_\gamma \simeq 10^{-26}$ cm^2. Thus, γ-irradiation of semiconductors is less effective than neutron irradiation as a means of generating stable lattice damage.

The effectiveness of γ-irradiation can be much higher in dielectrics, because in these materials γ-quanta can interact with matter by two important additional mechanisms, both of which postulate the conversion of electronic excitation (ionisation) energy into displacement energy. The first mechanism, put forward by Seitz[13], accounts for the formation of lattice displacements by local energy transfer following the annihilation of an exciton (excitons produced

by irradiation are annihilated whenever they encounter a local disturbance of the perfect periodicity of the crystal lattice). The recombination of radiation-induced hole–electron pairs in the vicinity of a lattice defect can also give rise to this effect.

The second mechanism, proposed by Varley[14], applies only to ionic compounds. Varley assumes that a negative lattice ion can undergo multiple ionisation under the influence of irradiation, and develop a positive charge. Such an ion, being surrounded by normal, positive lattice ions, finds itself in a highly unstable environment, and can easily move to an interstitial site before regaining its lost electrons. The postulated multiple ionisation can arise either by direct interaction between a γ-quantum and several outer electrons or in cascade (by the Auger process).

Varley's mechanism presents some fairly stringent requirements: the postulated positive ion must have time to transfer to an interstitial site before its charge is neutralised by recombination with the ejected electrons or by coulombic "repulsion" of the accompanying positive holes.

Some published results suggest[15] that both these mechanisms can, in principle, operate also in semiconductors.

Experimentally observed displacement effects caused by γ-irradiation of dielectrics include the decrease in ionic conductivity of alkali halide crystals under weak γ-irradiation, the decrease in thermal conductivity of artificial sapphire at low temperatures[16], and the appearance of colour centres and paramagnetic resonance absorption in aluminium oxide, quartz, etc.[17]

The irradiation of semiconductors and dielectrics by neutrons and charged particles produces far more significant effects. Electronic excitation and ionisation effects, and displacement of atoms and ions, are produced by the cascade processes initiated by irradiation of this type.

Neutrons interact with matter primarily by elastic collisions‡, leading to displacements. Ionisation effects, if present, are due to secondary processes.

Neutron irradiation can also result in the formation of appreciable quantities of chemical impurities by neutron capture and nuclear reaction if the irradiated material contains atoms of sufficiently large neutron capture cross-section.

Charged particles, whether primary or secondary, of energy $E > E_i$ undergo mainly inelastic collisions, giving rise to electronic excitation and ionisation[18]. Here $E_i = (M_1/m)I$, where M_1 is the mass of the moving particle, m the mass of an electron, and I the threshold excitation energy of an electron (comparable in magnitude with the width of the energy gap of the crystal). When $E < E_i$, elastic collisions (leading to displacements) predominate. It should be noted that ionisation processes can ultimately produce additional displacements by the mechanisms considered in the previous discussion of the effect of γ-irradiation.

Without considering these fast particle mechanisms in detail, we shall merely quote the formula[1] for calculating the total number of resulting displacements: $N_d = \varphi t N_0 \sigma_d \bar{\nu}$, where φ is the intensity of the stream of bombarding particles, t the time of irradiation, N_0 the number of atoms per unit volume of irradiated material, σ_d the cross-section for primary collisions, producing displacements, and $\bar{\nu}$ the average number of displaced atoms resulting from each primary displacement.

The value of σ_d depends on the type of interaction considered[19], but is of the order of 1 barn (1 barn = $= 10^{-24}$ cm^2). The quantity $\bar{\nu}$ is given[20] by the expression

$$\bar{\nu} = 0.5\left[1 + \ln\left(\frac{E_m}{2E_d}\right)\right], \text{ where } E_m = \frac{4M_1M_2}{(M_1 + M_2)^2}E.$$

E_m is the maximum energy which the collision can impart to the target atom; E_d the threshold displacement energy of the atom; E the energy of the bombarding particle; and M_1 and M_2 are the masses of the two atoms undergoing collision.

Estimates of the total number of radiation defects, based on these ideas, are usually found to agree in order of magnitude with the measured values (mostly derived from electrical measurements[1]).

Some changes in properties of semiconductors and dielectrics, resulting from corpuscular irradiation, will now be briefly considered. Irradiation of semiconductors has a strong effect on the free carrier concentration, and therefore on the electrical conductivity of the material. The effect on carrier mobility is much less marked. These effects do not decay, and their sign and magnitude are a function of the initial concentrations of electrons and positive holes. At some well-defined free carrier concentration, which is a characteristic of a given material, these changes become vanishingly small[1,21].

Irradiation of silicon, whether n- or p-type, usually alters the conductivity towards its intrinsic value. Specimens of n-type germanium are invariably converted into p-type as a result of irradiation, but in heavily p-type specimens the conductivity drops. Irradiation effects on InSb are very similar[5].

All these phenomena can be explained on the assumption that irradiation gives rise to donor and acceptor defects of different types, whose localised energy levels are distributed over such a wide band of energies as to produce the observed complexity and multiplicity of effects. In silicon, the induced donor and acceptor levels can be mutually compensating, and the Fermi level of the irradiated specimen is near the middle of the energy gap. In germanium, the acceptor centres are more prominent, and the Fermi level is shifted towards the lower half of the energy gap.

A detailed explanation of the electronic consequences of irradiation effects usually requires an exact knowledge of the energy parameters of the radiation defects involved. The most reliable information is obtained from measurements of the Hall effect as a function of temperature, and from studies of the spectral characteristics and of the transient behaviour of photoconductivity. Except in the case of germanium and silicon[1,5,22–26], our quantitative knowledge of these effects is inadequate.

Measurements of optical and magnetic properties provide the fullest information on the effect of fast particle irradiation of dielectrics. The commonest results of irradiation in these materials are changes in the absorption spectra, colour development, formation of paramagnetic centres, etc. Thus, the absorption spectrum of proton-irradiated NaCl crystals shows additional bands which can

‡ Elastic collisions are defined as processes in which the total kinetic energy of the colliding particles (but not the kinetic energy of the bombarding particle) is conserved.

be assigned to various defects (in particular, to the accumulation of F-centres[27]). Similar phenomena are observed[28] in neutron-irradiated quartz, and the optical spectra can be correlated with EPR measurements[29]. Neutron irradiation of α-Al_2O_3 produces comparable results[1].

A gradual change in properties (not tending, however, to reestablish the original properties) is frequently observed when fast-particle irradiation of specimens is interrupted. This is due to the trapping and reemission of non-equilibrium charge carriers, formed in ionisation processes, which occur at the same time as the time-independent displacement effects. As already remarked, these transient phenomena are most noticeable at the surface, where effective trapping centres are present in large numbers.

The removal ("annealing") of displacement defects can also cause changes in the properties of the specimen after cessation of the irradiation. In many cases, the initial properties of the material can be completely restored by this process. These phenomena have a diffusion mechanism, and are therefore greatly accelerated by a rise in temperature. Under conditions of prolonged irradiation, and therefore of high concentrations of structural defects, annealing effects can occur during the irradiation period, and set an upper limit to the radiation damage.

In conclusion, we may state that the band theory of the solid state offers a reliable description of the effects of irradiation on the electronic properties of semiconductors and dielectrics, provided that the concentrations and the energy parameters of the resulting defects can be evaluated. Modern theories of the interaction of solids with radiation enable us to evaluate (at least approximately) the number of radiation defects, but we are still entirely dependent on experimental information for a knowledge of the energy levels of the defects.

III. CHANGES IN THE ADSORPTION AND CATALYTIC PROPERTIES OF SEMICONDUCTORS AND DIELECTRICS UNDER THE INFLUENCE OF EXTERNAL γ-IRRADIATION

In view of the vast mass of published experimental material, no attempt will be made to include in the present review some of the older papers on the action of energetic electromagnetic radiations (and other forms of radiation) on solid adsorbents and catalysts. These have been adequately described by previous reviewers[30-32], who have also stressed the unreliability of some of the older work.

The effect of γ-radiation on the catalytic properties of zinc oxide, one of the best known and most widely used semiconductor catalysts, has been discussed in a number of papers. Barry and Roberts[33] studied the effect of γ-radiation on the catalytic activity of zinc oxide towards the synthesis of methanol from hydrogen and carbon monoxide. The catalyst, prepared by decomposing zinc carbonate in air at 300°, had n-type conductivity before irradiation. A ^{60}Co source was used to irradiate the material at a dose rate of 2.5×10^{19} eV g^{-1} h^{-1} whilst reaction was proceeding under a pressure of 1 atm. The catalytic activity of ZnO was found to be increased by irradiation, but only for reaction temperatures in the range 175°–250°. The results of three experiments, summarised in Table 1, show that the effect of irradiation is more pronounced at the lower temperatures.

TABLE 1. Synthesis of methanol on non-irradiated and irradiated zinc oxide.

Temp., °C	Rate of production of methanol, ml h^{-1}			Yield of methanol, molecules per 100 eV
	non-irrad.	irrad.	difference	
223	0.18	0.24	0.06	0.58
204	0.103	0.20	0.097	1.93
201	0.036	0.144	0.108	0.04

The authors conclude[33] that the mechanism of catalysis is not affected by the radiation, since the lower temperature limit of the irradiation effect is not very different from that for ordinary thermal catalysis. The observed effects can be ascribed to the free electrons produced by the γ-radiation. The adsorption of both hydrogen[34] and carbon monoxide[35] is known to be ionic over the temperature range of these experiments, a fact which the authors consider very significant[33].

Taylor and Wethington[36] have observed the opposite effect of γ-radiation on the catalytic properties of ZnO. The hydrogenation of ethylene at 0° is appreciably retarded by γ-irradiation of the zinc oxide catalyst. The ZnO specimens were irradiated for various times by γ-quanta from ^{60}Co (6000–10 000 r min^{-1}), in a vacuum and at 15° ± 5°. The specimens had been previously degassed at 0° (in a few cases, at 100°). An irradiation period of 3 months increased the time for 50% conversion in the catalytic reaction by more than a factor of 5. The usual activating procedures (high-temperature treatment and evacuation) were sufficient to restore the initial catalytic activity of the material.

The authors explain this radiation effect in terms of displacements induced by irradiation, but the possibility of catalyst poisoning (by the radiation-induced polymerisation of reactants or products) is not excluded.

On the other hand, zinc oxide irradiated with γ-quanta from ^{60}Co to a dose of 5×10^{18}–10^{19} eV g^{-1} shows a threefold to tenfold increase in catalytic activity towards the hydrogen–deuterium exchange reaction. Poisoning effects associated with oxygen were observed both before and after irradiation of the catalyst[31].

Mishchenko *et al.*[37] have reported very profound changes in the catalytic activity of TiO_2 towards the hydrogen–deuterium isotope exchange reaction as a result of irradiation. The TiO_2 specimens were heated at 500° under a pressure of 10^{-5} mm Hg for several hours, but in the absence of irradiation no catalytic activity could be detected at 0°. A ^{60}Co source (120 r sec^{-1}) was used to irradiate the material in a vacuum at liquid nitrogen temperature (integral dose 1.7×10^7 r). As a result, the catalytic activity of TiO_2 at liquid nitrogen temperature rose by at least 3–4 orders of magnitude.

The effect was found to decay rapidly, the rate constant at 0° decreasing by two powers of ten within an hour of removal from the liquid nitrogen bath. The authors[37] stress their observed correlation between changes in catalytic activity and in magnetic properties of the TiO_2 specimens. Specimens heated to 500° gave no EPR signal before

being irradiated. Irradiated specimens showed paramagnetic resonance absorption at liquid nitrogen temperature, which persisted as long as the material was kept at this temperature. Upon rapid heating to room temperature, the intensity and the shape of the EPR signal changed over a period of about an hour to give a new, stable line. The authors assume that the enhanced catalytic activity and the resonance absorption are due to the same impurity centres, induced by the γ-radiation.

Tsetskhladze and Kalandadze's interesting work[38] on the catalytic activity of γ-irradiated copper oxides calls for detailed discussion. These workers studied the dehydrogenation of ethanol, catalysed by CuO and Cu_2O. The catalysts were degassed in a vacuum at 10^{-5} mm Hg, irradiated with a ^{60}Co source, and used at 275°.

The variation of catalytic activity with dose of γ-radiation, shown in Fig. 1, implies that the catalytic properties of CuO and Cu_2O are affected in opposite senses. This is confirmed by the kinetic curves for irradiated and non-irradiated catalysts (Fig. 2).

In parallel with the measurements of catalytic activity, measurements of the electrical resistance of cold-pressed pellets of the copper oxides were carried out both before and after irradiation. The resistance of CuO was found to be increased, and that of Cu_2O decreased, by the irradiation. Both effects were considerable (at least an order of magnitude), but the authors were not able to establish a clear relationship between the dose and the change in resistance. Nevertheless, the observed correlation is not thought to be fortuitous, and an electronic mechanism to describe the effect of radiation has been put forward.

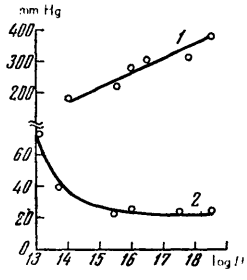


Fig. 1. Influence of irradiation dose (D, röntgens) of CuO (curve 1) and Cu_2O (curve 2) catalysts on hydrogen yield in the dehydrogenation of ethanol. Reaction time: 1 h.

Iron oxide is another oxide system in which γ-irradiation increases the "yield" of catalytic reactions. This oxide, after admixture of potassium carbonate and heating at 1000°–1300° for 4 h, has been used as a Fischer–Tropsch catalyst[39]. Specimens were degassed at room temperature before being irradiated (^{60}Co source). The measurements were made after irradiation.

The reaction kinetics before and after irradiation of the catalyst are illustrated in Fig. 3. Changes in catalytic activity are retained for surprisingly long times at 280°. The dependence on specimen geometry of the effect of irradiation is equally remarkable. The particle size of the catalyst to which Fig. 3 refers did not exceed 100–200 μ. When the particle size was decreased to 0.2–5 μ the percentage conversion was approximately doubled, but with 400–600 μ particles the effect of the same dose of γ-radiation was almost negligible. Pile irradiation (10^{18} neutrons cm^{-2}) was also ineffective under these conditions. There is evidence[31] that in these experiments the conductivity of the specimens was not affected by irradiation.

The authors[39] point out that in the initial stages of the reaction the effect of irradiation is slight (see Fig. 3), and therefore ascribe the observed effects to partial reduction of iron oxide, or formation of iron carbide (either of which can be expected to increase the catalytic activity), at the irradiation stage, rather than to a direct radiation effect such as electronic excitation or the production of structural defects.

Various oxide semiconductors (ZnO, TiO_2, etc.) have a catalytic effect towards certain radiation-induced chemical reactions, resulting from transfer to the reactants of the radiant energy absorbed by the semiconductor. Thus, the decomposition of potassium oxalate in aqueous solution under the influence of γ-radiation is intensified and accelerated[40] by a suspension of the semiconductor ZnO.

Among the dielectrics whose adsorption and catalytic properties are sensitive to γ-radiation, the various modifications of SiO_2 and Al_2O_3 have been most thoroughly investigated.

Kohn and Taylor[41] observed a large increase in the catalytic activity of silica gel towards the hydrogen–deuterium exchange reaction following irradiation. The rate of this

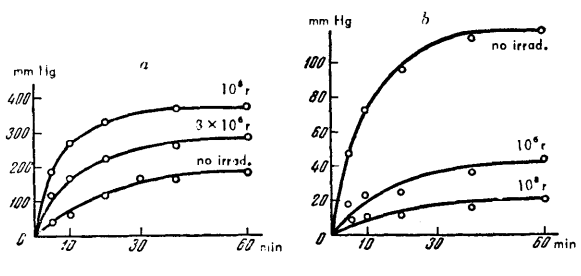


Fig. 2. Hydrogen evolution kinetics (mm Hg) in the dehydrogenation of ethanol on variously irradiated catalysts: (a) CuO, (b) Cu_2O.

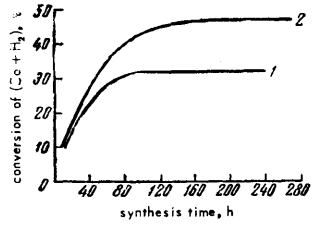


Fig. 3. Influence of γ-irradiation on the kinetics of hydrocarbon synthesis: temp. 280°, pressure 10 atm, irradiation dose 3.6×10^7 r: 1) before irradiation; 2) after irradiation.

reaction is only slightly increased, as a rule, by the presence of silica gel, and the room-temperature "half-life" is of the order of 100–1000 hours. This period was shortened to one hour by γ-irradiation of the silica gel with a dose of 10^{19} eV g^{-1}, which was shown to be vastly superior to conventional pretreatments for catalysts.

The investigation included, besides three specimens of silica gel, other modifications of SiO_2 and also three SiO_2–Al_2O_3 hydrocarbon cracking catalysts. All were degassed at 450°–700° and 10^{-5} mm Hg before being irradiated, at 25°, by γ-quanta from a ^{60}Co source (dose rate 1.2×10^{17} eV g^{-1} min^{-1}). The initial impurity content (Mg, Al, Fe, Mo) was in every case less than 10^{-1}–10^{-2}%.

The activation energy of the process before and after irradiation was deduced from measurements over a range of temperatures. Irradiation was found to lower the activation energy from 9 to 2 kcal $mole^{-1}$, which the authors interpret as evidence that a new path has been made available to the catalytic reaction. Since the activation energy is now small, a large number of active sites on the surface is no longer required. The results are set out in Table 2.

The authors believe that displacements induced in SiO_2 by the γ-radiation are responsible for these radiation effects. From data on the total number of displacements in SiO_2, deduced from EPR measurements and from calculations of the Compton scattering of γ-rays, they conclude that only about one displaced atom in a thousand gives rise to a catalytically active centre. "Yields" of catalytically active centres were calculated by dividing the measured rate constants K by the rate constants for a single active centre, which were evaluated by assuming an area of $\sim 16 \times 10^{-16}$ cm^2 per active centre, an activation energy of ~ 1 kcal $mole^{-1}$, and an average velocity of 1.5×10^5 cm $\times$ $\times$ sec^{-1} for a gas molecule at 25°.

In two subsequent papers[42,43], Kohn discusses the formation of colour centres and paramagnetic centres in irradiated silica gel. Colourless SiO_2 reddens on irradiation by X-rays or γ-rays and the colour does not disappear on heating to 250°. Hydrogen has an instantaneous bleaching effect, but the rate of bleaching decreases at low temperatures. Before irradiation, hydrogen was only weakly and slowly adsorbed, but after irradiation the extent and the rate of hydrogen adsorption increased. This was only a temporary effect, however, and hydrogen adsorption ceased as soon as the last trace of colour had disappeared. Starting from the dose of radiation and the amount of hydrogen adsorbed on the irradiated specimen, Kohn estimates that $\sim 3 \times 10^{18}$ colour centres were formed per gramme, each colour centre requiring the absorption of 100 eV of energy.

Ethylene, water vapour, and ammonia were also found to have a bleaching action, but oxygen had no effect. The colour centres were identified with holes, bound to excess oxygen in SiO_2. Bleaching results from the interaction of these holes with electrons donated by the gas. EPR studies of γ-irradiated silica gel showed that the paramagnetic centres are not related to the colour centres. A sample of SiO_2 irradiated at 50° gave an EPR signal which was stable at room temperature but not in the presence of ultraviolet radiation, oxygen, mercury vapour, or water vapour. The yield of these centres was 0.1 per 100 eV of energy absorbed. "Annealing" set in at 250°. The author ascribed this signal to electrons trapped in oxygen vacancies. The effect of oxygen suggests that we are dealing with a surface rather than a bulk phenomenon. Irradiation at -196° produced a new signal, insensitive to oxygen.

In an earlier paper[44], Taylor and Kohn had established that the catalytic activity of γ-Al_2O_3 towards the hydrogen–deuterium exchange reaction is strongly affected by γ-radiation.

The specimens, which were saturated with water when prepared, were degassed at high temperatures (~400°) for several hours, and irradiated *in vacuo* for 30 min at a dose rate of 2×10^{17} eV g^{-1} min^{-1}, using a cobalt source. Measurements of the rate of hydrogen–deuterium exchange at -78° showed a sevenfold increase in activity as a result of irradiation. The effect disappeared after storage for 2–4 h at room temperature, but could again be induced by repeating the irradiation. Specimens not previously degassed (and which were therefore catalytically inactive) showed an increase in activity of three orders of magnitude after irradiation, but the effect did not survive a few hours' storage, even at -78°. No significantly different results were obtained when irradiation was carried out during the course of the reaction, thus showing that fast-decaying processes do not play a major part. The authors explain these effects in terms of possible electron or hole trapping processes in the γ-Al_2O_3 lattice.

The study of this system was continued in a subsequent paper by the same authors[45]. Specimen pretreatment consisted, as in the previous work[44], in degassing at 200°–650°. In the absence of this treatment, the samples were catalytically less active, but more sensitive to irradiation. A study was made of the influence of degassing temperature on the radiation effect, and also of the effect of possible catalyst poisons (H_2O, H_2, C_2H_2). High degassing temperatures produced smaller radiation effects, and it was found that the sign as well as the magnitude of the effect could be influenced by the pretreatment, leading in some cases to loss of catalytic activity.

Poisoned specimens were shown to be more sensitive to radiation, and to regain their initial characteristics more rapidly. The authors suggest that radiolysis of the poison may be responsible for this, through either direct removal of the poison or the formation of compounds able to promote the reaction. They think it more likely, however, that electrons or holes trapped at unidentified localised states are responsible for the radiation effect. This view is supported by the effect of irradiation temperature on the increase in rate constant[45]. Specimens were irradiated at progressively decreasing

TABLE 2. Effect of γ-irradiation on SiO_2 and SiO_2–Al_2O_3 catalysts.

Catalyst	Degassing temp., °C	Rate constant at 25° before irradiation, min^{-1} m^{-2}	Radiation dose per unit surface area, eV m^{-2}	K after irradiation, min^{-1} m^{-2}	Yield of active sites per 100 eV	Yield of active sites per displacement
				25°		
Gel 1	450	$1.0 \cdot 10^{-8}$	$8.0 \cdot 10^{16}$	$2.4 \cdot 10^{-5}$	$1.3 \cdot 10^{-8}$	$1.3 \cdot 10^{-3}$
Gel 2	485	$1.4 \cdot 10^{-8}$	$3.6 \cdot 10^{16}$	$1.1 \cdot 10^{-5}$	$1.4 \cdot 10^{-8}$	$1.4 \cdot 10^{-3}$
Gel 3	525	$4.9 \cdot 10^{-9}$	$8.0 \cdot 10^{16}$	$5.5 \cdot 10^{-7}$	$3.1 \cdot 10^{-10}$	$3.1 \cdot 10^{-5}$
Quartz	500	$1.2 \cdot 10^{-4}$	$6.4 \cdot 10^{17}$	$>2.1 \cdot 10^{-3}$	$>1.6 \cdot 10^{-8}$	$>1.6 \cdot 10^{-3}$
Glass	500	$4.6 \cdot 10^{-4}$	$4.6 \cdot 10^{17}$	$>9.8 \cdot 10^{-3}$	$>9.4 \cdot 10^{-8}$	$>9.4 \cdot 10^{-3}$
Cristobalite	550	$8.1 \cdot 10^{-6}$	$4.7 \cdot 10^{18}$	$7.1 \cdot 10^{-3}$	$6.7 \cdot 10^{-9}$	$6.7 \cdot 10^{-4}$
"Cab-O-Sil"*	625	$1.1 \cdot 10^{-6}$	$2.5 \cdot 10^{17}$	$1.9 \cdot 10^{-5}$	$3.4 \cdot 10^{-10}$	$3.4 \cdot 10^{-5}$
		—78°		—196°		
SiO_2 – Al_2O_3	450	$8.8 \cdot 10^{-5}$	$3.8 \cdot 10^{17}$	$7.3 \cdot 10^{-5}$	$2.1 \cdot 10^{-7}$	$2.1 \cdot 10^{-2}$
SiO_2 – Al_2O_3	450	$2.2 \cdot 10^{-4}$	$8.3 \cdot 10^{17}$	$1.4 \cdot 10^{-4}$	$1.8 \cdot 10^{-7}$	$1.8 \cdot 10^{-2}$
SiO_2 – Al_2O_3	510	$1.7 \cdot 10^{-4}$	$2.7 \cdot 10^{18}$	$1.6 \cdot 10^{-5}$	$6.0 \cdot 10^{-9}$	$6.0 \cdot 10^{-4}$

* Anhydrous, particulate, colloidal silica made by Cabot Corp., USA. (Ed. of Translation).

temperatures (from 25° to -78°), and their catalytic activity was measured at -78° after each exposure. A plot of the logarithm of the rate constant for the exchange reaction against the reciprocal of the irradiation temperature is shown in Fig. 4. This graph defines the temperature dependence of the decay rate of the effect induced by irradiation. The corresponding activation energy (3 kcal × × mole^{-1}) is stated to be in tolerably good agreement with the depth of a typical trapping level for electrons or holes.

Kazanskii and Pecherskaya's report[46] that γ-irradiation of γ-Al_2O_3 at liquid nitrogen temperature induces paramagnetic resonance absorption at -196° is of relevance to Taylor and Kohn's results[44,45]. After two days at room temperature, the EPR signal had decreased tenfold. The Soviet workers point out that the symbathic relationship between the decrease in EPR signal and the loss of catalytic activity[45] of the γ-Al_2O_3 specimens allowed to reach room temperature is not fortuitous, and they suggest that both sets of phenomena are due to centres of a single type.

The influence of γ-irradiation on the catalytic properties of semiconductors and dielectrics is abundantly demonstrated by the work reviewed above. There have also been a number of publications on the effect of γ-irradiation on adsorption properties.

A paper by Starodubtsev *et al.*[47] discusses the adsorption properties of γ-irradiated silica gel. Changes in adsorption behaviour were observed by noting the pressure of a gas in a bulb containing the silica gel before and after irradiation. The silica gel specimens had previously been carefully heat-treated. Radiation was obtained from a ^{60}Co source of intensity 15×10^4–35×10^4 r h^{-1}, to give integral doses of 1.5×10^6–2×10^6 r.

A significant increase in the equilibrium adsorption capacity of silica gel towards various gases (H_2, N_2, C_2H_4, NH_3, CO, CO_2) was observed. Heating to 100° almost completely restored the initial adsorption properties of the silica gel, but annealing did not take place at room temperature (a hydrogen-filled bulb was stored for five months without significant change in hydrogen pressure). The authors ascribe the effect of irradiation to removal of hydroxyl groups with formation of free radicals on the surface of the adsorbent, and also to ionisation in the gas phase.

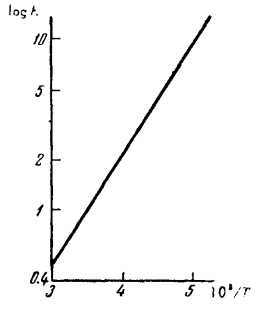


Fig. 4. Effect of irradiation temperature of a γ-Al_2O_3 catalyst on the rate constant (K, h^{-1} g^{-1}) of H_2–D_2 exchange at -78°.

Tagieva and Kiselev[48] studied the changes in adsorption properties of other modifications of SiO_2 (highly dispersed quartz and aerosil). The specimens were degassed at 200° under a pressure of 5×10^{-5} mm Hg; γ-irradiation from a ^{60}Co source was carried out at room temperature over a period of 24 h (integral dose 12×10^6 r).

The measured adsorption isotherms showed that the adsorption properties of SiO_2 towards water vapour had been reduced by the irradiation. The more highly hydrated specimen (quartz) was found to be more sensitive to radiation.

A decrease in surface hydration following γ-irradiation is also suggested by independent measurements of the structural water content of irradiated and non-irradiated specimens. Greatly increased (hundredfold) oxygen adsorption at room temperature following γ-irradiation, as compared with ultraviolet irradiation, is also reported in the same paper[48].

These authors[48] stress the appearance of a greyish colour on irradiation, which supports their theory that the observed effects are due to bond breaking in the adsorbed molecules or in the silanol groups. According to Molin and Voevodskii[49], this should produce paramagnetism in the irradiated specimens.

Kolbanovskii *et al.*[50] studied the effect of hydrocarbon adsorption (n-heptane, n-heptene, cyclohexane, benzene) on the EPR spectra of aluminium oxide before and after γ-irradiation. Commercial chromatographic alumina, and variously prepared mixtures of Al_2O_3 with Mo, Co, and Cr oxides, were used as adsorbents. The proportion of added oxides was normally kept below 10%. Doses of γ-radiation (^{60}Co source) between 6 and 120 Mr were applied at temperatures of -20°, -78°, and -196°. EPR spectra were recorded at different temperatures before and after irradiation. Irradiation produced profound changes in some of the EPR spectra. In some cases, signals due to radicals formed by homogeneous radiolysis were observed. The effect of temperature on the concentration of carriers with unpaired spins indicated the presence of activation energy barriers.

Special mention is due to the interesting results of Haissinsky and Siejka[51,52], who studied the effect of γ-radiation on the surface adsorption of various ions from aqueous solution: $^{144}Ce^{3+}$, $^{137}Cs^{+}$, $^{131}I^{-}$. In most experiments the adsorbent consisted of thin strips of platinum ($2 \times 1 \times 0.001$ cm^3) or stainless steel ($2 \times 1 \times 0.04$ cm^3), and the presence of a semiconducting film of oxide on the metal surface was found to be essential. Some measurements were also made on gold ($2 \times 1 \times 0.001$ cm^3) and poly(vinyl chloride) ($2 \times 1 \times 0.06$ cm^3) strips. The extent of adsorption was measured (in counts per minute) by monitoring the radioactivity of the adsorbent surface, since the cerium, caesium, and iodine isotopes used in the investigation were all radioactive.

Measurements before irradiation showed that cations and anions are adsorbed by different mechanisms. These results and the work of Balashova[53], led the authors to conclude that cation adsorption in their systems was mainly electrostatic, but iodine was chemisorbed.

The specimens were irradiated from a 650 c cobalt source during 7 days at temperatures between -1° and -2°. This was sufficient to saturate the radiation effect. Doses of 1.5×10^{19} eV and 36×10^{19} eV were absorbed by the platinum and the steel specimens respectively.

Irradiation increased the equilibrium adsorption of cations, and had a powerful effect on the adsorption kinetics and on the temperature coefficient. Kinetic curves for the adsorption of Ce^{3+} on platinum before and after irradiation are shown in Fig. 5.

The corresponding curves for the adsorption of I^- (Fig. 6) show a decrease in adsorption after irradiation, and vastly different adsorption kinetics. The activation energy of the process was unaffected by irradiation.

A special study was made of the effect on adsorption of degassing the adsorbents (500°) and the solution. The oxide film on platinum is partly dissociated at this temperature, whereas the oxide film formed by steel remains unchanged. This work (both irradiation and adsorption) was done in a vacuum.

After 30 min, cerium adsorption at ordinary temperatures was 2–3 times higher on the degassed (but not irradiated) specimens than on the initial specimens. Iodine adsorption decreased 80–100-fold on platinum, but not on steel. Irradiation of the degassed substrates lowered the adsorption of Ce^{3+} on platinum by a factor of 2 or 3, but produced a twofold increase in the adsorption of this ion on steel. The adsorption of I^- on platinum rose by a factor of 20, whereas the adsorption of I^- on steel was practically unaffected.

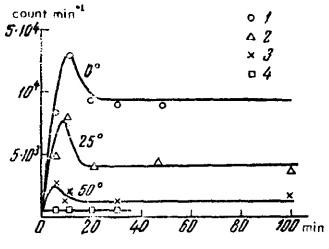


Fig. 5. Adsorption kinetics of Ce^{3+} on Pt: 1), 2), and 3) irradiated adsorbent; 4) adsorbent not irradiated.

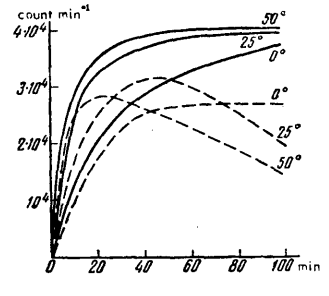


Fig. 6. Adsorption kinetics of I^- on Pt. Continous lines: adsorbent not irradiated; broken lines: irradiated adsorbent.

Haissinsky and Siejka interpret these observations by postulating that cation adsorption is mainly electrostatic, whereas iodine is chemisorbed. The results are consistent with the electronic theory of chemisorption and with the theory of the electrical double layer at a metal–solution interface.

IV. CHANGES IN THE ADSORPTION AND CATALYTIC PROPERTIES OF SEMICONDUCTORS AND DIELECTRICS RESULTING FROM EXTERNAL CORPUSCULAR IRRADIATION

The effect of neutron and charged particle bombardment on solid non-metallic adsorbents and catalysts has been investigated far less thoroughly than the effect of γ-radiation. Only two of the commoner catalysts, SiO_2 and Al_2O_3, have been studied in detail.

Weiss and Swegler[54] reported an increase in the catalytic activity of neutron-irradiated silica gel towards the isomerisation reaction of the double bond in hex-1-ene. The silica gel specimens, previously heated at 550° for 16 h, were irradiated in a reactor by a fast neutron flux of 7.5×10^{18} cm^{-2} (and approximately the same number of slow neutrons). The surface area of the specimens was not altered by irradiation.

The average percentage conversion of hex-1-ene on a catalyst which had not been irradiated, and on catalysts irradiated with 1.8×10^{18} and 7.5×10^{18} neutrons cm^{-2}, was 3.3, 4.6, and 9.4% respectively. The effect is ascribed to atomic displacements which, according to the authors' calculation, can amount to 1% of the total number of lattice atoms. Nuclear reactions are entirely negligible ($< 10^{-6}$%) because of the very small cross-sections involved ($\sim 10^{-27}$ cm^2). The authors also point out that neutron irradiation does not affect the catalytic activity of silica gel towards the cracking reaction of isopropylbenzene.

Lucchesi and coworkers[55,56] have reported a decrease in the rate of isomerisation of alkenes on an alumina–silica catalyst following irradiation. A study of the catalytic activity of SiO_2–Al_2O_3 catalysts towards isomerisation of the double bond in but-1-ene under pile irradiation conditions was carried out.

The catalyst contained 87 wt.% SiO_2. It was given a preliminary heat-treatment at ~540° for 16 h followed by 3 h at 675°.

Pile irradiation was applied as follows: fast neutrons (>0.5 MeV), 6.9×10^{18} neutrons cm^{-2}; thermal neutrons 6.1×10^{18} neutrons cm^{-2}; dose of γ-radiation, 1.2×10^{10} r. The induced radioactivity consisted of 2 MeV β-radiation (90%) and 0.5–2.6 MeV γ-radiation (10%).

Catalytic measurements, carried out at 65° during the 30 days following irradiation, showed that the activity of the catalyst had decreased as a result of irradiation (Fig. 7). The authors point out that atoms of Al, P, F, Mg, and Na may be formed in the lattice by nuclear reactions. Their concentration, however, is so small ($< 10^{-5}$–10^{-7}%) that they can hardly explain the observed effect. The number of displacements (a few hundreds per primary impact) is much larger, and an acceptable interpretation must involve these entities. Lastly, the effect of radiation on water, which is known to promote this catalyst, may also be important.

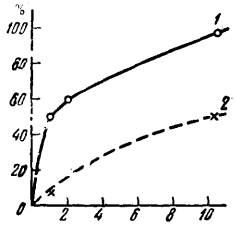


Fig. 7. Variation of percentage conversion of but-1-ene with reciprocal rate of admission in g h^{-1}. SiO_2–Al_2O_3 catalyst, not irradiated (curve 1) and irradiated (curve 2).

Kohn and Taylor's work[41], discussed in the previous section, had shown that the activity of silica gels in the hydrogen–deuterium exchange reaction and of SiO_2–Al_2O_3 catalysts in hydrocarbon cracking reactions was greatly increased by γ-irradiation. The effect of neutron irradiation on these systems was found to be even more striking. The impurity contents, and the pretreatment procedures adopted for the catalysts, are listed in Section III.

The specimens were irradiated in the pile with doses between 2.5×10^{15} and 2.2×10^{18} neutrons cm^{-2}. The catalytic activity rose to such an extent that the measurements had to be made at -196°. Table 3 lists the results, and also the authors' estimates for the numbers of displaced atoms and nuclear transformations, and for the yield of "catalytically active sites" per displaced atom. The rate constants observed before irradiation of the specimens are set out in Table 2.

It can be seen that neutron irradiation leads to calculated "yields" of active centres per displaced atom which are 100–1000 times smaller than in the case of γ-irradiation. This is interpreted by the authors as "aging" of the neutron-irradiated specimens, or as a demonstration of the greater effectiveness of the simple defects induced by γ-radiation, such as an isolated "vacancy–interstitial" pair, as compared with the more complex defects generated by neutron irradiation.

Kohn and Taylor[45] have studied the effect of neutron irradiation of γ-Al_2O_3 on the catalytic activity of the material in hydrogen–deuterium exchange reactions. The experiments on the effect of γ-radiation, and details of specimen purity, were summarised in the previous section.

The main conclusion of this work was that the reaction is significantly accelerated by neutron irradiation of the γ-Al_2O_3 catalyst.

Spitsyn *et al.*[57] have reported an interesting study of the effect of various types of radiation (including radiation from nuclear reactors) on the catalytic dehydration of n-decanol on Al_2O_3. The alumina used for this work contained 0.11% Fe_2O_3 and traces of SiO_2. The pile radiation had a neutron flux of $\sim 0.8 \times 10^{13}$ neutrons cm^{-2} sec^{-1}. The time of irradiation was varied between 1 and 10 days. The catalytic activity of the irradiated specimens was measured, in the temperature range 250°–400°, three days after irradiation. Typical results (for a temperature of 340°) are set out in Table 4.

It is interesting to note that the sign of the effect changes with the time of irradiation, and therefore with the integral dose of radiation: the catalytic activity is decreased by a brief irradiation, but increases on prolonged irradiation.

Measurements of temperature effects showed that storage during 49 days at 280° had practically no effect, whereas the same length of storage at 390° considerably decreased the effect of irradiation. The weak induced radioactivity (mostly due to the isotopes ^{24}Na and ^{59}Fe) cannot possibly account for the observed effects. However, irradiation with slow neutrons produces the short-lived radioactive isotopes ^{28}Al and ^{19}O of half-life 2.3 min and 29.5 sec respectively, which emit radiation of very high energy. The authors thus ascribe the observed effects to two opposing factors: on the one hand, to the appearance of lattice defects and production of electrical charges by radioactive decay, and on the other hand, to a decrease in the number of active sites at the surface due to the "polishing" effect of the radiation.

The loss of catalytic activity towards dehydration of n-decanol[58] induced by pile irradiation of the Al_2O_3 catalyst is given a similar explanation. The largest negative effect was observed with a specimen which had been kept for a long time (270 days) after 30 days' pile irradiation.

Yang[59] has reported enhanced physical adsorption of krypton on γ-Al_2O_3 as a result of fast neutron irradiation

TABLE 3. Effect of neutron irradiation on SiO_2 and SiO_2–Al_2O_3 catalysts.

Catalyst	Dose per m^2, *nvt*	No. of displaced atoms per m^2	No. of nuclear transmutations per m^2	k after irradiation at −196°, min^{-1} m^{-2}	Yield of active sites per displaced atom
SiO_2, gel 4*	$3.4 \cdot 10^{15}$	$1 \cdot 10^{16}$	$2.8 \cdot 10^{11}$	$1.2 \cdot 10^{-4}$	$1.2 \cdot 10^{-7}$
SiO_2, gel 2	$6.1 \cdot 10^{15}$	$1.8 \cdot 10^{14}$	$5 \cdot 10^{9}$	$9.3 \cdot 10^{-6}$	$5.4 \cdot 10^{-7}$
SiO_2, gel 3	$3.8 \cdot 10^{15}$	$1.2 \cdot 10^{13}$	$3.1 \cdot 10^{8}$	$2.5 \cdot 10^{-6}$	$2.3 \cdot 10^{-6}$
SiO_2–Al_2O_3	$1.6 \cdot 10^{15}$	$4.9 \cdot 10^{15}$	$1.2 \cdot 10^{12}$	$>1.1 \cdot 10^{-3}$	$>2.4 \cdot 10^{-6}$
SiO_2–Al_2O_3	$3.6 \cdot 10^{15}$	$1.1 \cdot 10^{16}$	$2.6 \cdot 10^{12}$	$>2.4 \cdot 10^{-3}$	$>2.3 \cdot 10^{-6}$
SiO_2–Al_2O_3	$1.2 \cdot 10^{16}$	$3.5 \cdot 10^{16}$	$8.5 \cdot 10^{12}$	$3.6 \cdot 10^{-3}$	$1.1 \cdot 10^{-6}$

* K on SiO_2 (gel 4) before irradiation had the value $9.3 \times 10^{-9} \times \times min^{-1}$ m^{-2} at 25°.

TABLE 4. Effect of neutron irradiation on the catalytic activity of Al_2O_3 towards dehydration of n-decanol.

Irradiation time, days	Radioactivity, mc g^{-1}	Yield of unsaturated hydrocarbons at 340°, %	Change in conversion relative to non-irradiated specimen, %
—	—	45	—
1	0.09	28	−38
1 (stored 49 days)	0.0002	37	−18
5	0.13	42	− 7
10	0.14	51	+13

(2×10^{18} neutrons cm^{-2}), and has attributed the effect to radiation defects in the crystal lattice of the adsorbent.

Very little has been published on the irradiation of solid non-metallic catalysts by charged particles. In the case of heavy charged particles, the lack of data is almost complete.

Kohn and Taylor's paper[45] on the effect of γ- and neutron irradiation on the catalytic properties of γ-Al_2O_3 towards the hydrogen–deuterium exchange reaction deals also with the effect of α-particles, which is found to be appreciable. Irradiation by the α-particles emitted by an Rn source (150 mc) adsorbed on the specimen was allowed to proceed for 102 days.

Gromov and Spitsyn[60] studied the sorption of dyestuff ions from solution on to barium sulphate as a function of electron and proton irradiation. Before irradiation, the barium sulphate was heated in a vacuum (10^{-3} mm Hg) at 300°–350°, and stored under nitrogen at 5 atm. Electron irradiation was carried out in a nitrogen atmosphere. An electron energy of 800 keV was used throughout, but the rate and total dose were varied. Irradiation with 1.5 MeV protons was carried out in a vacuum (10^{-5}–10^{-6} mm Hg); in this case the dose was 0.4×10^{21} eV g^{-1}. The specimens were heated to 100°–150° during irradiation; no induced radioactivity was detected. The specific surface of the specimens was practically unaffected by the irradiation. The sorption capacity of $BaSO_4$ decreased with increasing dose of electron irradiation, irrespective of the nature of the dyestuff. The sorption inhibition was more marked (for a fixed total dose and electron energy) at the lower dose rates.

Proton irradiation decreased the sorption of Acid Orange more markedly than electron irradiation. It was noticed that the colour of the specimens changed from white to light brown after irradiation. After a week at room temperature they lost their brown tint (both in air and in nitrogen), but did not recover their initial sorption capacity. 1 h at 200°–250° removed the colour, and also partly restored the original sorption capacity.

The authors consider that the external irradiation decreases the number of active sites on the surface ("polishing effect"), but they do not exclude the possibility of radiation defects in the $BaSO_4$ lattice.

Significant changes in the adsorption of sulphur trioxide on potassium sulphate were observed in a study[61] of the effect of electron irradiation on the isotope exchange of sulphur in the K_2SO_4–SO_3 system. The solid was irradiated during 10 min in a 5 MeV electron beam. Measurements at 840° showed that above a critical dose of the order of 10^{16}–10^{17} eV the rate of exchange increases in direct proportion to the dose absorbed by the substrate.

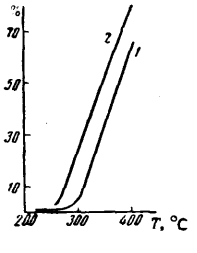


Fig. 8. Dehydration of n-decanol on Al_2O_3: 1) specimen not irradiated; 2) radiation dose 10^{20} eV g^{-1}.

Comparable doses of internal electron irradiation (produced by introducing a source of β-radiation into the bulk of the K_2SO_4) have a much more marked effect on the rate of exchange. This work is discussed in greater detail in the following section. The authors ascribe the effects to excitation of surface SO_4^{2-} ions under the influence of electron bombardment. The influence of electron bombardment on the gaseous SO_3 is significant, but much weaker.

The paper by Spitsyn *et al.*[57] on the dehydration of n-decanol on Al_2O_3 mentions the effect of electron irradiation on the activity of the catalyst. The catalyst and the alcohol vapour were irradiated for 10 min, during the reaction, with 760 keV electrons, to give a dose of 10^{20} eV $\times$ $\times$ g^{-1}. A significant increase in the rate of conversion of the decanol was observed, particularly at 250°–300°. The effect of temperature on the percentage conversion before and after irradiation is illustrated in Fig. 8. At 280° the yield of unsaturated hydrocarbons is increased by a factor of 10, but at higher temperatures the effect is less marked, due, no doubt, to "annealing" of the radiation defects. The authors describe the observed effects in terms of electron interactions with the Al_2O_3 lattice and excitation of the alcohol molecules.

Excitation and ionisation of atoms adsorbed on the Al_2O_3 surface are also invoked to explain the increased activity of an Al_2O_3 + 19.4% $CaCl_2$ catalyst towards dehydration of n-dodecanol[58] after electron irradiation (10^{20} eV g^{-1}).

We conclude this section with a discussion of an interesting paper by Roginskii, Zhabrova, and their coworkers[62] on the influence of electron bombardment on the topochemical processes involved in the decomposition of copper oxalate ($CuC_2O_4.\frac{1}{2}H_2O$) and nickel oxalate ($NiC_2O_4.2H_2O$).

The specimens were irradiated in air with different doses of electron (electron energy 0.6–2 MeV); the specimen thickness was of the same order as the depth of penetration of electrons of this energy. The heat thus generated did not raise the specimen temperature above 100°–150°.

Thermal decomposition of copper oxalate before irradiation begins at 225° *in vacuo* (to give Cu and Cu_2O) and at 250° in air (to give CuO). Non-irradiated nickel oxalate begins to decompose at 240° *in vacuo*, giving Ni, and at 300° in air, giving NiO.

Under the influence of radiation, the oxalates decompose in air some 200°–250° below the normal temperature of thermal decomposition, giving the same products as thermal decomposition in a vacuum. The depth of the effect increases with the dose of radiation. The radiation-chemical yield was found to be of the order of several tenths of a molecule per 100 eV.

Previous irradiation has a very marked effect on the decomposition kinetics of the oxalates (Fig. 9). Non-irradiated copper oxalate gives typically autocatalytic kinetic curves, with a long induction period which decreases with increase in temperature. Irradiation speeds up the reaction and shortens the induction period even at low temperatures. Really large doses (10^9 rad) can mask the autocatalytic effect.

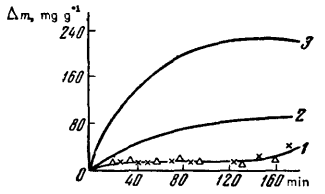


Fig. 9. Effect of previous irradiation on the decomposition kinetics of copper oxalate *in vacuo* at 225°: 1) non-irradiated specimen (Δ) and specimen irradiated with a dose of 2.2×10^8 rad (×); 2) specimen irradiated with 6×10^8 rad; 3) specimen irradiated with 1.1×10^9 rad.

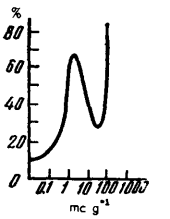


Fig. 10. Variation of percentage exchange with specific activity of $K_2S^*O_4$.

The authors[62] describe their observations in terms of excess electrons and holes, formed as a result of irradiation. The shortening of the induction period is ascribed to aggregation of the metal atoms formed by irradiation, giving crystallites (or nuclei) of a new phase.

V. CHANGES IN THE ADSORPTION AND CATALYTIC PROPERTIES OF SEMICONDUCTORS AND DIELECTRICS RESULTING FROM "INTERNAL" RADIOACTIVE RADIATION

The present section is devoted to the numerous papers on the control of the adsorption and catalytic properties of various solid catalysts by radioactive emitters of positive or negative particles, incorporated into the bulk of the catalyst (see Spitsyn's reviews[63,64]).

An effect of internal β-radiation on surface properties was first observed by Spitsyn and Mikhailenko, in their study[65] of the isotopic exchange of sulphur in the $K_2S^*O_4$–SO_3 system. These workers reported that the level of radioactivity of their preparations had an influence on the rate of isotopic exchange. The $K_2S^*O_4$ specimens were prepared by introducing a small amount (0.04–3%) of sulphur-labelled sodium sulphate into a solution of potassium sulphate, evaporating to dryness, and heating the residue to 800°. The exchange reaction was brought about by heating at 840° for 10 min. The rate of exchange was shown to be unaffected by inactive Na_2SO_4.

Within the limits of activity used in that investigation (0.02–19.2 mc g^{-1}), the extent of exchange was found to rise to a maximum at 2–2.3 mc g^{-1}, and then fall off again. The system was reinvestigated by the same workers[66] in greater detail and over a wider range of activities (up to 130 mc g^{-1}), with the results shown in Fig. 10. The formation of Cl^- ions by radioactive decay is not thought to affect the degree of exchange: an experiment in which 0.12% of KCl was added to a K_2SO_4 preparation of activity 0.06 mc g^{-1} gave 11.6% exchange, *i.e.* practically the same as in the control experiment.

A variation in the extent of exchange with specific activity of the solid of the type shown in Fig. 10 was observed also for the system $Na_2S^*O_4$–SO_3. The authors suggest that in both systems isotopic exchange of sulphur involves a reaction between SO_3 and SO_4^{2-} ions on the surface, with formation of the ionic intermediate $S_2O_7^{2-}$. The initial increase in the degree of exchange (see Fig. 10) is ascribed to the appearance of positive surface charge as a result of the continuous emission of β-particles; the subsequent drop can be explained by neutralisation of the positive charges setting in above a certain rate of electron emission. Lastly, the third, sharply rising portion of the curve is thought to be largely controlled by "activation" of the crystal lattice of the solid sulphate and of the SO_3 molecules under the influence of β-particles. The point was confirmed by comparing the results of Fig. 10 with those obtained in a parallel investigation[61]: the doses of external radiation required[61] to influence the amount of exchange in K_2SO_4 are effectively the same as the doses of internal electronic radiation experienced by the $K_2S^*O_4$ preparation whose specific activity corresponds to the beginning of the third section of the curve of Fig. 10. This is clear evidence that the two phenomena must be related.

The authors' suggestion of a change in mechanism for the sulphur isotope exchange reaction at different levels of radioactivity of the substrate has been confirmed by measurements of the rate constant for the exchange reaction in the $Na_2S^*O_4$–SO_3 system in the temperature range 700°–800°, leading to the activation energies of the process: 23–24 kcal $mole^{-1}$ and 18–19 kcal $mole^{-1}$, respectively, for specific activities of 0.02–1 mc g^{-1} and 10–25 mc g^{-1}.

Spitsyn and Finikov[67] reported very similar effects in their study of the oxygen isotope exchange in the $Na_2S^{*16}O_4$–$^{18}O_2$ system between 600° and 800°. By working over a range of temperatures, they were able to show that the activation energy of the process is a function of the specific activity of the sample. An energy minimum of 4 kcal $mole^{-1}$ was observed for activities of 1–2 mc g^{-1}, but at high specific activities the activation energy was even higher than the 54 kcal $mole^{-1}$ which characterise the process in the absence of radiation effects.

These workers noticed a "build-up" of the radiation effect with time, as shown in Table 5. These results confirm that the main effect of radiation takes place in the solid rather than in the gas phase, since the effect increases with time elapsed after irradiation as well as with the initial radioactivity. The specimens became greyish violet and the intensity of the colour increased with specific activity and with storage time. The colour was bleached by heating the solid to 600°.

Spitsyn and his coworkers studied the direct influence of internal radiation on adsorption properties[68–70]. We have already discussed their work[60] on the adsorption from

TABLE 5. Isotopic exchange of oxygen in the $Na_2{}^{*16}O_4$–$^{18}O_2$ system.

Temp., °C	Specific activity, mc g^{-1}	Storage time, days	Amount of exchange in 8 h, %	
			before storage	after storage
786	0.5	4	5.6	6.3
782	10.0	15	26.8	—
785			—	40.6
780	25.0	8	18.5	38.6
760		6	24.8*	29.6

* Specimen kept for 2 days before the first measurement.

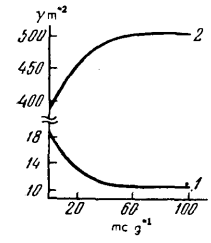


Fig. 12. Effect of initial radioactivity of BaS^*O_4 on dye sorption: 1) Methylene Blue; 2) Acid Orange.

solutions of ions of the dyestuffs Acid Orange and Methylene Blue, using barium sulphate adsorbents subjected to external electron and proton irradiation. The same workers investigated the influence of "internal" β- and α-radiation on the system[68] by coprecipitation of the isotopes ^{35}S and ^{226}Ra with the barium sulphate.

The equilibrium sorption curves (Fig. 11) show that sorption of the coloured cations of Methylene Blue decreases with increasing β-activity of the BaS^*O_4, whilst sorption of the coloured anion of Acid Orange increases under the same conditions. Internal α-radiation produces even stronger effects, but in the opposite sense.

Another basic dye, Brilliant Green, showed the same behaviour as Methylene Blue.

The measured sorption capacity of BaS^*O_4 is plotted in Fig. 12 against specific β-activity. The authors interpret these curves by invoking the accumulation of electrical charge on the $BaSO_4$ surface, the surface charge being positive for β-radiation and negative for α-radiation. The difference in behaviour between basic and acidic dyestuffs is, of course, consistent with this model. Gromov and Spitsyn's results[60] suggest that different mechanisms are involved in the interaction of external electronic and of proton radiation with a given system.

The same school has investigated[69,70] the effect of internal β-radiation on the adsorption capacity of potassium and barium sulphates towards various gases. The adsorption

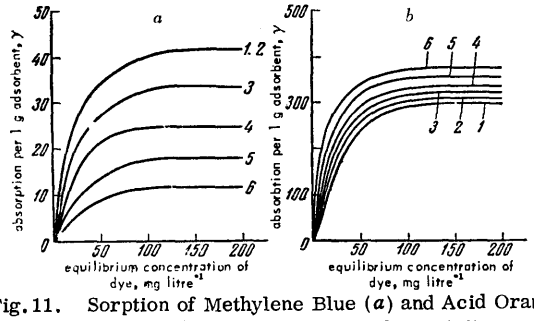


Fig. 11. Sorption of Methylene Blue (*a*) and Acid Orange (*b*) by precipitated BaS^*O_4 of varying specific activity: 1) inactive; 2) 0.01 mc g^{-1}; 3) 0.1 mc g^{-1}; 4) 1 mc g^{-1}; 5) 4 mc g^{-1}; 6) 10 mc g^{-1}.

of methanol on a $K_2S^*O_4$ specimen of specific activity 17.2 mc g^{-1} is 20% higher than on an inactive specimen. A $K_2S^*O_4$ specimen of specific activity 0.08 mc g^{-1}, which had been allowed to decay during 473 days, had an adsorption capacity 40% higher than an inactive sample.

Radioactive BaS^*O_4 was found[70] to have a much higher adsorption capacity towards n-hexane, benzene, and other vapours, than inactive specimens. The BaS^*O_4 was prepared by precipitation from solutions of $BaCl_2$ and $Na_2S^*O_4$, the latter containing varying proportions of ^{35}S. Specimens having an initial specific activity of ~85–100 mc g^{-1} were obtained. These were stored for various times, and degassed at 200°, before the adsorption measurements.

The main outcome of this work was the failure to observe a "build-up" effect, repeatedly detected in previous work. The adsorption measurements could be duplicated exactly after storage of the adsorbent for two months.

These effects are ascribed to the formation of a non-uniformly active adsorbing surface by incorporation of $Na_2S^*O_4$ during preparation of the BaS^*O_4, rather than to modification of the specimen surface by the subsequent radioactive decay.

Balandin, Spitsyn, and their coworkers[71–74] first observed an effect due to "internal" radioactive radiation on the catalytic properties of solids when studying the dehydration of cyclohexanol on MgS^*O_4. Atoms of ^{35}S and ^{45}Ca, introduced as $Na_2S^*O_4$ and Ca^*Cl_2 respectively during preparation of the material, were used as sources of internal β-radiation. Control specimens were prepared with identical admixtures of inactive Na_2SO_4 and $CaCl_2$. The reaction was studied between 350° and 420°, the percentage dehydration of cyclohexanol being used as a measure of the catalytic activity.

Pure $MgSO_4$ was found to have the highest catalytic activity (significantly decreased by additions of inactive Na_2SO_4 or $CaCl_2$). Radioactive $Na_2S^*O_4$ and Ca^*Cl_2 do not themselves catalyse the reaction, but appreciably increase the extent of dehydration when added to $MgSO_4$. Clearly, the action of radiation on the $MgSO_4$ has an important effect on the catalytic process.

Apparent activation energies were calculated, and found to be somewhat lower for the radioactive specimens.

The authors' curves for the increase in percentage conversion of cyclohexanol, Δ, as a function of the specific activity and of the dose rate of self-irradiation of the

MgS^*O_4 (Fig. 13) have some interesting features. Curve *2* of Fig. 13*a* is reversible: the spontaneous decay of radioactivity upon storage is accompanied by a proportional fall in Δ. It follows that "build-up" of the catalytic effect of radiation does not occur in this system.

The difference between curves *1* and *2* of Fig. 13 is thought to arise from the difference in β-energy of ^{35}S (E_{max} = = 0.167 MeV) and ^{45}Ca (E_{max} = 0.254 MeV), and hence to involve secondary radiation effects on the catalyst.

Irradiation of the catalyst, during the reaction, with a beam of 800 keV electrons had no effect whatever on the extent of conversion.

A paper by Krohn and Smith[75] should be considered in conjunction with the work just discussed[71–74]. These workers studied the effect of X-rays on the dehydration of cyclohexanol (catalysed by $MgSO_4$ and $MgSO_4$–4% Na_2SO_4) using dose rates of 113 and 123 rad min^{-1}, but failed to observe any changes in catalytic properties.

Krohn and Smith point out that X-radiation produces high-energy electrons in the bulk of the material, and should therefore be equivalent to radiation from previously incorporated ^{35}S atoms. They calculate that their X-ray treatment should produce an effect at least equal to that of a specific radioactivity of 14 mc g^{-1}. Yet, this level of activity in MgS^*O_4 catalysts had been found[74] almost to double the rate of reaction, whereas X-rays had no effect on the catalytic properties of $MgSO_4$. Krohn and Smith conclude that the effects reported by the Soviet workers[74] are due to the conversion of ^{35}S into ^{35}Cl, and not to electron emission.

It should be noted that Spitsyn *et al.* have themselves published some results[57] which contradict their other findings[73]: the isotope ^{144}Ce, when introduced into Al_2O_3, had practically no effect on its catalytic activity towards the dehydration of n-decanol, whereas external electron irradiation had given a large positive effect. On the other hand, the isotope ^{45}Ca had sharply increased[58] the catalytic activity of Al_2O_3 with respect to the dehydration of n-dodecanol, the effect being suppressed by electron irradiation (energy 800 keV, dose 10^{20} eV g^{-1}) during the reaction. Thus, the effect of internal radioactive radiation on the surface properties of solids is seen to be highly specific.

A paper by Spitsyn *et al.*[76] should be mentioned in this context. These workers made a special electron-microscopic study of the effect of radioactive radiation on the surface structure of various solids, including $K_2S^*O_4$, MgS^*O_4, BaS^*O_4, and Mo^*O_3. The solids were examined in the inactive condition, as well as at various levels of specific activity. Inactive specimens had a much less developed surface than the radioactive ones, even when the latter were examined immediately after preparation. This confirms the authors' conclusion[70] reached independently that radioactive radiation affects the formation of the surface during specimen preparation by crystallisation. The subsequent effect of radiation on the crystal lattice of the solid must, of course, also be considered. The authors point out that this conclusion is confirmed by measurements on inactive K_2SO_4, irradiated by an external electron beam: in spite of a higher dose of radiation, the surface development in this material was less than in the radioactive specimens.

We conclude this section by discussing two interesting papers[77,78] on the effect of internal radioactive radiation upon semiconductor catalysts. The isotopes introduced into the specimens in this work (^6Li and ^{10}B) were not themselves radioactive, but they gave α emitters when irradiated by thermal neutrons because they present a very large cross-section to the (n, α) reaction.

The paper by Sayto *et al.*[77] describes the decomposition of nitric oxide on NiO, SnO_2, and Al_2O_3. The SnO_2 and Al_2O_3 catalysts contained additions of B_2O_3 (10%) and Li_2O (10%); the NiO contained 10% B_2O_3 and 1% Li_2O. The preparations were heated for 2.5 h at 750° and exposed to a neutron flux of 10^{11} neutrons cm^{-2} sec^{-1} during 3 h. The catalytic measurements were made one month after irradiation.

Apparent activation energies and relative values of the frequency factor (Table 6) were calculated from the temperature dependence of the percentage decomposition of nitric oxide.

The slight negative effect (decrease in catalytic activity) observed with NiO, a *p*-type semiconductor, is thought to be due to a decrease in hole concentration, resulting from the removal of excess oxygen ions from their equilibrium sites under the influence of α-radiation. SnO_2, an *n*-type semiconductor, shows a fairly large positive effect, which is also explained by an increase in the number of donor levels of the oxygen vacancy type as a result of irradiation, leading to a higher concentration of electrons in the material. Lastly, the behaviour of Al_2O_3 is ascribed to the dielectric properties of this compound.

Braun and Maxim[78] studied the effect of pile irradiation on the catalytic activity of NiO doped with Li_2O (2.5 mole %) towards the oxidation of CO. The specimens were heated for 3 h at 850° and exposed to pile radiation (2×10^{11} thermal neutrons and 7×10^9 fast neutrons cm^{-2} sec^{-1}). However, the time of irradiation (over 150 h) was much longer

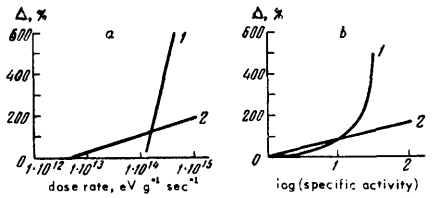


Fig. 13. Increase in the degree of conversion (Δ) of cyclohexanol with dose rate experienced by the catalyst (*a*) and with specific activity (mc g^{-1}) achieved (*b*): 1) $MgSO_4$ + + Ca^*Cl_2; 2) $MgSO_4$ + $Na_2S^*O_4$.

TABLE 6. Catalytic properties of NiO, SnO_2, and Al_2O_3, before and after irradiation, towards the decomposition of nitric oxide.

Catalyst	NiO				SnO_2				Al_2O_3			
	Li_2O		B_2O_3		Li_2O		B_2O_3		Li_2O		B_2O_3	
	before	after	before	after	before	after	before	after	before	after	before	after
Relative values of the frequency factor	1.7	1	1.1	1	1	2.9	1	2.5	1.6	1	1	2.5
Apparent activation energy, kcal $mole^{-1}$	22	23	19	19	21	20	43	20	23	23	23	24

than in the previous work[77], so that the effect of the reaction $^6Li(n, \alpha)^3H$ was to some extent masked by the normal effect of external neutron irradiation. An increase in the catalytic activity of NiO towards the oxidation of CO was observed (Fig. 14).

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In spite of the wealth and diversity of our fund of factual information concerning the influence of irradiation upon the adsorption and catalytic properties of non-metallic solids, a unified description and a quantitative interpretation of these phenomena are still awaited. This is not surprising, in view of the complexity of adsorption and catalytic systems, and of the inadequacy of our understanding of radiation defects.

However, the experimental papers discussed here (and also in recent review articles[30-32,79,80]) give the impression that most workers prefer to rely on electronic concepts to explain the observed effects§. The electronic nature of these phenomena is most strikingly demonstrated by the correlation between changes in adsorption and catalytic properties, on the one hand, and electrical, optical, magnetic, and other solid state properties on the other. Thus, a successful interpretation of these phenomena must, in all probability, involve a synthesis of modern theoretical concepts on the effects of radiation on solids[1] and of the electronic theory of chemisorption and catalysis[81].

Vol'kenshtein[82] has taken the first step in this direction by formulating the problem of radiation effects on the adsorption and catalytic properties of semiconductors in terms of the electronic theory of solids, and giving a possible mechanism for the effect.

The electronic theory teaches that surface electrons and holes, either free or localised on surface defects, are responsible for the adsorption and catalytic properties of solids. The equilibrium concentrations of these charge carriers are defined by the position of the Fermi level at the surface, which itself depends on the position of the bulk Fermi level. Clearly, any radiation effect which alters the position of the Fermi level in the specimen can influence the adsorption and catalytic properties. As already stated, the main effects of radiation are ionisation, displacement of atoms (or ions), and nuclear transmutations in the crystal lattice of the solid.

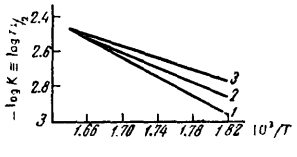


Fig. 14. Arrhenius plots for the catalytic oxidation of CO on (NiO + 2.5% Li_2O): 1) before irradiation; 2) 80 h pile irradiation; 3) a further 80 h irradiation.

Ionisation processes destroy the electronic equilibrium in the crystal and create non-equilibrium charge carriers both in the bulk and at the surface, thus significantly affecting the adsorption capacity and the catalytic activity of the material. Basically, this mechanism is the same as the photoadsorption and photocatalytic mechanism quantitatively analysed by Vol'kenshtein[82]. Changes in adsorption capacity, adsorption kinetics, and rate of catalytic reaction under the influence of ionising radiation are correlated, and it is shown that if the irradiation conditions are fixed, the magnitude and sign of the effect are a function of temperature and of the original position of the Fermi level. We should stress that the ionisation effect decays rapidly because of the short lifetimes of non-equilibrium charge carriers: in the absence of electron or hole trapping processes, the effect should be observable only during the irradiation period. This suggests an experimental test for distinguishing between this and other, more stable, effects.

The various lattice defects formed at the surface or in the bulk as a result of atomic or ionic displacements behave as electron donors or acceptors, and therefore cause the Fermi level to move in the appropriate direction, with a consequent effect on the surface properties of the crystal. Depending on what determined the initial adsorption capacity and catalytic activity of the crystal, the major effect could be due either to changes in the free carrier concentrations or to changes in the population of localised surface states. This mechanism accounts for more persistent changes in surface properties. "Annealing" of the defects involves diffusion and can only occur at high enough temperatures.

Nuclear transmutations produce chemically foreign species, which affect the surface properties by much the same mechanism. The only difference is that these changes are irreversible, and do not respond to "annealing".

Irradiation can produce electronic effects even when the bulk and the surface Fermi levels remain almost unaffected. This situation will arise in the presence of large concentrations of free carriers, as a result of mutual compensation of radiation defects, and for other reasons. When these defects reach the surface, however, they can give rise to new active sites from the point of view of adsorption and catalytis. The electron (or hole) occupancy of these states, and therefore also the efficiency of the mechanism, are determined by the original position of the Fermi level.

The efficiency of any mechanism involving lattice defects, it should be noted, depends on the concentration of defects produced and on the position of their energy levels in the energy band diagram of the semiconductor or dielectric. It is highly desirable, therefore, that adsorption and catalytic measurements should be accompanied by observations of the influence of radiation on other solid state properties, so as to characterise the resulting defects.

We have considered some general mechanisms which can be deduced directly from the effect of radiation on solids and from the electronic theory of adsorption and catalysis. Other effects of a more specialised nature can also be very important: charging of the specimen during

§ Some new experimental papers in general agreement with the views presented here have been published after the manuscript had passed the editorial stage. We shall not mention these individually, but refer the reader to the authoritative review by R. Covkelbergs, A. Cruck, and A. Frennet, Advances in Catalysis, 13, 55 (1962).

self-irradiation or external irradiation, for example, in which charge "leakage" is a significant factor.

Charge accumulation in the specimen can affect its adsorption and catalytic properties in various ways. One likely effect of charge accumulation is a shift in the Fermi level of the specimen, which then leads to the observed phenomena. Processes in which the solid acts as an energy moderator between the radiation and the reactant molecules in the gas phase or in solution can also be of importance.

Lastly, phenomena such as radiolysis of surface promoters or poisons, radiation polymerisation of organic substances, radiochemical reactions in the gas phase or in solution, etc., must be kept in mind, even though their influence has proved decisive only in a few concrete instances. As a rule, they play a secondary part, and tend to mask the major effects.

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CHEMICAL CHANGES DURING β-DECAY PROCESSES

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I. INTRODUCTION

The study of the chemical consequences of nuclear transformations is one of the most interesting and at the same time one of the most complex fields of radiochemistry; it has been called the chemistry of hot and excited atoms[1-11]. Studies in this field are of considerable theoretical and practical interest for both radiochemistry and chemistry in general, since they make it possible to obtain important information on the characteristic features of the behaviour of atoms of elements existing in particular energy and charged states and in completely new and unusual experimental conditions. From the practical view point, the study of the behaviour of atoms produced in different kinds of nuclear process is of considerable importance for the concentration of radioactive isotopes, the separation of nuclear isomers, and the preparation of various labelled compounds.

The study of the chemical changes during β-decay processes has revealed new possibilities in studies of this type. The processes of the electron- and positron-decay of atoms have provided a new method of exciting and ionising molecules and an original source of positive and negative molecular ions of any degree of complexity and with different initial localisation of the charge and excitation. Such ions may be generated both in highly rarified (gaseous) and in condensed (liquid and solid) phases. This makes it possible to examine how their behaviour is influenced by effects associated with the possibility of transfer of excitation energy to the surrounding medium, reaction with this medium, and other processes. Comparison of the consequences of excitation produced by the β-decay of atoms with other forms of molecular excitation (electron collision, photoionisation) makes it possible to observe the characteristic features of the redistribution of the energy of the nuclear transformation between the emitted β-particle and the molecular system and also to study the ways in which the excitation energy is redistributed in the molecular ion.

Methods making use of the chemical effects accompanying β-transformations and based on the processes of stabilisation and breakdown of molecular ions make it possible to prepare compounds of the daughter element with the highest possible specific activity, extremely difficult to prepare by ordinary methods. These new methods may be particularly important for the preparation of compounds of typical radioactive elements such as polonium, francium, and astatine. Moreover, in recent years extremely simple and elegant methods have been developed for the separation of radioactive isotopes by making use of the phenomenon of chemical-bond rupture during β-decay.

The importance of studies of chemical changes during β-decay processes extends beyond the limits of radiochemistry and the general chemistry of the elements, since such studies in a number of cases make it possible to reach conclusions regarding the nuclear transformations themselves. On the other hand, it is impossible to explain the chemical changes accompanying β-decay without making use of the results of special nuclear or related studies. It will therefore be appropriate to begin with a description of those factors in the field of nuclear physics which determine the state of the daughter atoms produced during β-decay processes.

II. FACTORS DETERMINING THE STATE OF DAUGHTER ATOMS

By the factors determining the state of daughter atoms we mean those factors which influence the energy and charged states of these atoms and thus determine their distribution between the stable and labile forms of the element possible under the given conditions. These factors include the kinetic energy of the daughter atom (recoil energy), acquired as the result of the emission of β-particles, conversion electrons, or γ-quanta; the internal conversion of the γ-radiation of the daughter atom in its electron shells; and changes in the electron shells of the atoms as a result of the sudden change in the charge of the nucleus [12,13].

The final chemical state of the elements formed in β-decay processes is influenced to a considerable extent by the chemical state of the mother elements and the conditions under which breakdown of the mother molecule takes place.

1. Recoil during β-Decay

The atoms produced in nuclear transformations very often acquire a high kinetic energy, many times greater than the average energy of thermal movement. These atoms are called hot atoms.

The maximum recoil energy for β-decay is calculated from the formula:

$$E_{M(\max)} = 548\frac{E_{\beta(\max)}}{M} + 536\frac{E^2_{\beta(\max)}}{M}, \qquad (1)$$

obtained with allowance for the relativistic dependence of the mass of the β-particles on velocity [1]. In this formula the maximum recoil energy $E_{M(\max)}$ is expressed in eV, the maximum energy of the β-particles in MeV, and M, the mass of the recoil atom, in atomic mass units.

For light nuclei exhibiting a high maximum β-radiation energy, the recoil energy may reach very high values. For ^{12}B, for example, the maximum recoil energy is 8.68×10^3 eV, and for ^{8}Li it is as high as 11.7×10^3 eV. For intermediate and heavy nuclei and the maximum β-radiation energies most frequently encountered (1-2 MeV), the recoil energy is close to the energy of the chemical bond formed by the atoms. In the case of heavy nuclei with low β-particle energy, the recoil energy may be much less than the chemical bond energy. This is the case, for example, for the transformations RaD(^{210}Pb)–RaE(^{210}Bi), ThB(^{212}Pb)–ThC(^{212}Bi), etc. For RaD–RaE the maximum recoil energy for the emission of a β-particle is only 0.04 eV.

Formula (1) can be used to calculate the maximum recoil energy, *i.e.* it is applicable only for those comparatively rare cases of β-decay where the energy removed by the neutrino is equal to zero. In the general case, the energy of the β-particles emitted during the decay of a given isotope varies from zero to a certain maximum value. The difference between the maximum energy and the actual energy of the β-particle is removed by the neutrino. Thus in the general case, in the calculation of the energy of recoil atoms, it is necessary to make allowance for the simultaneous emission of two particles (the β-particle and the neutrino). The observed recoil energy in this case will depend on the distribution of the total energy of decay between these particles and also on the angle between the directions of their escape. Since there are different combinations of energy distribution between the β-particle and the neutrino and the directions of their escape, the recoil atoms have different energies. We therefore have to deal with a recoil atom energy spectrum. The calculation of this energy spectrum involves a number of difficulties. The available data on the angular correlation of the β-particle and neutrino are indefinite, and this prevents rigorous quantitative calculation of the energy spectrum of recoil atoms.

The proportion of recoil atoms with energies above certain minimum depends to a marked extent on the nature of the angular correlation between the β-particle and the neutrino [2]. Fig. 1 gives the energy spectra of recoil atoms for an atom with mass 100 and $E_{\beta(\max)} = 2.0$ MeV, for different types of angular correlation: (a) escape of β-particle and neutrino in the same direction, (b) escape of β-particle and neutrino in opposite directions, and (c) isotropic radiation.

Thus the angular correlation between the β-particle and the neutrino should influence the efficiency of chemical-bond rupture resulting from recoil phenomena. This forms a basis for obtaining qualitative information on correlation phenomena during β-decay.

β-Decay is often accompanied by the emission of γ-rays and conversion electrons, which also bring about recoil effects. It is easy to make allowance for these effects and they are not usually important†.

Suess [14] showed that for diatomic molecules, the recoil energy used up directly for bond rupture depends on the ratio $R/(R + M)$, where R is the mass of the molecular residue and M the mass of the recoil atom. This means that only a fraction of the recoil energy, equal to $E = E_M\frac{R}{R+M}$, where E_M is the recoil energy, can be used up in bond rupture. The remaining fraction of the recoil energy is realised as the kinetic energy of the whole molecule.

When the part played by the phenomenon of recoil is assessed, we find that in different cases of β-decay, recoil may have a decisive influence or an insignificant influence

† The recoil energy for the emission of γ-quanta is calculated from the formula $E_M = 536E^2_\gamma/M$, where E_M is the recoil energy in eV, $E\gamma$ the energy of the γ-quanta in MeV, and M the mass of the atom in atomic units. In the case of emission of conversion electrons, the recoil energy is greater than that for the emission of the corresponding γ-quantum and is given approximately by the formula $E_M = 541E_e/M$, where E_M is the recoil energy in eV, E_e the energy of the conversion electron in MeV, and M the mass of the recoil atom in atomic units.

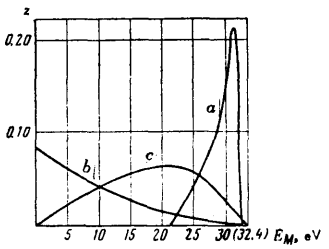


Fig. 1. Energy spectrum of recoil atoms for different cases of corelation between β and ν.

on chemical-bond rupture. The contribution of the phenomenon of recoil can be estimated in each individual case with satisfactory accuracy.

2. Excitation and Ionisation of an Atom during β-Decay

The excitation and ionisation of atoms during radioactive transformations may be produced by three factors which are approximately independent: (a) recoil of the nucleus (kinetic activation of the recoil atoms), (b) direct reaction of the radiation emitted by the nucleus with the atomic electrons, and (c) the sudden change in the charge of the nucleus.

These factors influence the degree of excitation or ionisation of the atoms to different extents during β-decay. The perturbations undergone by different electrons of the same atom also differ. For some electrons they may arise slowly (adiabatically) and for others suddenly (non-adiabatically).

By means of the criterion of sudden perturbation, formulated by Pauli[12,15], it can readily be shown that during β-decay (and also α-decay) the velocity acquired by the atom as a result of recoil is insufficient to bring about ionisation of even the outer electrons. (Ionisation as a result of recoil takes place, for example, during nuclear fission, where the divergence of the fission fragments is adiabatic only with respect to the internal electrons[16-19].)

Migdal[20], Feinberg[21], and others have shown theoretically that in the general case the direct reaction of β-particles with atomic electrons is negligible.

In β-decay, the chief part in the excitation and ionisation of recoil atoms is played by another mechanism. Migdal[20], Feinberg[21], Schwartz[22], Levinger[23], Winther[24] and others have shown that the chief part in the excitation and ionisation of recoil atoms in the emission (or absorption) of charged particles is played by the effect of the "shaking" undergone by the electrons as a result of the sudden change in the charge of the nucleus. The perturbation undergone an electron shell of the atom during β-decay is nonadiabatic, since the β-particle leaves the atom at a velocity immeasurably greater than the rate of movement of the orbital electrons. According to theoretical calculations, the probability of ionisation during the sudden change in the charge of the nucleus is proportional to $1/Z^2_{\text{eff}}$ (Z_{eff} is the effective charge of the nucleus).

Calculations carried out using the hydrogen-like wave function for atoms with a nonadiabatic approximation concern chiefly the K, L, and M shells. The results of the calculation, by different authors, of the probabilities of ionisation in these shells for atoms with high values of Z are compared in Table 1.

Screening decreases the effective charge of the nucleus Z_{eff} fairly rapidly, so that the electrons in the outer shell have the highest probability of excitation to the state of ionisation.

The most detailed quantum-mechanical calculations of the excitation and ionisation of daughter atoms have been made by Winther[24,25] for the $^6He \xrightarrow{\beta^-} {}^6Li$ transformation, since for this case the wave function describing the ground state of helium and several states of lithium is known. The distributions of the daughter atoms with respect to excitation energies, obtained by Migdal and Winther, show a sharp decrease in the probability of conversion into the excited state with increase in the excitation energy, and up to 70% of the daughter atoms are formed in the ground state. At the same time calculations show that 25% of the $(^3He)^+$ has 20.5 eV excitation relative to the ground state, and for 17% of the $(^6Li)^+$ the figure is about 60 eV.

Green[26] has carried out theoretical calculations of the probabilities of ionisation of daughter atoms for the case of $^{79}Kr \xrightarrow{\beta^-} {}^{79}Rb$ decay. These results were later tested experimentally and satisfactory agreement with theory was obtained.

Serber and Snyder[27] made a theoretical estimate of the average excitation energy for β-decay by averaging the probabilities of distribution for conversion from the ground state of the mother atom to different final states of the daughter atom. They obtained the following expression for the average excitation energy for the case of heavy nuclei:

$$\Delta E = 22.85\, Z^{2/5}(Z' - Z)^2,$$

where ΔE is the mean excitation energy of the daughter atom in eV, and Z and Z' are the atomic numbers of the elements. As already noted, however, this expression does not give a picture of the actual distribution of the daughter atoms with respect to excitation energies.

Theory predicts[20,23] that the effect of "shaking" during positron-decay is of approximately the same magnitude as that for β^--decay.

In general, published calculations of the probabilities of ionisation during β-decay are inaccurate because of the approximations made. In this connection it is important to estimate the applicability of the nonadiabatic approximation used in these calculations; this is fairly satisfactory for the inner shells of heavy atoms. For other cases the accuracy of the nonadiabatic approximation decreases with increase in the shell number and with increase in the charge of the nucleus. For the outer electrons of the cloud, the

TABLE 1. Calculated values of the ionisation probability for the β-decay of atoms.

Shell	Ionisation probability $\times Z^2_{\text{eff}}$, from:			
	Migdal[20]	Feinberg[21]	Schwartz[22]	Levinger[23]
K	0.6	0.64	0.66	0.65
L	6.8	—	2.26	2.1
M	14	—	4.28	—

"shaking" resulting from change in the charge on the nucleus will be "delayed" and not so powerful as that for the electrons of the inner shells. Nevertheless the probability of ionisation during decay increases with increase in the shell number, since the outer electrons are less firmly bound and the effective nuclear charge with respect to these electrons is low.

Experimental confirmation of the "shaking" theory was until recently based on absolute counting of the characteristic X-radiation accompanying β-decay. The calculated and experimental values of the probabilities of ionisation of the internal electron shells were compared. The results obtained confirm the theory over a wide range of atomic numbers. Examples include the data given by Renard[28] for ^{32}P and RaE, Robinson and Howland[29] for ^{35}S, Michalowicz[30] for ^{90}Sr–^{90}Y and RaE, Boehm and Wu[31] for ^{147}Pm and RaE, Langevin-Joliot[32,33] for ^{147}Pm, and by other authors[34,35].

Despite the importance of such studies, it must be remembered that they can be used for the experimental verification of Migdal's theory only for the inner electron shells. The first experimental studies of the effect of "shaking" on the outer electron shells were made by Wexler for the case of the β-decay of tritium, ^{14}C, and ^{41}Ar.[36] The results of these experiments (Table 2) show that in all cases (even for the atoms of elements such as carbon, for which the "shaking" effect should be strongest), the average charge of the daughter atoms is close to unity. This is apparently due to the fact that the presence of a relatively small quantity of ions with multiple charges (chiefly doubly charged) could not be recorded with sufficient accuracy by the methods used.

Basic information on the effect of "shaking" on the outer electron clouds of atoms has recently been given by the charge spectrometry of recoil atoms. Snell and Pleasonton[37–39] have made a systematic study of the charge spectra of recoil atoms during the β-decay of various isotopes of the inert gases. The use of the monatomic inert gas for the observations made it possible to avoid the influence of molecular effects. The results of the studies[39] of the charge spectra of recoil atoms during the β-decay of ^{6}He, ^{39}Ar, ^{85}Kr, and ^{133}Xe (Table 3) show that singly charged ions predominate in the charge spectra. In the case of β-decay the singly charged ion is produced directly by the emission of a nuclear β-particle and the resulting increase in the charge of the nucleus by one unit. Thus in 80–90% of all decays there is insufficient excitation energy for ionisation. The loss of one orbital electron leads to a charge of +2. Thus in the case of pure β-decay, the relative yield of the ion with charge +2 in the charge spectrum gives almost exactly the probability of ionisation of the outer shell as a result of the "shaking" effect. The experiments show that this

TABLE 2. Average charge of the daughter atoms for the β-decay of T, ^{14}C, and ^{41}Ar.

Isotope	Chemical formula	Maximum energy of β-particles in MeV	Average charge of daughter atoms
T	T_2	0.018	0.9±0.1
^{14}C	$^{14}CO_2$	0.155	1.0±0.2
^{41}Ar	Ar	1.245	1.0±0.1

TABLE 3. Charge distribution of recoil atoms for the β-decay of various isotopes (% of total number of decays).

charge	Isotope ^{6}He	^{39}Ar	^{85}Kr	^{133}Xe
1+	89.4±3	86 ±3	79.2 ±0.4	80
2+	10.6±1.0	10.5±2.0	10.9 ±0.2	8
3+	0.04±0.01	2.5±0.8	3.91 ±0.12	4
4+	—	0.9±0.4	3.12 ±0.13	3
5+		0.3±0.2	1.51 ±0.07	—
6+		<0.05	0.66 ±0.04	~5
7+			0.40 ±0.02	
8+			0.18 ±0.02	
9+			0.093±0.01	
10+			0.026±0.006	
11+			<0.003	

removal of one of the outer electrons takes place in approximately 10% of all decays. If the primary ionisation takes place in an inner shell, the atom may be even more extensively ionised as a result of subsequent Auger transitions. The relatively small quantity of ions with multiple charge in the charge spectrum indicates that the removal of the inner orbital electrons is much less frequent than removal of the outer electrons. These results confirm Winther's data[25] for the $^{6}He \xrightarrow{\beta^-} {}^{6}Li$ transformation. According to the theoretical calculations of the author, the loss of one electron takes place in 10.5 ± 5% of cases and the loss of two electrons in less than 0.1%. These calculations show good agreement with the experimental data (10.6 ± 1.0 and 0.04 ± ± 0.01% respectively).

On the whole, the data at present available show fairly good agreement with the model based on the "shaking" resulting from sudden changes in atomic number.

3. The Emission of γ-Quanta by the Excited Nuclei of Daughter Atoms and the Phenomenon of Internal Conversion during β-Decay

β-Decay leads fairly frequent to excited states of the nuclei of daughter atoms and the daughter nucleus may return to the ground state by two competing processes: radiation of the excess energy in the form of γ-quanta, or internal conversion[40,41]. The phenomenon of γ-quanta emission by excited nuclei may itself lead to additional, albeit weak, effects (recoil during the emission of the γ-quantum).

The probability of the discharge of the excited state of nuclei by internal conversion, *i. e.* by direct transfer of the excitation energy of the nucleus to the electron shells of the atom, depends to a considerable extent on the atomic number of the element and the energy, nature and multipolarity of the radiation. These processes are most marked in the case of heavy nuclei[40,41].

Internal conversion leading to the removal of electrons from deeply lying shells, for example the K or L shells, is often followed by Auger transitions without radiation. It is now well known that the cascade of vacancies developing in the process leads to the accumulation of a considerable positive charge (multiple ionisation of the atom). The development of analogous cascades of vacancies is due to capture of an orbital electron (K-capture) and also, to a slight extent, to processes of β-decay as a result of the ionisation of inner electron shells when the nuclear charge changes suddenly.

Experimental confirmation of these ideas is provided by the work of various authors on the determination of the average charge of the daughter atoms when conversion phenomena are involved in the case of K-capture and isomeric transition[42-49]. The examples which have been studied in most detail include K-capture in ^{37}Ar. In the first work on the determination of the charge state of ^{37}Ar atoms by collection of the ions in an electrical field[42-44], average charge values close to +3 were obtained.

Snell and Pleasonton[47,48] made a detailed study of the charge distribution of recoil atoms for K-capture in ^{37}Ar by the methods of mass-charge spectroscopy. The distribution with respect to the charges of the recoil atoms, expressed as percentages of the total number of disintegrations, is given in Fig. 2. This distribution of recoil atoms with respect to charges arises because the cascades of vacancies are the predominating processes. The "shaking" effect is shown to a much smaller extent than with β^--decay, since the change in the nuclear charge is smoothed out to some extent by the loss of the K-electron. This feature was first noted by Primakoff and Porter[49].

The high efficiency for ionisation of the atom, shown by the processes of internal conversion, can be seen from the charge spectrum (Fig. 3) of the recoil atoms formed during the decay of ^{131m}Xe (isomeric transition, converted to the extent of 98%). The average charge in this case is +7.9.[48] An even higher charge state (+10.5) was obtained by Wexler[36] for the decay of ^{80m}Br (in the form of C_2H_5Br).

In addition to these charge spectra for simple cases (pure β-decay, Table 3; K-capture, Fig. 2; highly converted isomeric transition, Fig. 3), Snell and Pleasonton[48] give data on the spectra of recoil atoms for the case of complex decay schemes. These complex spectra are as it were, composed of simple spectra and have several maxima due to different processes.

Conversion phenomena are of considerable importance with elements of high atomic number which are very soft β-irradiators; the nuclei of the daughter atoms from these elements are in intermediate excited levels immediately after decay. This is particularly true of the chains: RaD(^{210}Pb)–RaE(^{210}Bi), ThB(^{212}Pb)–ThC(^{212}Bi); RaB(^{214}Pb)–RaC(^{214}Bi), etc. As shown below, the study of the chemical state of RaE, ThC, and RaC, produced by the decay of RaD, ThB, and RaB in certain organolead compounds shows that the phenomenon of internal conversion is one of the

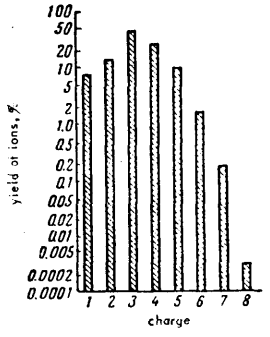


Fig. 2. Charge distribution of recoil atoms for K-capture in ^{37}Ar.

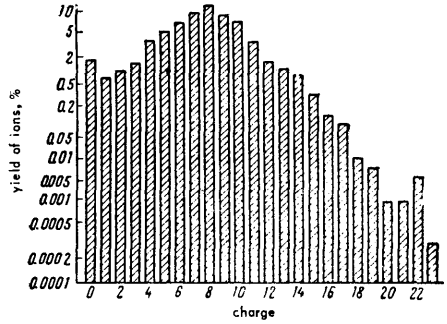


Fig. 3. Charge distribution of recoil atoms for ^{131m}Xe.

main causes of chemical-bond rupture during the β-decay of these isotopes. This is indicated, in particular, by the fact that the internal conversion coefficients coincide with the maximum yield of the inorganic forms of RaE, ThC, and RaC.

We shall conclude this description of the various mechanisms of excitation and ionisation of atoms during β-decay by considering the process noted by Wolfsberg and Perlman[51], who suggest that the emission of conversion electrons brings about electrostatic "shaking" analogous to that which is observed during the sudden change in nuclear charge, and that this may lead to excitation and ionisation of atoms. There are no experimental data in support of this mechanism and it may be assumed to accompany Auger transitions to some extent.

III. PROCESSES DEVELOPING IN MOLECULAR SYSTEMS DURING β-DECAY

Since after emission of a β-particle the daughter atom may possess a single positive charge even in the absence of further ionisation, it is obvious that if the decaying atom is part of a molecule, the first direct result of the β-decay process will be the production of a primary molecular ion with an electronic charge of +1. Data obtained in theoretical and experimental studies show that a considerable proportion of the primary molecular ions exists in various excited levels immediately after their formation. Here we may have not only electronic excitation but also the excitation of vibrational and rotational levels of the molecular ion. The main cause of the electronic excitation is the nonadiabatic character of the β-decay processes ("shaking" effect), whereas the initial excitation of the vibrational and rotational levels is due chiefly to the effect of radioactive recoil.

It should be remembered that a particularly important factor in the behaviour of the primary molecular ions is the change in the chemical nature and charge state of one of the atoms of the molecular system and the resulting thermodynamic stability or instability of these molecular ions. The Frank–Condon principle shows that for adiabatic transitions the cause of the excitation of the vibrational levels of the molecular ions is the change in the chemical nature and charge state of the decaying atom. The configuration of the nuclei in the molecular ion at the moment of its

formation is "inherited" from the initial molecular system and will not in general correspond to the minimum potential energy of this ion. This means that the so-called vertical transitions on the potential-energy diagram, associated with the change in the chemical character and electronic state of the atom, will lead to the production of molecular ions existing in different excited vibrational levels.

The behaviour of excited molecular ions depends on many factors: the nature of the initial molecular system, the composition and structure of the molecular ions, their stability in the ground level and excited levels, the distribution function of the daughter atoms with respect to energies, the extent and rate of the transfer of the excitation energy of these atoms to the molecular ion, and the surrounding medium, etc. Subsequent changes may involve either stabilisation processes or fragmentation processes, depending on the energy state of the initial molecular ion and the above factors. Either type of process leads finally to stable chemical forms of the daughter elements. Processes involving neutralisation of the primary molecular ions, existing in ground levels, by electrons and negatively charged ions may lead to the formation of stabilisation products of these ions. Processes involving the fragmentation of excited molecular ions lead to the production of various types of fragment, which may be stabilised in the form of different chemical products.

The use of β-decay processes for the preparation and further study of molecular ions is an extremely effective method compared with classical techniques using relatively inefficient methods of excitation. Another important advantage of these processes is the possibility of bringing about excitations and ionisations which initially are highly localised. An interesting feature is that whereas in β^--decay in molecular systems, positively charged ions are produced, positron-decay should lead to the appearance of negatively charged molecular ions. This is of particular interest for the production of negatively charged ions in condensed phases.

Despite the intensive theoretical and experimental studies of the consequences of β-decay for atomic systems, until recently very little theoretical work had been done on the nature of excitation processes and their consequences in molecular systems. Existing work includes the general theoretical studies of Schwartz[22], Cantwell[52], and Wolfsberg[53], on the excitation of molecular systems during β-decay processes. These studies were based on quantum-mechanical methods. The approximate calculations showed that, as in the case of atomic systems, a large proportion of the singly charged ions formed in β-decay exist in ground levels or levels with similar energies. For excitation resulting from the $^{14}C \xrightarrow{\beta^-} {}^{14}N$ transition, Wolfsberg[53] showed that as a first approximation the probability of transition to the ground level is the same for molecular and atomic systems. Cantwell[52] calculated the probabilities of transition from the ground electronic state of TH and T_2 to different vibrational levels of their daughter products.

The data obtained in these theoretical studies were verified experimentally for the decay of tritium in the TH and T_2 systems and for ^{14}C in the $^{14}CH_3-{}^{14}CH_3$ system[54-56]. The theoretical and experimental results are of the same order of magnitude, but the problem as a whole is too complex for detailed theoretical solution. The problem is even further complicated on going to the real polyatomic molecular systems studied, for which the number of different vibrational and rotational states is extremely high.

Recent studies by Wexler and others, which we shall examine in more detail later, show that the behaviour of the complex molecular ions formed during β-decay processes may in some cases be described quantitatively by means of the statistical theory of fragmentation, developed by Eyring, Rosenstock, and others for electron collision[57-59]. The application of this theory to β-decay processes by Wexler and others is based on the fact that an analogy should exist in the behaviour of identical molecular ions formed on β-decay and electron collision. For example, there is no essential difference between the $C_6H_5^+$ ion formed by the β-decay of monotritiated benzene and the analogous ion formed by benzene on electron collision, apart from the total energy and its distribution. We may thus also expect an analogy in the appearance of the different type of fragmentary ion formed during the decay of a corresponding mother ion. In this connection an extremely important factor in the kinetics of the monomolecular decay of the mother ion is the relationship between the potentials at which the different ionic fragments appear and their relative yields.

The basis of the theory put forward by Rosenstock and others[57-59] for this monomolecular decay process is that the excess electronic energy acquired is not localised in a definite bond but is distributed throughout the various degrees of freedom of the whole molecular ion by means of radiationless transitions. The subsequent decay of the vibrationally excited mother ions takes place by competing quasi-equilibrium monomolecular processes. The initial postulates of this theory are confirmed by a number of experimental facts established in the study of phenomena accompanying electron collision in polyatomic molecules (the lack of proportionality between the yield of molecular ions and the number of corresponding bonds, the detection of so-called metastable peaks, etc.)[60].

A fundamental feature of the work of Rosenstock and others is the statistical approximation, which is useful for polyatomic molecules. A disadvantage of this method is the somewhat indefinite nature of the choice of parameters. Moreover, this theory can hardly be applied to the description of phenomena accompanying β-decay in condensed phases, although it may serve for a qualitative description of the processes taking place. It should be noted that other theoretical approaches to the problem of electron collision also exist[61-65].

In the foregoing discussion we did not deal with the important question of the possibility of formation of multiply charged molecular ions. The production of multiply charged ions is an important consequence of β-decay. A similar effect is also apparently to be expected for molecular systems. It has been shown that a particularly marked accumulation of positive charge takes place in internal conversion processes. Since the phenomenon of internal conversion often accompanies β-decay processes, it will have a considerable effect on the behaviour of the original molecular system. Intensive molecular breakdown is obviously to be expected when internal conversion processes start cascades of vacancies. Recent work[66] showed that the most important result of this type of process for molecular systems is the rapid internal redistribution of charge in the molecular and the subsequent coulombic repulsion. The distribution of the fragments with respect to mass and charge in isomeric transition in $CH_3{}^{80m}Br$ and $CCl_3{}^{80m}Br$ has been studied. The distribution with respect to charge for ^{80}Br, ^{35}Cl, and ^{12}C atoms in isomeric transition in $CCl_3{}^{80m}Br$ is shown in Fig. 4.

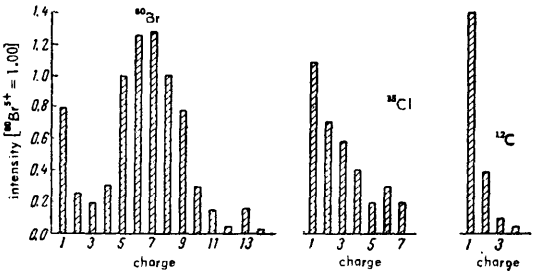


Fig. 4. Charge distribution of recoil atoms for isomeric transition in $CCl_3{}^{80m}Br$.

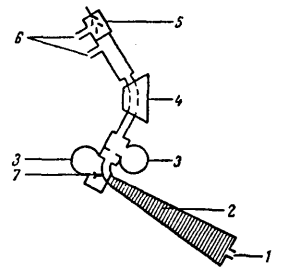


Fig. 5. Diagram of charge mass-spectrometer:
1) gas inlet, 2) system of rings, 3) 450 litre sec^{-1} pump, 4) 60° magnetic analyser, 5) photomultiplier, 6) to pump, 7) reflector.

It can be seen that in this case, in addition to ^{80}Br atoms with multiple charges of up to +14 (the maximum lies at +7), the spectrum shows ^{35}Cl and ^{37}C atoms with multiple charges of up to +7 and ^{12}C atoms with charges of up to +4. The charge spectra of the carbon and chlorine atoms show that although internal conversion and subsequent Auger transitions take place in the bromine atom, the charge is distributed throughout the whole molecule. This internal charge transfer is a fairly rapid and intensive process leading to extensive molecular breakdown as a result of the coulombic repulsion of the distributed charges.

IV. EXPERIMENTAL METHODS OF STUDYING CHEMICAL CHANGES DURING β-DECAY PROCESSES

The following experimental methods are used at present to study the chemical changes during β-decay processes: (1) the charge mass-spectrometry of the fragments formed as a result of radioactive decay, and (2) the radiochemical study of the final products of radioactive transformations (the use of compounds with more than one labelled atom is a special form of the second method).

A special mass-spectrometer can be used to measure the charge of the ions formed as a result of decay in a highly evacuated gas. Measurement of the distribution of the resulting fragments with respect to mass and charge in this way before the ions collide with other ions or molecules can give a detailed picture of the changes resulting from the radioactive decay of the atoms present in different molecules. The charge mass-spectrometer used by Wexler[67] is illustrated in Fig. 5. The radioactive gas passes through a capillary opening into a conical source with a volume of 80 litres, where it decays at a pressure of 10^{-6}–10^{-5} mm Hg. The conical source contains a system of rings to which is applied a potential of 150–500 V in such a way that the positively charged ions formed during radioactive decay are directed towards the apex of the cone. On leaving the cone, the ions are accelerated between two grids with a high accelerating potential (up to 600 V). After passing a reflector and condenser (to separate the ions from neutral molecules) the positively charged ion beam is directed into a magnetic analyser which measures the relative quantities of ions of different charge. After further acceleration to 3600 V the ions are detected by means of an electron multiplier. High differential evacuation is maintained throughout the whole system to prevent the passage of radioactive gas into the region of the detector. Apparatus of other design has also been described[66,68].

Charge mass-spectrometry is extremely effective for establishing the initial picture of the distribution of the fragments with respect to mass and charge. It makes it possible to study the consequences of radioactive decay in isolated atoms and molecules, and the daughter atoms may not be radioactive.

In the radiochemical method of studying chemical changes during nuclear processes in general and β-decay in particular, the initial distribution of the fragments with respect to mass and charge is estimated from the composition of the final products. Essential conditions for the application of this method are that the daughter atom should be radioactive and that there should be no isotopic exchange reactions which might lead to breakdown of the initial distribution of the daughter element between different chemical forms. The method of isotopic carriers is widely used for the identification and determination of the quantity of the different chemical forms of the daughter element. For the same purpose, use has recently also been made of a chromatographic method which in many cases makes it possible to do without carriers.

An extremely valuable method for studying the chemical consequences of β-decay is that using compounds labelled with more than one atom. The radioactivity of the radicals and groups combined with the decaying mother atom in this case makes it possible to follow the fate not only of the mother atom but also the other fragments of the molecule. The extensive introduction of this method is restricted by the low degree of development and complexity of the synthesis of compounds labelled with more than one atom[69].

When radiochemical methods of analysis are used to study the consequences of β-decay, it must be remembered that the observed chemical forms may appear as a result of the rearrangement of the mother molecule (survival), as a result of the recombination of fragments, or as a result of the interaction of certain forms with one another, with carriers, and with the surrounding medium. On this basis the chemical forms of the daughter element may be classified as primary, secondary, and tertiary. The primary forms are those produced as a result of the transformation of the molecular ions formed directly after β-decay. The secondary forms are those produced as a result of the recombination of fragments. Such processes would be expected to have a high probability under conditions of decay in

crystals, since the migration of the fragments formed during decay is almost impossible in this case. In addition to processes leading to the appearance of primary and secondary forms, we may also have subsequent redistribution of the daughter element as a result of the reaction of these forms with the surrounding medium and with carriers. The forms thus produced may be described as tertiary forms.

V. REVIEW OF EXPERIMENTAL WORK

1. Inorganic Systems

The study of the chemical changes during the β-decay of atoms in inorganic molecules, until recently, was carried out exclusively by radiochemical methods. In work of this kind, an essential condition is that the daughter element should be able to exist in several stable valence states or in different stable compounds incapable of undergoing isotopic exchange under the conditions of the separation. It is particularly difficult to satisfy these conditions for inorganic systems and this makes correct interpretation of the results difficult.

Charge mass-spectrometry is to a considerable extent free from these disadvantages, and this method has been used to study three very simple gaseous inorganic molecules: tritium hydride (TH), tritium (T_2), and carbon dioxide ($^{14}CO_2$).[48,54,55] The compounds were studied at a pressure of 10^{-5}–10^{-6} mm Hg, which excluded the possibility of intermolecular and interionic interaction. The ions formed as a result of β-decay were recorded by the spectrometer in a time interval of 10^{-4}–10^{-5} sec. This is much longer than the time required for radiative transitions (10^{-8} sec) and, more particularly, the period of atomic vibrations (10^{-14} sec), so that the energy of the excited molecular ion produced initially can be redistributed through all the degrees of freedom, and, in addition to the primary molecular ions, experiment reveals ions formed by the decay of the excited molecular ion. The results of a study of the distribution of the ions formed during the β-decay of tritium in the simplest inorganic molecules are given in Table 4.

The data on the decay of TH were obtained on two spectrometers with markedly different ionic optics and may give some idea of the reproducibility of the results obtained using different experimental techniques.

TABLE 4. Mass and charge distribution of ions formed during the β-decay of tritium in TH and TT.

Molecule	Ions formed	Concentration of ion, %	
		results of Snell et al.[56]	Wexler's results[55]
TH	$^3HeH^+$	93.2 ±1.9	89.5±1.1
	$^3He^+$	5.1 ±0.3	8.2±1.0
	H^+	1.55±0.16	2.3±0.4
	$^3He^{2+}$	0.14±0.01	
TT	$^3HeT^+$		94.5±0.6
	$T^+ + {}^3He^+$		5.5±0.6

The first noteworthy feature is that after decay a large proportion of the molecules remain combined in the form of the helium hydride ion $(^3HeH)^+$ or the helium tritide ion $(^3HeT)^+$. This is a stable combination, familiar in mass-spectrometry. The data also show how sharply the removal of an electron takes place by the "shaking" mechanism. This mechanism should lead unavoidably to the appearance of H^+ or He^{2+}, but the observed total intensity of these ions amounts to only 1.7% (2.3% according to Wexler). Moreover, this is an upper limit, since H^+ and He^{2+} may be formed in other ways. This value of 1.7–2.3% is comparable with the theoretical value of 2.5%[20] for the probability of removal of an electron in the conversion of atomic tritium into the ^3He ion. Comparison of the yields of $(H^3He)^+$ and $(T^3He)^+$ (89.5 and 94.5%) shows that the heavy isotopic molecules are more stable towards dissociation as a result of β-decay. This is due to the slight difference in the zero-point energies of the TH and TT molecules. An interesting feature is that similar effects associated with mass were observed for H_2, D_2 and T_2 molecules on electron collision[70,71].

The molecular changes accompanying the β-decay of atoms in diatomic molecules may be discussed from the viewpoint of Frank–Condon transitions, since the movement of the nuclei is very slow compared with that of the electrons and nuclear particles. The logical application of the Frank–Condon principle to explain the dissociation of TH and T_2 during β-decay has been carried out by Wexler[55].

Of considerable importance in the study of the chemical change accompaying β-decay is the ^{14}C isotope, which has been used in a large number of organic and biochemical studies. Here we shall examine some data on the consequences of β-decay in ^{14}C in the $^{14}CO_2$ molecule[48]. Mass-spectrometric studies have been made with radioactive carbon enriched to the extent of 38% in ^{14}C. Data on the decay of $^{14}CO_2$ (Table 5) show that the nitrogen atom formed as a result of the β-decay of ^{14}C remains for the most part bound in the form of $(NO_2)^+$. The formation of the $(NO_2)^{2+}$ ion is undoubtedly due to the "shaking" effect, leading to the removal of one orbital electron without further dissociation of the ion. In this case it would be extremely interesting to observe the negative oxygen ions, since this would make it possible to construct a more complete picture of the processes of molecular breakdown in this system.

There are a number of papers devoted to the study of the consequences of β-decay in inorganic systems by radiochemical methods. Davies[72] tried to explain the influence of certain primary processes accompanying β-decay on the valance state of the daughter element for the chain $^{143}La \xrightarrow{\beta^-} {}^{143}Ce$. One result of the primary changes may be an increase in the valence of the daughter atom by one unit on β^--decay.

TABLE 5. Distribution of ions for the β-decay of $^{14}CO_2$.

Ion	Yield, %	Ion	Yield, %
NO_2^+	81.4±1.6	O_2^+	0.2 ±0.4
NO^+	8.4±0.4	NO^{2+}	0.06±0.04
O^+	5.9±0.6	N^{2+}	0.02±0.01
N^+	3.6±0.4	O^{2+}	<0.01
NO_2^{2+}	0.4±0.06		

This process may be represented schematically as follows:

$$(^{143}La)^{3+} \xrightarrow{\beta^-} (^{143}Ce)^{4+}.$$

The $(^{143}Ce)^{3+}$ and $(^{143}Ce)^{4+}$ were separated by adsorbing the Ce^{4+} on zirconium iodate. It was found that in nitric acid solution, ~60% of the ^{143}Ce is in fact in the quadrivalent state. This result is not rigorous, since a considerable part of the $(^{143}Ce)^{3+}$ might be formed by exchange with stable Ce^{3+}, which is a common impurity in lanthanum. Exchange in the $Ce^{3+} + (^{143}Ce)^{4+} \rightleftharpoons (^{143}Ce)^{3+} + Ce^{4+}$ system is very rapid.

Davies[72] also studied the chemical changes taking place in the chains: $^{83}Se \xrightarrow{\beta^-} {}^{83}Br$, $^{84}Se \xrightarrow{\beta^-} {}^{84}Br$, and $^{132}Te \xrightarrow{\beta^-} {}^{132}I$. In the case of these systems it was possible to study the influence of the chemical state of the mother element on the form in which its decay products exist. In the decay of radioselenium, a study was made of the distribution of the resulting radiobromine between the bromate ion and its reduced forms. It was found that the quantity of radiobromine existing in the form of the bromate ion at pH 7–11 amounts to ~35% of the total quantity of radiobromine and does not depend to any significant extent on whether the mother element exists as selenate or selenite ions. When ethylene bromide, which is capable of reacting only with atomic bromine, was introduced into the system, ~23% of the radiobromine was transferred to the organic phase. This appears to indicate the formation of extremely reactive atomic bromine during the β-decay of radioselenium. The fact that the ratio of the quantities of radiobromine formed in the oxidised and reduced states is approximately constant may indicate that the decay of radioselenium is accompanied by complete breakdown of the original selenite and selenate ions. The nature of the subsequent reaction of the bromine atoms with the surrounding molecules (chiefly water molecules) is almost independent of the initial chemical state of the mother element.

The processes taking place during decay in the chain $^{132}Te \xrightarrow{\beta^-} {}^{132}I$ show a certain similarity to the processes taking place during the decay of radioselenium. The greatest proportion of the radioiodine is again present in the reduced form, although there also appears to be some dependence on the chemical state of the mother substance. The breakdown of the initial structure of the tellurite ion in this case is apparently due to internal conversion, accompanying the β-decay of ^{132}Te.

Burgus and Kennedy[73] studied the valence state of the radiochromium produced by the positron-decay of ^{51}Mn and investigated the part played by various factors determining the chemical state of the daughter atoms. They made a large number of studies of the valence states of radiochromium formed during the β^+-decay of ^{51}Mn in $Cs^{51}MnO_4$, $^{51}MnO_2$, and $^{51}MnCO_3$ and accumulating in solutions and crystals of these compounds. They studied the distribution of radiochromium only between Cr^{3+} and Cr^{6+} since other valence states of chromium are unstable or capable of exchange under the separation conditions. The main results of this work are summarised in Table 6.

Change in the temperature (from room temperature to -180°) at which the accumulation of ^{51}Cr took place had no significant influence on the distribution of chromium between the different valence states.

The observed chemical changes are evidently extremely complex and result from various simultaneous little-studied processes. One of the most interesting results is the detection of a considerable proportion of chromium (30%) in the highest valence state when ^{51}Cr accumulates in $^{51}MnCO_3$ crystals. The appearance of sexivalent chromium as a result of decay indicates considerable ionisation, since otherwise the transition $(^{51}Mn)^{2+} \xrightarrow{\beta^+} (^{51}Cr)^+$ should have taken place. The detection of Cr^{6+} in this case, however, may also result from the fact that the chromium is stabilised in $MnCO_3$ crystals in some intermediate form capable of undergoing rapid isotopic exchange with the chromate ion. The fact that during accumulation in solution almost all the radiochromium is found in the lower valency state was attributed to reduction reactions, activated by radioactive recoil, with water molecules. The possibility of such processes in the case of the hot atoms produced in $(n\gamma)$ reactions was pointed out earlier[74]. Experiments carried out with the aim of decreasing this effect (by decreasing the mole fraction of water by the addition of acetone of dioxan) also support this suggestion. The fact that the reduction of $(^{51}Cr)^{6+}$ is not complete during accumulation in permanganate solutions is probably due to the transfer of kinetic recoil energy to the entire group of atoms CrO_4^{2-} and not to the individual chromium atom. In this case the kinetic energy of the CrO_4^{2-} amounts to only 44% of the Cr^{6+} recoil energy.

TABLE 6. Valency states of ^{51}Cr produced by the decay of ^{51}Mn.

Compound	Accumulation conditions	Quantity of radiochromium in the form of Cr^{3+}, %
$^{51}MnCO_3$	*a*) in solution with carriers	98 ±2.0
	b) in solution with molar fraction of acetone or dioxan 0.6	88 ±2.0
	c) in crystals	70.5±2.0
$Cs^{51}MnO_4$	*a*) in solution at different pH and concentrations	49 ±2.0
	b) in crystals	0.4±1.3
$^{51}MnO_2$	suspension in solutions	43.8±0.6

On the whole, the study of the chemical changes accompanying the process of β-decay in inorganic systems by radiochemical methods, despite the considerable difficulty of interpreting the results, are of considerable interest for the chemistry of various elements. By changing the experimental conditions valuable information may be obtained on the types of chemical reaction undergone by the daughter element: radioactive decay may lead to the appearance of quite unusual chemical species, whose study is of importance for the development of general chemical theory.

2. Organic Systems

Until comparatively recently no papers had been published on the study of the chemical changes accompanying the β-decay of atoms in organic molecules. One reason for this was the absence of radioactive decay chains for isotopes of carbon, hydrogen, sulphur, and other elements found in organic compounds. At the same time the chemical changes accompanying the β-decay of ^{14}C are of considerable interest, since this isotope is widely used as a radioactive tracer in chemical and biological studies and moreover is found in considerable quantities in the biosphere[75,76]. The use of compounds labelled with more than one atom and, more particularly, the use of mass-charge spectrometry have brought the first significant results in this field.

The first work in this direction was carried out by Wolfgang *et al.*[56]. Using double labelling with ^{14}C, they studied

the rupture and stability of the C–N bond during the β-decay of ^{14}C in the molecule of doubly labelled ethane ($^{14}CH_3$–$^{14}CH_3$).

The use of double isotopic labelling makes it possible to observe some of the stable daughter atoms thanks to the radioactivity of the second atom. With decay of one of the carbon atoms in $^{14}CH_3$–$^{14}CH_3$ and preservation of the bond formed by the daughter atom, the ethane molecule should be converted into methylamine. This change should apparently take place according to the scheme

$$^{14}CH_3–^{14}CH_3 \xrightarrow{\beta^-} [^{14}CH_3–^{14}NH_3]^+ \longrightarrow {}^{14}CH_3–NH_2 + H^+.$$

The use of a gaseous compound as starting material eliminates to a considerable extent the complications associated with various types of secondary process. The work was carried out essentially as follows: $^{14}CH_3$–$^{14}CH_3$ (enriched with ^{14}C to the extent of 25%) was prepared and kept until sufficient decay products had accumulated. Stable methylamine was then added to the system as carrier, the components of the mixture were separated, purified thoroughly, and identified. The proportion of $^{14}CH_3$–$^{14}CH_3$ molecules whose decay was accompanied by the formation of $^{14}CH_3NH_2$ was found by determining the activity of the methylamine or its derivatives. Special careful control experiments showed that the $^{14}CH_3NH_2$ produced is in fact a primary product, *i.e.* it is formed as a result of the preservation of C–N bonds during the β-decay of ^{14}C and not as a result of secondary reactions such as exchange reaction with the carrier or reaction under the influence of radiation, etc. The results show that the $^{14}CH_3$–$^{14}CH_3$ molecule, after β-decay of one of the carbon atoms, gives methylamine ($^{14}CH_3NH_2$) in 47 ± 2% of all decays.

The processes taking place during the β-decay of ^{14}C in ethane were examined theoretically by Wolfsberg[53]. Approximate quantum-mechanical calculation gave for the "survival" of the C–N bond a value of 60 ± 20%.

Thus the available data on the β-decay of ^{14}C (decay in $^{14}CO_2$ was examined earlier) show that a considerable proportion of the atoms formed remain in the original molecule, which undergoes an internal rearrangement not accompanied by extensive decomposition. From this it may be assumed that the formation of complex nitrogen-containing organic molecules should take place readily and simply if the primary molecule contains a radioactive ^{14}C atom. It is not impossible that such processes might be one means of formation of various amino-derivatives in nature.

The mass spectrometric method has been used to study the consequences of the β-decay of tritium in the following organic compounds: CH_3T,[48] C_2H_5T,[67] i-C_3H_7T, n-C_3H_7T,[77] C_6H_5T,[68] α-$CH_2TC_6H_5$, *o*-$CH_3C_6H_4T$, *m*-$CH_3C_6H_4T$, *p*-$CH_3C_6H_4T$,[77] and of the β-decay of ^{82}Br in 1,2-C_2H_4. $^{82}BrBr$[66,67], and $^{82}BrCCl_3$.[66] Table 7 gives as an example the yield of ions obtained during the decay of tritium in C_2H_5T.[67]

A noteworthy feature of the results obtained for C_2H_5T is that the C–He bond is broken in almost every β-decay act, the charge remaining on the organic fragment. This initial $C_2H_5^+$ mother ion is preserved in 78% of decays, whereas in the other cases a greater velocity of ions is obtained, forming a spectrum similar to that for C_2H_6 on electron collision. The process may be represented schematically as follows:

$$C_2H_5T \xrightarrow{\beta^-} C_2H_5He^+ \rightarrow C_2H_5^+ + He$$
$$\sim 13 \text{ fragments (22\%)}$$

TABLE 7. Yields of ions in the decay of tritium in C_2H_5T.

Ion	Yield, %	Ion	Yield, %
$C_2H_5{}^3He^+ + C_2H_5T$	<0.2	C_2H^+	4.1±0.4
Mass 31	1.0±0.5	C_2^+	1.7±0.2
$^{12}C^{13}CH_3^+$	1.5±0.5	CH^+	<1.0
$C_2H_5^+$	76 ±1	$^3H^3He^+$	<0.2
$C_2H_4^+$	<0.5	H_2^+	<0.2
$C_2H_3^+$	6.5±0.7	H^+	<0.2
$C_2H_2^+$	6.9±0.7		

An even greater variety of fragments is observed in the decay of tritium in compounds with a large number of carbon atoms. The yield of the initial mother ion always predominates, however. We shall not consider the complete composition of the spectra in detail, but shall give only the ratios of the number of initial mother ions to the total number of ions detected. These ratios, corresponding to cases of decay which do not lead to appreciable excitation of the primary molecular ion, are given in Table 8.

The results vary on the average between 70% and 80%, with the exception of those for propane. An interesting feature is that for propane, the splitting of H_2 from $C_3H_7^+$ requires very little energy and it is probable that some of the mother ions with low excitation energy are capable of overcoming the corresponding energy barrier. Thus for the propane the sum of $C_3H_7^+$ and $C_3H_5^+$ represents with a high probability transitions to low-lying levels of the propyl ion. This sum amounts to 70% for n-C_3H_7T and 63% for i-C_3H_7T.

Theoretical calculations[20] show that for the decay $T \xrightarrow{\beta^-} He^+$, 70% of the transitions take place to the ground state of He^+, 25% to the first excited level with energy 20.5 eV, 2.5% to a level with energy 54.1 eV, and 2.5% to He^{2+}. An analogous distribution also appears to be obtained in the case of molecular system containing tritium. The data in Table 8 show that in fact 70–80% of the molecular ions are formed without appreciable excitation energy.

Certain general features of the changes in organic molecules during the β-decay of tritium may be noted: (1) after the conversion of RT into $(R^3He)^+$ the C–He bond is always broken, since the strength of the bond between an element and an inert gas is in all cases close to zero — an exception being the case of the $(H^3He)^+$ ion; (2) on rupture of the C–He bond, the positive charge remains on the organic fragment, the ^3He splitting off in the form of the neutral atom, since the ionisation potential of helium is much higher than that of organic radicals; (3) after the helium has split off, the initial mother molecular ion is preserved in 70–80% of all decays, and in the remaining cases of β-transitions the initial molecular ion acquires an excitation energy

TABLE 8. Yield of primary ions in the β-decay of tritiated hydrocarbons.

Substance	Mother ion	Concentration of ion in the spectrum, %	Substance	Mother ion	Concentration of ion in the spectrum, %
CH_3T	CH_3^+	83	α-C_7H_7T	$C_7H_7^+$	79
C_2H_5T	$C_2H_5^+$	78	*o*-C_7H_7T	$C_7H_7^+$	78
i-C_3H_7T	$C_3H_7^+$	56	*m*-C_7H_7T	$C_7H_7^+$	79
n-C_3H_7T	$C_3H_7^+$	41	*p*-C_7H_7T	$C_7H_7^+$	76
C_6H_5T	$C_6H_5^+$	72			

sufficient for subsequent fragmentation; (4) there is some analogy with the process of electron collision in the formation of various types of fragment ion, but the relative yields of fragments are different for the processes of β-decay and electron collision.

It was previously shown that the ionisation produced by the β-decay of nuclei with high values of Z takes place chiefly in the outer electron shell. Thus if the decaying atom is part of a molecule it is probable that, initially, the excitation energy will affect chiefly the bonding and other valency electrons of the ion undergoing the change. This localised excitation may be accompanied by an isomeric effect. There exist, however, certain rapid processes which take place in the time interval between the excitation of the molecule and its fragmentation, and these smooth out the effects of localised excitation. These are, firstly, the non-radiative transitions postulated by the theory of quasi-equilibrium monomolecular dissociation, as a result of which the excitation energy is rapidly redistributed throughout the molecule, and, secondly, the migration of an H atom through the carbon chain, or other transformations which eliminate the structural differences in the initial molecular ions. Wexler *et al.*[77] tried to study these effects for the case of the isomers of propane and toluene, labelled with tritium in different positions.

Experimental data on the yields of different ions during the β-decay of tritium in α-, *o*-, *m*-, and *p*-tritiumtoluenes (Fig. 6) show that the yields of different fragments agree not only qualitatively, but also quantitatively, showing that the localised excitation in these systems is eliminated by the rapid redistribution of the excitation energy and by transformations preceding fragmentation. Analogous observations have been made in the study of the consequences of electron collision for monodeuterated toluenes[78]. According to Wexler *et al.*, this confirms that fragmentation is preceded by the transformation of the tolyl and benzyl structures to a seven-membered ring, the tropylium ion, in which the carbon atoms, like the hydrogen atoms, are indistinguishable. A possible scheme for the fragmentation of the isomers of tritiated toluenes, resulting from β-decay, is shown in Fig. 7.

The above characteristic features of the fragmentation of tritiated organic derivatives do not result from the

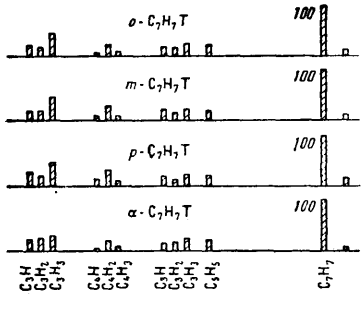


Fig. 6. Yields of ions for the β-decay of tritium in toluenes.

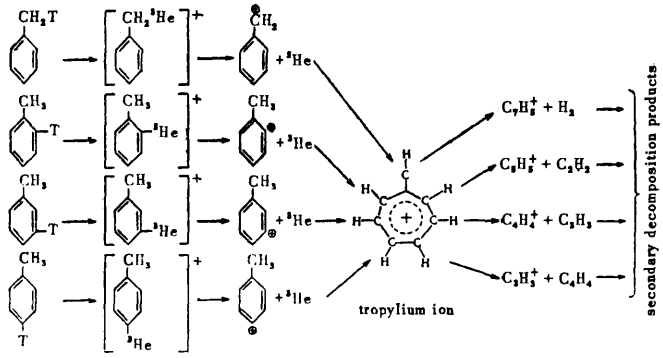


Fig. 7. Fragmentation of tritiated toluenes.

characteristic features of the nuclear transition $T \xrightarrow{\beta^-} {}^3He$. This assertion is based, in particular, on the fact that the spectrum of ions for the β-decay of ^{82}Br in $1,2\text{-}C_2H_4 \cdot {}^{82}BrBr$ [66,76] and $^{82}BrCCl_3$ [66] shows all the features characteristic of the spectrum of ions formed during the decay of tritium. As in the case of the β-decay of tritium, the initial mother ions $C_2H_4Br^+$ and CCl_3^+ predominate in the spectra of the organic derivatives (69.8 ± 2% and 64 ± 1.4% respectively). The C–^{82}Kr bond is always broken and the positive charge remains on the organic fragment. In 30–35% of the nuclear transitions, the initial ions acquire sufficient excitation energy for subsequent fragmentation. It should also be noted that the β-decay of ^{82}Br appears to be accompanied by very little removal of orbital electrons, as indicated by the absence of doubly charged ions in the spectra. This may, however, be due to the breakdown of molecular ions with a charge greater than unit, as a result of coulombic repulsion, so that they are not recorded in the mass-spectrometer.

3. Organoelemental Systems

The study of the consequences of β-decay organoelemental systems is now attracting increasing attention. These compounds have a number of advantages in studies of this type, including the extensive possibilities for preparing compounds with different physical and chemical properties for the elements studied; the absence or retardation, in many cases, of isotopic exchange reactions which distort the initial picture of chemical changes; etc.

The first investigation in this direction was made as early as 1934 by Martenson and Leighton[79], who studied the possibility of retention of the initial structure by molecules of organoelemental derivatives during β-decay in the chain $RaD(^{210}Pb) \xrightarrow{\beta^-} RaE(^{210}Bi) \xrightarrow{\beta^-} RaF(^{210}Po)$. They studied the readily volatile tetramethyllead $Pb(RaD)(CH_3)_4$. If decay had been accompanied by complete decomposition of the original molecule, the resulting radiobismuth and polonium would have been obtained in inorganic forms and would not have exhibited the volatility of the methyl derivatives of these elements. When $Pb(RaD)(CH_3)_4$ was kept for a period sufficient for the accumulation of RaE and RaF, the authors detected the β-activity of RaE and the α-activity of RaF in the volatile fraction. On this basis they suggested that these

processes involved the formation of the organometallic compounds of bismuth $^{210}Bi(CH_3)_3$ and polonium $^{210}Po(CH_3)_2$ according to the following possible scheme:

$$^{210}Pb(CH_3)_4 \xrightarrow{\beta^-} {}^{210}Bi(CH_3)_3^+ + CH_3;$$

$$^{210}Bi(CH_3)_3^+ + e \rightarrow {}^{210}Bi(CH_3)_3;$$

$$^{210}Bi(CH_3)_3 \xrightarrow{\beta^-} {}^{210}Po(CH_3)_2 + CH_3;$$

$$^{210}Po(CH_3)_2^+ + e \rightarrow {}^{210}Po(CH_3)_2.$$

In 1953 Edwards *et al.* [80] made a more detailed study of the same system and examined the distribution of the β-activity of ^{210}Bi between the volatile and non-volatile fractions for different conditions of accumulation in solutions and in the gaseous phase. For accumulation in solution in benzene, octane, and carbon tetrachloride, at sufficiently high molar fractions of $Pb(RaD)(CH_3)_4$, they found that the greater part of the RaE (60–80%) was present in the form of a non-volatile fraction. The appearance of this fraction was evidently due to processes of internal conversion and cascades of vacancies [81–84], leading to complete decomposition of the original tetramethyllead molecule. On the other hand, in the decay of $Pb(RaD)(CH_3)_4$ in solutions at low concentrations of this compound and in the gaseous phase, an anomalously low yield of radiobismuth (up to 10%) in the form of the non-volatile fraction was observed. It is possible, however, that the last result is due to an experimental error as a result of the formation of stable aerosols or of secondary effects [85], particularly since the forms in which the radiobismuth was obtained were not identified.

Essentially the same method was used in more recent work by Baulch *et al.* [86] in a study of the consequences of the decay of RaD in tetramethyllead. These authors examined the relationship between the quantity of radiobismuth deposited on the walls of the vessel during the decay of $Pb(RaD)(CH_3)_4$ in the gaseous state and the vapour pressure of the gas. They found that the percentage of radiobismuth deposited on the walls was low (5–30%) and decreased with increase in pressure. On this basis they concluded that the processes of excitation and internal conversion either are insufficiently effective for complete breakdown of the original tetramethyllead molecule or are suppressed by secondary processes before the molecule reaches the walls of the vessel. It was also concluded that the molecular ion $Bi(CH_3)_4^+$ formed – $^{210}Pb(CH_3)_4 \xrightarrow{\beta^-} {}^{210}Bi(CH_3)_4^+$ – is more stable than previously assumed, and that when it acquires sufficient excitation energy it decomposes according to the scheme: $Bi(CH_3)_4^+ \rightarrow {}^{210}Bi(CH_3)_3 + CH_3^+$. Thermochemical calculation showed that this process is more probable than that involving the removal of a neutral methyl radical.

It should be noted that in these cases the forms in which the daughter elements were obtained were not identified.

Here it would be desirable to use other improved methods such as mass-charge spectrometric study of the resulting fragments or gas chromatography.

Another series of studies was made of the consequences of β-decay in organometallic systems with aromatic derivatives. The aromatic derivatives have the advantage not only of stability and variety of chemical form, but also the possibility of exact identification and determination of the distribution of the daughter element between these forms.

The first study of the chemical state of the RaE produced by the decay of RaD in the phenyl derivatives $Pb(RaD)(C_6H_5)_4$ and $Pb(RaD)(C_6H_5)_3Cl$ was that of Nefedov and Andreev [87], who used the isotopic carrier method with subsequent chemical separation to study the distribution of radiobismuth between the forms $Bi(C_6H_5)_3$, $Bi(C_6H_5)_3Cl_2$, and inorganic bismuth, with accumulation in crystals and in solutions of these compounds. The most interesting result of the study was the detection of a considerable proportion of RaE atoms in the form of the complex organometallic compounds $Bi(C_6H_5)_3$ and $Bi(C_6H_5)_3Cl_2$. It was found that the yield of radiobismuth in the form of these compounds for accumulation in crystals is greater than that for accumulation in solutions. This may be due both to an increase in the probability of recombination of the fragments of the decomposing molecule in the crystals and also possibly to the nearby presence of analogous molecules, facilitating the rapid redistribution of the excitation energy between the identical entities.

Comparison of the data on the distribution of RaE between the different compounds in the decay of RaD in $Pb(RaD)Ph_4$ and $Pb(RaD)Ph_3Cl$ indicates that the nature of the mother molecule has a marked influence on the chemical form of the daughter RaE. For example, the decay of $Pb(RaD)Ph_4$ gives almost no RaE in the form of $BiPh_3Cl_2$, whereas in the decay of $Pb(RaD)Ph_3Cl$ it is one of the chief products. Moreover, it was found that the maximum yield of radiobismuth (~70%) for accumulation in solution is obtained in inorganic forms. An interesting feature is that this value lies in the range of values of the total conversion coefficients for RaD (60–80%) found by different authors [81–84]. The presence of RaE in inorganic form is undoubtedly related to the process of internal conversion, which generally leads to complete breakdown of the original molecule.

Analogous results were obtained in a study [88] of the chemical state of ThC formed by the decay of ThB in the phenyllead derivatives $Pb(ThB)(C_6H_5)_4$ and $Pb(ThB)(C_6H_5)_3Cl$. The most interesting result of the comparison of these with the previous data is the influence of the decay schemes of different lead isotopes (RaD and ThB) on the yield of different forms of radiobismuth, particularly its inorganic form. The yield of ThC in inorganic form with accumulation in the crystals was found to be 21%. For accumulation is solutions, the yield of inorganic forms of radiobismuth (ThC) (30%) almost coincides with the total internal conversion coefficient for the decay ThB $\xrightarrow{\beta^-}$ ThC. [89] These results indicate that the bismuth isotopes formed by the β-decay of different lead isotopes show different behaviour.

Detailed studies have been made of this problem [90,91]. Special experiments were carried out to study the influence of the decay schemes of the natural lead isotopes RaD, ThB, and RaB on the yields of radiobismuth in different forms. For this purpose, as well as identical conditions of synthesis, accumulation, etc., identical methods of analysis of the compounds containing the different radioactive lead isotopes were used. In addition, two different radioisotopes of lead were introduced simultaneously into the same compound with subsequent radiochemical and radiometric analysis.

The results of studies of the isotopic effects for RaD and ThB by the carrier method (Table 9) indicate firstly that the different bismuth isotopes (RaE and ThC) show different behaviour. In particular, in the case of $BiPh_3Cl_2$, displacement of the isotopic composition was revealed by the relative enrichment of this form with ThC. The data in Table 9 also show that the experimentally observed displacement of the isotopic composition did not depend significantly on whether the mother substance had been labelled separately or simultaneously. The difference in the chemical behaviour of the bismuth isotopes can be due only to

TABLE 9. Isotopic effects in the β-decay of RaD and ThB.

Mother substance	Daughter substance	Fraction of RaE in a given form, %	Fraction of ThC in a given form, %
Pb (ThB) Ph_3Cl	$BiPh_3Cl_2$	19±1	50±2
Pb (RaD)Ph_3Cl	Bi^{3+}	43±3	17±1
Pb (ThB, RaD) Ph_3Cl	$BiPh_3Cl_2$	17±1	49±2
	Bi^{3+}	42±3	17±3

differences in the radioactive decay schemes of the mother isotopes. Data obtained by chromatrographic analysis of compounds containing the other lead isotope (RaB) are given in Table 10.

These show clearly the characteristic types of isotopic effect for the β-decay of the natural lead isotopes (RaD, ThB, RaB) in complex organometallic compounds. The observed effects are due chiefly to differences in the values of the total internal conversion coefficients (60–80% for RaD,[81-84] 30% for ThB,[89] and 15% for RaB[92]); this is shown by the fact that the yield of inorganic forms is directly proportional to the internal conversion coefficients.

The previous papers showed the complex character of the changes taking place during the β-decay of the central atom in organolead derivatives, revealed primarily in the variety of chemical compounds formed by the daughter radiobismuth. The appearance of higher organometallic bismuth compounds ($BiPh_3$ and $BiPh_3Cl_2$) as a result of the rearrangement of the mother molecule is possible only when the latter contain a sufficient number of radicals. It may, however, be suggested that the formation of these compounds is due, albeit only partly, to such processes as interaction with the surrounding molecules (particularly molecules of the mother substance).

The part played by individual processes leading to the appearance of higher organometallic bismuth derivatives was examined in a study[93] of the chemical changes accompanying the β-decay of RaD in the radical-deficient lead derivative $Pb(RaD)(C_6H_5)_2Cl_2$. It was found that for this compound the yield of higher bismuth derivatives $BiPh_3$ and $BiPh_3Cl_2$ is very low. It was therefore concluded that the chemical changes accompanying the β-decay of the central lead atom in the organometallic derivatives in this case do not involve the surrounding molecules.

An analogous study[94] was made of the chemical state of the RaE obtained by the β-decay of RaD in $(PbPh_3)_2$, $PbPh_3NO_3$, and $PbPh_2(NO_3)_2$.

These studies were made using the isotopic carrier method and established a number of characteristic features of the β-decay of lead isotopes in complex organometallic compounds. The isotopic carrier method cannot, however, reproduce all the complex features of the changes taking place, since a number of latent changes and intermediate or unstable forms are not detected. Chromatography, particularly on paper, is a more precise method. An important advantage of this method is often the possibility of isolating daughter forms without carrier. Fig. 8 gives as an example the chromatogram for the decay products of $Pb(RaD)Ph_3Cl$, obtained by successive elution with benzene and petroleum ether without the use of carriers[95]. This method gave more fundamental information on the essential features of the processes accompanying the decay of the central atom in phenyllead derivatives and, in particular, revealed a new, previously unknown form of RaE and the processes of its evolution, and also the evolution of other forms of radiobismuth under different conditions.

Important information on processes taking part in organometallic compounds may be obtained by studying the β-decay of other radioisotopes. Thus, studies have been made of the chemical changes accompanying the β-decay of ^{125}Sb in the derivatives $Sb(^{125}Sb)R_3$ and $Sb(^{125}Sb)R_3Cl_2$ (where R represents the phenyl or *p*-tolyl radical)[96]. The various chemical forms of the resulting ^{125m}Te were separated by paper chromatography. The results confirm the marked influence of the chemical state of the ^{125}Sb on the yield of ^{125m}Te in different forms. With accumulation in the $Sb(^{125}Sb)R_3$ crystals, the ^{125m}Te was found chiefly in the form of the two compounds TeR_2 (60–63%) and TeR_3Cl (27–29%), and with accumulation in $Sb(^{125}Sb)R_3Cl_2$ the ^{125m}Te was found chiefly in the form of TeR_2Cl_2 (83–90%).

These results can be explained qualitatively on the basis of the theory of molecular-ion fragmentation. In the β-decay of ^{125}Sb in $^{125}SbR_3$, a direct result of decay in the absence of further excitation should be the appearance of the primary molecular ion $^{125m}TeR_3^+$, formed according to the scheme: $^{125}SbR_3 \xrightarrow{\beta^-} {}^{125m}TeR_3^+$. The TeR_3Cl found in 27–29% yield is probably the product of the stabilisation of this primary molecular ion. As shown previously, however, a considerable proportion of the molecular ions formed during β-decay are in an excited state. Electron-collision studies of organometallic and similar compounds[97] and other studies[86] show that the most probable form of realisation of the excitation energy in these cases is the removal of positively charged radicals. The removal of a positively charged radical from the excited molecular ion $^{125m}TeR_3^+$ according to the scheme $^{125m}TeR_3^+ \rightarrow {}^{125m}TeR_2 + R^+$ leads to the stabilisation of a considerable proportion of the ^{125m}Te (60–63%) in the form of TeR_2.

TABLE 10. Isotopic effects in the β-decay of RaD, ThB, and RaB.

Daughter substance	Mother substance Pb^*Ph_3Cl yield of daughter substance, %	Mother substance Pb^*Ph_4 yield of daughter substance, %
RaE^{3+}	47±1	45±1
ThC^{3+}	24±2	25±2
RaC^{3+}	11±1	10±1

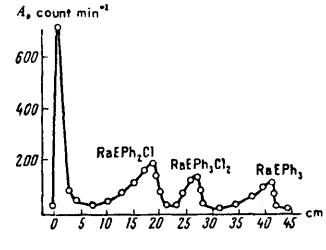


Fig. 8. Chromatogram for the decay products of $Pb(RaD)(C_6H_5)_3Cl$.

In the β-decay of ^{125}Sb in $Sb(^{125}Sb)R_3Cl_2$, the primary molecular ion is $^{125m}TeR_3Cl_2^+$. Such structures are not characteristic of organic compounds of tellurium, so that this ion is thermodynamically unstable. Assuming that the breakdown of this ion should also involve the removal of a positively charged radical, the greater part of the ^{125m}Te should be found in the form of TeR_2Cl_2, produced according to the scheme: $^{125m}TeR_3Cl_2^+ \rightarrow {}^{125m}TeR_2Cl_2 + R^+$. The experimental results in fact show that with accumulation in $Sb(^{125}Sb)R_3Cl_2$ crystals a high yield of ^{125}Te in the form of TeR_2Cl_2 (83–90%) is obtained.

A number of studies have been made of the decay $^{131}Te\ \beta^-,\ ^{131}I$ in organoelemental compounds[98,99]. An attempt was made to find the stable form of the radioactive iodine during the decay of ^{131}Te in dibenzyltellurium[98]: the radioiodine appears in the form of different compounds (C_6H_5I, CH_3I, etc.). The separation method (fractional distillation) which they used, however, introduces considerable errors and makes it difficult to establish the nature of the primary chemical changes. Nevertheless the use of β-decay processes to prepare various organic derivatives of radioiodine is of considerable interest.

Keneshea and Kahn[99] also showed the possibility of preparing iodobenzene labelled with ^{131}I, by the β-decay of ^{131}Te when a mixture of tellurium tetrachloride and benzene is irradiated in a reactor.

The use of β-decay processes in organoelemental compounds for the synthesis of a variety of products on the one hand and for the separation of radioactive isotopes without the use of carriers on the other is of considerable theoretical and practical interest. These two possibilities result from the use of different aspects of the same process. When the original bonds are preserved and the changes in the original molecule are slight in β-decay processes, we may expect the production of various compounds of the daughter element. An important feature is that in a number of cases these compounds can be obtained without carriers, with the highest possible specific activity. If, however, the decay of the isotope is accompanied by marked excitation of the original molecule, leading to its complete breakdown, the daughter isotope is obtained in a chemical form differing sharply from that of the mother element and can be easily separated from the latter.

A good illustration of this is provided by work on the synthesis of new organic compounds of polonium[100,101] and work on the separation of various radioisotopes when chemical-bond rupture takes place as a result of β-decay[87,88,104,105].

The exceptional progress observed in recent years in the chemistry of organoelemental compounds as a whole has not extended to a number of elements such as francium, astatine, and polonium, althought the ability of these elements to form such compounds is indicated by their position in the Periodic System and from the general features first noted by Mendeleev and later formulated in modern terms by Nesmeyanov[106,107].

Murin *et al.*[100] were the first to show conclusively that organic compounds of polonium (RaF) are produced during the β-decay of RaE in various aromatic derivatives, as a result of the stabilisation and fragmentation of the molecular ions formed. The polonium accumulated in $Bi(RaE)(C_6H_5)_3$ and $Bi(RaE)(C_6H_5)_3Cl_2$ crystals. The chief task was to isolate and identify the daughter compounds of polonium (RaF). The chief method used was paper chromatography. The analogous tellurium derivatives $Te(C_6H_5)_3Cl$, $Te(C_6H_5)_2Cl_2$, and $Te(C_6H_5)_2$ labelled with ^{127m}Te were used as "markers" to establish the positions of the various organic compounds of polonium on the chromatogram. The chromatograms were analysed radiometrically from the α-activity of the polonium and the β-activity of the ^{127m}Te, and the α-active peaks of the various polonium compounds were identified by comparing their positions with those of the analogous β-active tellurium derivatives. Fig. 9 shows a chromatogram obtained for the case of accumulation in $Bi(RaE)Ph_3$ crystals, using ethyl acetate as mobile phase. As in the decay of different isotopes of lead and antimony, the chemical state of the RaF has a marked influence on the yield of the different forms of polonium. Fig. 10 gives for comparison a chromatogram for the products of the decay of $Bi(RaE)Ph_3Cl_2$, obtained under identical conditions. This influence makes it possible to use the chemical changes accompanying the β-decay of RaE to synthesise certain organic derivatives of polonium.

These studies were continued in work[101,102] on the chemical state of polonium produced by the β-decay of RaE in various p-tolyl and α-naphthyl derivatives. An analogous method was used to isolate and identify another series of new polonium compounds:

$$Po(p\text{-}CH_3C_6H_4)_2,\ Po(p\text{-}C_7H_7)_2Cl_2,\ Po(p\text{-}C_7H_7)_3Cl,$$
$$Po(\alpha\text{-}C_{10}H_7)_2,\ Po(\alpha\text{-}C_{10}H_7)_3Cl,\ Po(\alpha\text{-}C_{10}H_7)_2Cl_2,$$

and to study the distribution of polonium between these compounds under different conditions.

It is clear that methods of synthesis based on the chemical changes accompanying β-decay processes will make it possible in the near future to open up a new field of knowledge — the chemistry of organic derivatives of polonium.

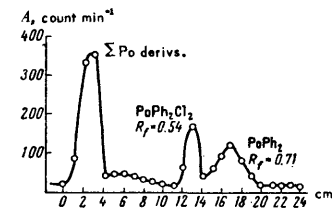


Fig. 9. Chromatogram for the decay products of $Bi(RaE)(C_6H_5)_3$.

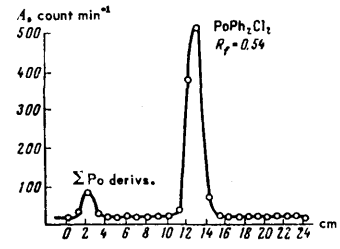


Fig. 10. Chromatogram for the decay products of $Bi(RaE)(C_6H_5)_3Cl_2$.

Analogous methods can be used successfully for other typical radioactive elements such as astatine and francium.

It was pointed out earlier that under certain conditions the radioactive recoil and secondary processes in electron shells of the daughter atoms may lead to conversion of the greater part of the daughter atoms into the simplest inorganic forms. This phenomenon has been used very successfully to isolate a number of radioactive isotopes without the use of carriers. The chief advantages of these methods are that the differences in the physicochemical properties of the original compound of the mother element and the simplest forms of the daughter element are incomparably greater than the differences in the physicochemical properties of any inorganic compounds of these elements.

Examination of the table of isotopes suggests the possibility of using analogous methods to isolate numerous valuable radioactive isotopes. Systems for study include the transformation chain formed by radioelements obtained by fission, spallation reactions, radiative neutron capture, ordinary cyclotron reactions, and decay in series. In particular, the method may be used to isolate the following radioactive isotopes without the use of carriers: ^{32}P, ^{68}Ga, ^{71}Ge, ^{72}As, ^{93}Nb, ^{99m}Tc, ^{113m}In, ^{119}Sb, ^{125}Sb, ^{132}I, ^{178}Ta, ^{188}Re, ^{191}Au, ^{193}Pt, ^{200}Tl, ^{210}Bi, ^{212}Bi, and others. Up to the present, methods have been developed for separating the following radioactive isotopes and nuclear isomers without the use of carriers, based on chemical-bond rupture during β-decay processes: ^{188}Re,[103] RaE,[87] ThC,[88] ^{99}Tc,[102] and ^{113}In.[104] The specimens of radioactive isotopes and nuclear isomers obtained have been used successfully in studies in nuclear physics and chemistry. An important feature is that in the great majority of cases, long-acting sources of short-lived isotopes of a number of elements can be produced. A characteristic feature of these methods is the simplicity of the isolation of the radioactive isotope without the use of carriers after the preparation of the source. For example, ^{99m}Tc and ^{188}Re have been isolated by extraction from chloroform solutions of the hexacarbonyls $Mo(^{99}Mo)(CO)_6$ and $W(^{188}W)(CO)_6$ with distilled water. The isotopes ^{210}Bi and ^{212}Bi were isolated by adsorbing inorganic bismuth from solutions of organic radiolead compounds.

In conclusion, the authors express the hope that the study of the chemical changes accompanying β-decay processes will attract the attention of a wider circle of research workers and will find a number of new and extremely important applications in various fields of study. The undoubted interest in this topic is indicated by the considerable number of papers by Soviet and other authors, published while the present paper was in the press[108-125].

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ADVANCES IN THE USE OF INFRARED SPECTROSCOPY FOR THE CHARACTERISATION OF OH BONDS

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I. INTRODUCTION

The study of the structure of molecules and ions by infrared spectroscopy is based on the observed characteristic frequencies of vibration of such functional groups as OH, CH, NH, C=O, N=O, and many others. The existence of an absorption band in the frequency region typical of a given group conclusively demonstrates its presence in the compound under investigation.

The position of an absorption band within the characteristic frequency region depends on the interaction with neighbouring groups within the molecule and on intermolecular interaction; the shift of an absorption band within the characteristic region can thus be used to establish the position of the studied group relative to others and its reaction with neighbouring molecules.

This review is concerned with the spectroscopic characteristics of groups consisting of oxygen and hydrogen atoms, and only single groups of those atoms bound by a substantially covalent bond will be considered; groups containing hydrogen and oxygen bonded by purely ionic or hydrogen bonds will not be considered.

All the ions and molecules which we shall discuss below have at least one O–H bond. The hydrogen atom of this bond may be free or may participate in hydrogen bonding, so that all the systems which we shall consider can be represented by the formula $R_1-O-H\cdots R_2$, where R_1 is any atom or radical and R_2 is any proton-accepting molecule.

Modern methods have shown that hydrogen and oxygen atoms produce only the groups OH^-, OOH^-, $H\overset{O}{\diagdown\diagup}H$, HOOH, and the pyramidal $\begin{matrix}H\\H\end{matrix}\!\!\diagdown\!\overset{+}{O}\!-H$. For convenience we shall call these all oxygen–hydrogen or O_mH_n groups. When investigating the structure of new types of compound or evaluating their ability to form a hydrogen bond (alcohols, acids, carbohydrates, proteins) the nature of the O_mH_n groups present has always to be investigated.

Despite its importance this matter has not been sufficiently broadly discussed in Soviet or other literature. This review is the first to do so, and some of the conclusions may be controversial; it therefore includes, without exception, all the Soviet and available foreign literature from 1953 to May 1962 inclusive. The object of the review is to find methods for determining the form of O_mH_n groups and certain of their parameters by infrared spectroscopy, and to this end it compares the spectroscopic characteristics of compounds differing either in the form of their O_mH_n groups, the nature of neighbouring groups in the same molecule, or in intermolecular interaction.

There is no doubt of the advantage of infrared spectroscopy, since all physicochemical methods used for the analysis of such groups involve decomposition of the sample, and any O_mH_n groups present in the compound are converted into H_2O molecules and are only then recorded by some means. For example, the ignition of an organic compound containing hydrogen, whatever its nature, produces water; in some cases inorganic substances also give water molecules on ignition. In such cases the true nature of the oxygen and hydrogen in the initial compounds remains unknown. The formula for inorganic compounds is normally written as the oxides of the individual elements, with hydrogen as so many water molecules (nH_2O).

Since the bonding and mutual disposition of the oxygen and hydrogen atoms were unknown and could not be established from the water given off on decomposition of the sample, it is more correct under these conditions to use the above concept of oxygen–hydrogen groups (O_mH_n groups).

In reviewing the nature of the bond between hydrogen and oxygen atoms we meet with a number of obsolete concepts and terms, and we must therefore consider briefly the ideas which have existed up to the present, together with their foundations. A very large number of minerals and inorganic compounds give off water when heated, most frequently with a concomitant change in various physicochemical properties of the material; these changes, recorded by various methods, have served as a basis for the development of the concept of different "waters". Clearly the word "water" as used here has nothing in common with the concept of a water molecule, and it does not clarify the nature, bonding, or mutual disposition of the hydrogen and oxygen atoms; hence no method used for the investigation of "water" in inorganic compounds and which is associated with the removal of water can determine any of these parameters. Thus the concepts of constitutional, plus, zeolitic, cationic, etc., water which have arisen by the use of such methods must be considered as characterising the method of study rather than the form of the O_mH_n groups. We shall illustrate this with some concrete examples.

Chemical analysis of O_mH_n groups in inorganic compounds consists in the determination of the loss of water by the substance on heating. The use of this method led to the concepts of *minus "water"* (O_mH_n groups removed at temperatures up to 100°–110°) and *plus "water"* (O_mH_n groups removed above 100°–110°). The use of X-ray structural analysis for studying crystal hydrates led to the introduction of the concept of *structural "water"*, *i.e.* O_mH_n groups, the oxygen atoms of which occupy a definite position in each elementary cell of the crystal. The removal of these groups produces a change in the structure of the crystal.

Mineralogy uses its own system of classification of water in crystals. Structural "water" is divided into *cationic* and *anionic*. Cationic "water" comprises water which increases the basic properties of the cation in a salt formed fron a strong acid and a weak base; the oxygen atoms of this water form regular polyhedra around the cations. Anionic "water" comprises water which increases the acidic properties of the anion in a salt formed from a weak acid and a strong base; this water is normally directly attached to several cations.

In addition mineralogy uses the concept of *zeolitic* "water", which is intermediate between structural and adsorbed water. Zeolitic water is given off without destruction of the crystal lattice and without change in the anisotropy or transparency of the crystal. Moreover, as distinct from structural water, the removal of zeolitic water is accompanied by a decrease in specific gravity and refractive index (these parameters increase when crystal hydrates are dehydrated). On the other hand, zeolitic water differs from *adsorbed* water, which is removed without any change in the properties of the compound. Without considering

intermediate states, this concept of adsorbed water itself embraces two fundamentally different states; these are water *adsorbed in a mono-layer* and the *capillary-condensed* phase. *Interlayer* "water" found in layer minerals and allocated by mineralogists to a separate group, also has a number of specific properties. Interlayer water, like zeolitic, is removed over a wide range of temperatures without changing the crystal structure, but, like structural water and unlike zeolitic, with an increase in specific gravity and refractive index.

The spectroscopic study of compounds containing oxygen–hydrogen groups (usually the OH stretching frequencies are used) employs the terms *strongly bound* and *weakly bound* "water" or an OH group *disturbed by strong or weak hydrogen bonding*.

The most widely used terms are Pauling's *crystallisation* and *constitutional* "water". Crystallisation "water" is the water accompanying the compound when it is crystallised from an aqueous solution; constitutional "water" is water the loss of which changes the chemical nature of the substance. However, even these more valid concepts do not reflect the form of the O_mH_n groups, and even less do they reflect their geometrical and energetic parameters.

These examples show that each of the concepts named characterises either individual properties of the O_mH_n groups themselves (plus, minus, structural, strongly bound, capillary-condensed, water in a monolayer) or the influence of the O_mH_n groups on certain properties of the whole compound (constitutional, zeolitic, crystallisation), and none of these concepts discloses the basic characteristic of the O_mH_n groups, namely their type; hence they are purely arbitrary. This is because the methods of investigation have been indirect. Thus thermography, study of weight loss, change of refractive index, coefficient of refraction, solubility, and even X-ray structural analysis do not give direct information on the form of the O_mH_n groups. Data obtained by these methods are so indirect, and the definitions so imprecise, that they cannot be directly compared; thus it is impossible to establish any correlation between such apparently close concepts as zeolitic and crystallisation "water", or zeolitic and adsorbed "water", and so on.

These matters can only be clarified by using methods which can observe the oxygen–hydrogen groups directly. Such a method is infrared spectroscopy, which is also the simplest, most rapid, and requires small specimens.

II. SPECTROSCOPIC CHARACTERISTICS OF OH_n GROUPS

The object of this review is to analyse spectroscopic studies using infrared spectroscopy to investigate the form of O_mH_n groups†. We have collected more than 300 studies, relating to the spectra of 1500 compounds. In all these cases the nature of the OH_n groups was known beforehand, and the absorption bands ascribed to them have been reliably interpreted. Although the distribution of the compounds studied among the different classes is very uneven, a number of important and useful regularities can be observed.

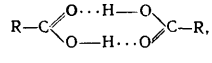
† Since of all possible O_mH_n groups having more than one oxygen atom only hydroperoxide groups are known, and as will be shown these are a special case of OH group, we shall in future refer only to OH_n groups.

The collected literature was analysed systematically so as to detect the spectroscopic properties of the OH_n groups in relation to their type or the nature of the atoms and bonds surrounding them. We first considered compounds containing the OH group, then systems having the $H\diagup O \diagdown H$ molecule, and finally compounds containing the ion OH_3^+.

Compounds containing the OH group formed the largest class, and it is therefore with these that it is easiest to follow the influence of the immediate and more distant environment on the vibrational properties of the OH group. Organic acids, alcohols, phenols, hydroxy-compounds, and oximes all contain the same C–O–H group, but in these various compounds the carbon atom of this group forms different bonds with different atoms. Comparison of the spectra of these compounds will enable the influence of the more distant environment to be observed. By comparing the spectra of various inorganic acids, organoelemental acids, hydroperoxides, surface OH groups, and hydroxides we can trace the influence of the atom directly bonded to the OH group on the vibrational properties of the latter. Finally, comparison of the spectra of acids, their acid salts, and organo-substituted acids will determine the influence of cations on the vibrational spectrum of the OH group.

1. Absorption Spectra of Hydroxyls (the O–H Group)

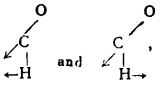
Organic acids are very convenient for study and were investigated long ago. The great expansion in polymer chemistry, biophysics, and medicine has increased interest in these compounds. Bellamy[1] has reviewed work on organic acids published up to 1953. The experimental data which had even then been accumulated enabled certain regularities to be established. Thus it was found that in the liquid and solid and sometimes even in the vapour phase acids exist as the dimers:



or higher polymers. The complexes are formed through strong hydrogen bonding, which leads to the reduction of the stretching frequencies of the OH group to 3000–2500 cm^{-1}. Most frequently these bands have a large half-width and lie in the region from 2750 to 2500 cm^{-1}. The integral and peak intensities differ substantially.

Most acids in the liquid state exhibit a band at about 935 cm^{-1}, which on deuteration is displaced to 675 cm^{-1}. In the crystals the intensity of this band falls and the half-width increases. Nearly all workers ascribe it to non-planar deformational vibrations of the C–O–H group.

Two strong bands in the range 1320–1210 cm^{-1} are related to combinations of the planar deformational vibration of the C–O–H group and stretching of the C–O group. The forms of these vibrations were later found:



and even to a first approximation cannot be considered as purely deformational vibrations of the COH group[2]. Others have also come to the same conclusion[3-12].

The deformational OH vibration becomes characteristic of the type of group only when the OH group is disturbed by hydrogen bonding or the hydrogen is replaced by deuterium[12,13]. The intermolecular vibrations of the associated molecules, or in other words the vibrations of the actual hydrogen bond[14,15] appear in the range 240–155 cm^{-1}.

Recent work confirms that the OH stretching frequencies normally lie in the region 3000–2500 cm^{-1}, but some studies on associated acids[14,16-18] have found absorption bands in the region 3300–3100 cm^{-1}.

Investigators as a rule do not indicate the degree of polymerisation of the substance studied, and the concentrations of solutions used cannot definitely establish this. The frequencies given in Table 1 under the heading "organic acids (free)" relate only to acids which were shown to be actually monomeric. All results obtained for dimeric and polymeric acids and for acids present in the crystalline state are given under the heading "organic acids disturbed by H bonding". This division is intended to demonstrate the great variation of the spectroscopic characteristics of OH groups with hydrogen bonding. Table 1 shows that there is practically no overlap between the regions of the stretching modes of OH groups disturbed and not disturbed by hydrogen bonding. An exception is given by Josien[23], who relates the bands at 3490–3420 cm^{-1} to the monomeric form of the acids because of their small half-width ($\Delta S_{\frac{1}{2}}$ = 50–100 cm^{-1}). As we shall see below, the band half-width is not a definite criterion of the formation of a hydrogen bond, although in most cases it increases the band width to several hundreds of reciprocal centimetres. This broadening with increasing polymerisation is seen particularly well with formic acid[16].

Alcohols. The spectroscopic characteristics of alcohols have also been reviewed previously[1]. The stretching frequency of the OH groups depends on the strength of the hydrogen bond. A weak bond reduces the frequency by 100–200 cm^{-1} and does not increase the band width ($\Delta S_{\frac{1}{2}}$ = = 50 cm^{-1}). With strong hydrogen bonding the frequency is reduced to 3400–3200 cm^{-1} and the half-width increases to 200 cm^{-1}. In the succeeding years a large number of alcohols of different types have been investigated. Comparison of these results shows that monomeric alcohols exhibit OH stretching frequencies of at least 3500 cm^{-1}, with a half-width of 20–70 cm^{-1}. A reliable assignment of the observed bands to dimers, trimers, and tetramers of the alcohols has only been made by Van Thiel and coworkers[52] and Cannon and Stace[53], so that, as with the acids, we have divided the alcohols only into free alcohols and those disturbed by hydrogen bonding (Table 1).

A typical spectrum of a highly dilute alcohol is that of t-butanol (Fig. 1)[55]. It contains a narrow band at about 3630 cm^{-1} due to undisturbed OH groups and two broad bands below 3500 cm^{-1} due to vibrations of the OH groups in associated molecules. Fishman and Drickamer[54] obtained the spectra of butanol at pressures from 1 to 12 000 atm; this experiment, in which any influence due to solvents was avoided, showed that a decrease in the distance between reacting molecules increases the probability of formation of complexes and very slightly affects the vibrations of free OH groups.

The frequency of planar and non-planar deformational vibrations of the OH group is very much less dependent on the degree of association of the molecules: thus the frequencies of the planar deformational vibrations are only increased by 120 cm^{-1} on passing from monomers to polymers (Table 1).

Phenols have been comparatively little studied, and their degree of association has not been determined. Gaseous phenols and their dilute solutions in inert solvents[126-128] exhibit bands of half-width $\Delta S_{\frac{1}{2}}$ = 15–60 cm^{-1} with a maximum at about 3730–3540 cm^{-1}. Phenols in the liquid

TABLE 1. Frequencies of the fundamental vibrations of hydroxyl-containing compounds in cm^{-1}*.

System	ν_{OH}	References	δ_{OH}	References	γ_{OH}	References
Organic acids	3590—3490	13,14,16,19—23	1284—1057	2,13,16,20,22,24	650—538	13,16,22
(free)	(2653—)	13,19,20	(973—865)	13,20,24	(546—421)	13
Organic acids	3300—2500	4,13,14,16—18,20, 21,25—38	1450—950	2,6,7,13,14,16, 18,20,29—33, 38—42	975—830	4,10,11,13,16—18, 27,28,30,31,36, 43—46
(disturbed by H bonding)	(—2260)	13,31	(1090—940)	13,31	(701—690)	13,31
Alcohols	3720—3500	9,14,23,33, 48—62	1330—1010	39,47—51,62—70	670—640	50,66,68
(free)	(2760—2655)	9,48—51,58	(950—770)	47—51,63—66	(490—475)	50,66,68
Alcohols	3530—2900	9,14,33,47—50, 52—57,60,71,72	1440—1140	9,14,18,33,50, 57,65—70,73,74	1090—858	57,74,75
(disturbed by H bonding)	(2577—2200)	47—50,72	(1100—875)	9,39,50,63,68,72		
Inorganic acids	3590—1900	25,33,76—91	1430—1000	76,79—93	1050—650	79—83
	(2655—2200)	83—86	(1086—860)	83—85,92		
Acid salts	3300—2200	77,82,86,88,89, 94—99	1400—1030	82,86,88,89,94—101	1020—400	82,89,95—100
Surface OH *groups* (free)	3770—3730	102—109	870—790	103—105,110		
Surface OH *groups* (disturbed by H bonding)	3660—3300	106—109,111,112	1150—935	110—112		
Metal hydroxides (alkali and alkaline earth)	3680—3530	113—120,129				
Metal hydroxides (other than alkali and alkaline earths)	3600—2800	61,120—124	1160—840	81,116,121—125		

* Frequencies in parentheses relate to the corresponding deuterated analogues.

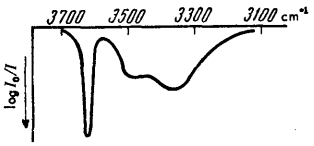


Fig. 1. Solution of t-butanol in CCl_4. C = = 0.2 M. [55]

state and their solutions in proton-accepting solvents, *i.e.* phenols with OH groups disturbed by hydrogen bonding, exhibit a wide band [3,128-131] in the region 3580–2250 cm^{-1}. The deformational vibrations of phenolic OH groups [3,5,14,129] lie in the region 1410–1170 cm^{-1}. In addition to these, salicylaldehyde has a band at 715 cm^{-1} which is also due to vibrations of the OH group. Deuterophenols have only been studied by two groups of workers [5,128]; the stretching and deformational modes lie in the ranges 2700–2480 and 980–925 cm^{-1} respectively.

Hydroxy-compounds. Of the compounds under consideration the hydroxy-compounds form the most complex and varied group, and the frequencies due to the OH groups of these compounds would be expected to appear over a wider range than in the case of other compounds, but the results of 22 studies which we have collected do not bear this out. All the compounds [132-140] exhibit OH stretching frequencies from 3620 to 2760 cm^{-1}, and deuterated hydroxy-compounds [138] from 2610 to 2200 cm^{-1}. The planar deformational vibrations of OH groups [8,134-147] and OD groups [138,142-145] have frequencies at 1475–915 and 1280–830 cm^{-1} respectively. Non-planar deformational vibrations appear [8,138-140,147] in the region 880–400 cm^{-1}.

Oximes have been the least fully investigated, and the existing information is not always fully accepted or sufficiently definite. A shift of the OH stretching frequency bands towards lower frequencies when hydrogen bonding occurs has been reliably established; thus it has been shown [148] that monomeric oximes and their deuterated analogues absorb at about 3650 and 2690 cm^{-1} respectively. Solutions in which the OH groups of oximes are somewhat disturbed by solvent molecules [149] have an absorption band at about 3500 cm^{-1}. Oxime polymers containing strong hydrogen bonds [148-150] have absorption bands right down to 2340 cm^{-1} and below [151]. The bands of planar deformational OH vibrations, in the presence or absence of hydrogen bonding, lie in the range [148,149,152,153] 1480–1200 cm^{-1}. We have quoted the overall range of frequencies, since although hydrogen bonding produces some increase in the frequency of deformational OH vibrations [148,152], the increase is less than the frequency changes occurring within the general class of oximes. The frequencies of the deformational vibrations thus cannot serve as a criterion of hydrogen bonding. Non-planar deformational OH vibrations have frequencies [148,150] from 930 to 420 cm^{-1}.

Dimethylglyoximes have been studied by two sets of investigators [150,151], who each recorded a large number of bands and suggested various interpretations. The bands at about 1800–1650 cm^{-1} are ascribed to stretching or deformational vibrations or to splitting of the levels in the two-humped potential valley.

Inorganic acids are a good class of compounds for investigating the influence of the radical R_1 in the compound R_1OH on the vibrations of the OH group. The published results on the absorption spectra of inorganic acids show convincingly that the stretching and deformational OH vibrations of all the compounds studied lie in the same regions of frequencies (Table 1). The vibrations of OH groups in organic-substituted acids also lie in the same regions [76,93].

Inorganic acids are not very volatile and form hydrogen bonds very readily, so that even their solutions in inert solvents cannot be considered *a priori* to contain monomeric forms, and hence all results obtained for the acids in the liquid or crystalline phase we have related to their polymeric forms, *i.e.* we have considered the acidic OH groups as being disturbed by hydrogen bonding. A characteristic of such compounds is the overlapping of the bands, which have half-widths of several hundreds of reciprocal centimetres. Aqueous solutions of inorganic acids cannot be compared with their solutions in other solvents, since the dissociation of strong acids in water produces the ion OH_3^+ (this matter will be considered in more detail below). Great care is needed therefore in the interpretation of the bands observed in the spectra of acids in the presence of water molecules.

Acid salts. The OH groups of acid salts exhibit frequencies in the same region as the corresponding acids (Table 1). The observed coincidence in the main frequencies of the OH vibrations would be expected, since the acidic OH groups in acids and acid salts are very similar in nature. The slight differences in the frequency ranges for the two types of compound must be related to their slightly different nature and to the fact that different materials were investigated. For the same reasons as in the case of the inorganic acids, all acid salts present in the solid and liquid phases are considered to be polymeric.

Some acid salts have two absorption bands in the OH stretching frequency region [100,154-156], the band with the lower frequency being in the region 2400–1900 cm^{-1}. This may be due either to different types of association of OH groups in the compound or to splitting of the energy levels because of the presence of two minima on the potential curve of the hydrogen bond.

The interpretation of the bands at about 1850–1580 cm^{-1} observed in certain acid phosphates, arsenates, and iodates [99,100,156-158] is even more indefinite. On the basis of their shift on deuteration these bands have been ascribed to vibrations of R–O–H groups, but the type of vibration has not been established, and the types of vibration suggested by different workers are very different [99,156,157]. They have been assigned to OH stretching vibrations, to OH deformational vibrations, and to vibrations of the H_2PO_4 group. In the first case the low frequency of the bands was ascribed either to very strong hydrogen bonding or to the appearance of a second minimum on the potential curve. The difficulty of interpretation is removed if it is assumed that in addition to acidic OH groups the compounds contain the OH_3^+ group, for which absorption in this region is characteristic (see below); the workers cited did not consider this possibility. The frequencies of these bands will not be taken into account in further discussions.

Hydroperoxides behave in the same way as the other types of compound considered above in respect of the spectroscopic characteristics of their OH groups.

Monomeric hydroperoxides have OH stretching vibration bands[159-162] at about 3580–3530 cm^{-1}. When hydrogen bonding occurs the frequency is reduced[161-172] to 3500–3000 cm^{-1}. As with the other compounds, monomeric hydroperoxides have narrower bands than their polymeric forms.

Deformational vibrations of the OH groups of polymeric hydroperoxides[163-168,170-172] lie in the region 1420–940 cm^{-1}, which also contains the frequencies 1320 and 1000–930 cm^{-1} found for hydroperoxide monomers[159,160]. Since there have only been two such studies, no definite conclusion can be drawn from these data. Bands due to non-planar deformational vibrations of the OH groups have been observed only for hydrogen peroxide[167] and isopropylbenzene hydroperoxide[166]; these bands lie in the region 880–700 cm^{-1}. Bands were also observed[167] at about 650–530 cm^{-1} and have been ascribed to intermolecular vibrations.

Organoelemental compounds. The OH groups of organoelemental compounds have stretching frequencies at from 3690 to 2300 cm^{-1}, depending on the degree of hydrogen bonding[56,156,173-179]. The formation of a hydrogen bond, as with other compounds, lowers the frequency of the vibrations and broadens the band to a width of several hundreds of reciprocal centimetres[56,156,175-177]. Bands due to planar deformational vibrations of the OH groups have been observed[156,177-181] at 1400–800 cm^{-1}. The frequency is increased slightly when hydrogen bonding occurs, but the increase is less than the frequency range in which the deformational vibrations of the various organoelemental compounds are observed. The bands due to non-planar deformational vibrations, observed in crystals of mono-, di-, and tri-methyl borates, lie[177] at about 650 cm^{-1}.

In addition to these bands some organic phosphorus compounds[156] have bands in the region 2350–1900 cm^{-1} and[156,173,174] at about 1700 cm^{-1}. As in the case of acid salts, these bands are shifted on deuteration, and can therefore be related to OH vibrations, but, again as with the acid salts, the type of vibration is unknown. These bands will not therefore be considered in future discussions.

Surface OH groups, because of their unusual situation, should not exhibit any particular spectroscopic characteristics, but Table 1 shows that this conclusion is incorrect. Free surface OH and OD groups[102-104] are characterised by narrow bands not more than 100 cm^{-1} in width[105,107]. The presence of even weak hydrogen bonding[111] broadens the band and shifts it from 3770 to 3300 cm^{-1}. The bands due to deformational vibrations of the free OH groups lie in the region 870–790 cm^{-1}; when disturbed by hydrogen bonding they are shifted to 1050 cm^{-1} (Table 1).

Hydroxides have been much studied, but the spectra obtained differ considerably (Table 1). They may be divided into two groups. The first group contains the alkali and alkaline earth metal hydroxides, which have very narrow bands (half-width 4–60 cm^{-1}) in the region 3680–3610 cm^{-1}. Their deuterated analogues[113-115] have bands in the range 2715–2630 cm^{-1}. When hydrogen bonding occurs, the bands due to OH stretching frequencies are shifted[115,116,129] to 3570–3530 cm^{-1}. No bands due to deformational vibrations were observed[116] in the spectra of these compounds in the usual region of 1800–400 cm^{-1}. The Raman spectra of these compounds[117] exhibit bands with frequencies of from 360 to 50 cm^{-1}, but these could not be interpreted.

The hydroxides of other metals have a quite different type of spectrum. The hydroxides of iron, aluminium, gallium, indium, zinc, etc., have broad diffuse bands in the region 3600–2800 cm^{-1}, due to OH stretching vibrations. The spectra also have bands due to deformational vibrations at about 1160–840 cm^{-1}. In addition to bands at 1060 and 841 cm^{-1}, technetium hydroxide[124] has a band at 1543 cm^{-1}.

The hydroxides of copper and vanadium apparently occupy a position intermediate between the above two types of compound; they exhibit stretching and deformational vibration bands at about 3570–3530 cm^{-1} and 790–470 cm^{-1} respectively[182].

2. Absorption Spectra of Water Molecules (the OH_2 Group)

So far we have considered compounds of the formula R_1OH, where R_1 is any radical or atom other than hydrogen. We shall now deal with the molecule H–O–H.

In the vapour state the various water molecules have the frequencies given in Table 2.

The investigation[188] of *water* in a nitrogen *matrix* at 20°K has enabled the spectroscopic characteristics of water molecules in various polymeric forms to be established; the frequencies and half-widths of the absorption bands are given in Table 2 and Fig. 2. Similar studies of water in a matrix of krypton, argon, or xenon[189,190] have shown the stretching frequency of water molecules to be in the range 3770–3660 cm^{-1} in each case. A distinct rotational structure has been observed in the region of deformational vibrations of H_2O, HDO, and D_2O molecules, the most intense bands[189] having the frequencies 1608–1602, 1413, and 1195 cm^{-1}. The spectra obtained for water in a nitrogen matrix are in complete agreement with Thiel's results[188] (Fig. 2). Investigation of water vapour in an atmosphere of nitrogen and carbon dioxide at 50 atm has shown that reaction between nitrogen and water molecules does not cause any substantial change in the spectrum of the latter, but carbon dioxide molecules, on the other hand, form hydrogen bonds with H_2O and D_2O molecules and so increase the frequency of their deformational vibrations[191] to 1610 and 1190 cm^{-1}.

The spectra of water dissolved in various solvents were investigated in another group of studies of

TABLE 2. Frequencies of the fundamental vibrations of water molecules.

	Composition	ν_3	ν_1	$\nu_2 = \delta_{OH}$	$\Delta S_{1/4\nu}$ and $\Delta S_{1/4\delta}$	$2\nu_2$	References
Vapour phase	H_2O	3755.8	3656.6	1594.6			183,184
	HDO	3707.5	2726.7	1402.2			183—186
	D_2O	2788.0	2671.5	1178.3			183—186
	$D_2^{18}O$	2764±5	2657±2	1169±2			187
In a nitrogen matrix at 20°K	monomer	3725	3627	1600	~20 ~8		188
	dimer	3691	3546	1620	~20 ~6		188
	trimer	3510	3355	1635	80 and 365		188
	polymer	3320	3240	1635	~30		188
Liquid phase	H_2O	3480±20	3425±10	1645±5		3290±20	
	D_2O	2580±20	2510±10	1215±5		2435±20	
	HDO	3420±10	2510±5	1460±5		2930±10	

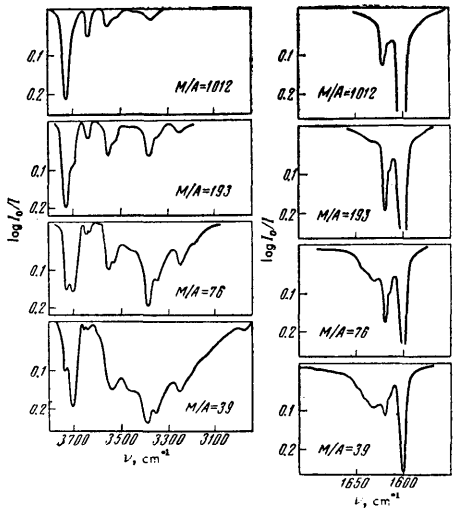


Fig. 2. Spectra of water in nitrogen matrices[188] at 20°K and molar ratios of from 1:1012 to 1:39.

OH_2 groups. Two bands were observed in the OH stretching frequency region, with half-widths less than 70 cm^{-1}; these frequencies, of 3705–3575 and 3650–3520 cm^{-1}, are very close to the frequencies for water vapour given in Table 2, so that as with the water vapour bands they are ascribed to antisymmetric and symmetric vibrations of the H_2O molecule respectively[129,192-195]. With D_2O molecules analogous bands of half-width 50 cm^{-1} have been observed[193,196] in the ranges 2766–2700 and 2655–2600 cm^{-1}.

A detailed study of water–pyridine binary mixtures and water–pyridine–carbon tetrachloride ternary mixtures has shown that when hydrogen bonding occurs the water spectrum loses the doublet character typical of solution in an inert solvent[194]. The bands due to OH stretching vibrations are shifted to 3500–3200 cm^{-1}, and the band due to deformational vibrations is shifted to 1665–1640 cm^{-1}. Similar results were obtained in another study[192].

Water in the liquid or crystalline phase consists wholly of H_2O molecules disturbed by hydrogen bonds. The spectroscopic data on water have been discussed in detail[194]. In the liquid phase, water of any isotopic composition exhibits broad absorption bands in the region of OH stretching vibrations. In the case of H_2O and D_2O molecules three maxima can be distinguished on the broad band, ascribed to symmetric and antisymmetric stretching vibrations and to the first overtone of the deformational vibration of the water molecule. There has as yet been no reliable allocation of the observed bands to ν_s and ν_{as} vibrations.

The suggested interpretation and the frequencies of the observed absorption bands are given in Table 2. Later studies have confirmed these results[197-201]. Slight variations in the frequencies obtained are due to the different experimental conditions and to insufficient experimental accuracy. A change of temperature of 20° is required to produce such a shift of frequency[200]. Since we are here concerned only with general characteristics, we shall not pursue this matter in any more detail.

In addition to the absorption bands mentioned, liquid water exhibits bands[201-203] at about 2100 and 710–645 cm^{-1}, due respectively to vibrations of the type $\delta_{OH} + \omega$ and ω. Recent work in the far infrared[204] has detected six bands in the region 230–140 cm^{-1} in the spectra of liquid light and heavy water. This is the first observation of the fundamental frequencies of the hydrogen bond in an absorption spectrum.

The first spectroscopic investigation of *ice*[205] detected absorption bands in the regions 3380–3140, 1650–1580, and 850–820 cm^{-1}. More recent studies[199,201,203,206,207] agree in general with these values. The spectrum of ice is little dependent on external conditions. Thus with reduction of the temperature from 0° to -170° the OH stretching frequency (ν_{OH}) is lowered by 60–40 cm^{-1} and the deformational (δ_{OH}) and intermolecular (ω) vibration frequencies are increased[207] by 25 and 15 cm^{-1} respectively. Similarly the external pressure has little effect on the spectrum of ice: increasing the pressure from 1 to 9000 atm only slightly increases the frequency due to OH stretching vibrations to 3600 cm^{-1} and slightly increases the intensity of the band due to deformational vibrations[208].

Depending on the temperature of freezing, water vapour produces either hexagonal or cubic ice[201,205]. Although both forms absorb in approximately the same region their spectra are quite different; thus cubic ice, obtained by condensation of the vapour at below -80°, has much narrower bands (Fig. 3).

The frequencies of intermolecular vibrations have been found from the Raman spectrum: they are[207] 310, 299, 230, and 212 cm^{-1}. Thus under different conditions the spectrum of ice may contain bands due to OH stretching vibrations of half-width from 50 to 300 cm^{-1} and with maxima over a wider range of frequencies (Table 3) than had previously been indicated[205].

The dependence of the spectrum of water on the nature of salts and acids dissolved in it has often been studied. Neither the concentration nor the nature of the ions produces any substantial change in the spectrum of the water[129,193,209-214]. The OH and OD stretching vibrations appear in the regions 3460–3260 and 2560–2470 cm^{-1} respectively. The deformational vibrations of H_2O and HDO molecules are found in the regions 1655–1620 and 1475–1450 cm^{-1}. Investigation of the fine effect due to influence of various ions on the spectrum of water has shown[129,211] that the position of the absorption bands of the water is more sensitive to the nature of the anion and less sensitive to the nature of the cation. Replacing

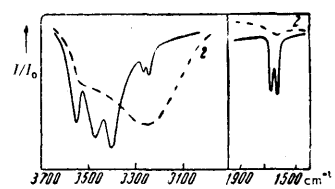


Fig. 3. Spectra of ice obtained by condensation of water vapour[201] at: 1) -80°; 2) -22°.

TABLE 3. Frequencies of the fundamental vibrations of water molecules.

System	ν_{OH}	References	δ_{OH}	References	γ_{OH}	References
In a crystalline phase	3600—3090	199,201,205, 207,208	1660—1580	199,201,205,207, 208	850—650	201,203,205, 208
Adsorbed on a surface	3580—3300	103,105,108, 215—217	1645—1620	102,103,105,108, 110,216—218		
In hydrated salts of oxygen-containing inorganic acids	3620—2700	33,77,80,82, 88,94,96,116, 123,129,195, 219—239	1670—1590	33,77,80,82,88, 94,96,116,123, 129,223—233, 240,241		
In hydrated halides	3600—2900	89,121,242—250	1670—1590	89,121,242—250		
In hydrated salts of organic acids	3530—3050	34,199,222, 251—253	1650—1614	34,199,222, 251—253		
In other crystal hydrates	3600—3120	254—263	1670—1600	255—254		

I^- ions by F^- ions reduces the OH and OD stretching frequencies by 160 and 90 cm^{-1} and increases the frequency of the HDO deformational vibrations by 50 cm^{-1}. The presence of Cl^- ions in solution does not produce any marked change in the spectrum of pure water. The presence in solution of various alkali and alkaline earth metal cations only produces a shift of 30 cm^{-1} in the band due to the OD stretching vibration.

In the adsorption of water molecules on an adsorbent the geometrical and force parameters of the water may be slightly altered, and its vibrational spectrum would then be expected to show a marked change. Most workers have studied the adsorption of water on silica gel; cellulose and Cellophane have also been studied as adsorbents[216,218]. Of course, as the coverage of the surface by the adsorbed material increases, interaction between individual adsorbed molecules will begin to show itself. The extreme cases of this coverage are a monolayer and capillary condensation. The frequency of the deformational vibration of water molecules adsorbed in a monolayer is 1620 cm^{-1}, and that of water molecules in a capillary condensed phase[102,103] is 1640 cm^{-1}. The bands due to OH and OD stretching vibrations in molecules adsorbed in a monolayer are narrower and have frequencies 150 cm^{-1} higher than in the corresponding bands for capillary condensed molecules. Other workers have given similar values for the frequencies. Table 3 gives the generalised data.

Crystal hydrates form the most fully investigated class of compound. Analysis of the collected results demonstrates convincingly that water molecules present in the most varied compounds all exhibit the same spectroscopic pattern. Crystal hydrates of salts of inorganic oxo-acids, halogen acids, and organic acids and hydrates of alkalis and other more complex compounds all have absorption bands due to water in the same frequency ranges (Table 3).

In all cases the OH stretching frequencies lie within the range 3620–2700 cm^{-1}. Only once[225] has a frequency outside this range been recorded (3690 cm^{-1}), but in another investigation[227] the same compound gave a different result (3570 cm^{-1}); we have therefore taken the value 3620 cm^{-1} for the upper limit of the OH stretching vibrations. The half-width of these bands varies from 70 to 400–500 cm^{-1}, but in such arbitrary fashion that it cannot be correlated with any parameters of the compounds. A good example is uranyl nitrate, for which the half-width of the bands due to the OH stretching vibrations is six times as great in the hexahydrate as in the dihydrate (Fig. 4).

The deformational vibrations of water molecules (δ_{OH}) in most crystal hydrates have a frequency of from 1670 to 1590 cm^{-1}; in very rare cases (5 out of 450 bromates, benzene sulphonates, and phosphates[77,249,264]) the frequency is increased to 1680 cm^{-1}. A δ_{OH} band below the normal lower frequency limit has been observed only in $CuCl_2.2H_2O$ and $MgCl_2.6H_2O$, which have a band at about 1560 and 1576 cm^{-1} respectively[244,247]. These deviations from the normal position of the δ_{OH} bands do not affect the discussion which follows, and are mentioned here only to demonstrate how few they are.

A different question arises in respect of other investigations[77,96] in which, in addition to bands at 1640–1620 cm^{-1}, bands were observed with frequencies at 1705–1680 cm^{-1}. As we shall see later, the question of the presence in crystal hydrates of water molecules having a deformational vibration frequency of above 1670 cm^{-1} is very important, and we shall therefore consider this matter in more detail. Three main facts must be borne in mind when evaluating the reliability of these reported results. Firstly, the spectra in which bands of frequency 1705–1680 cm^{-1} were found[96] have also been investigated by other workers, who give lower frequencies, namely[80] 1690 cm^{-1} instead of 1705 cm^{-1} and[77] 1670 cm^{-1} instead of 1680 cm^{-1}. We must therefore be very circumspect in considering the accuracy of the determination of these frequencies. Secondly, in all three investigations the observed bands were assigned to δ_{OH} vibrations on the tacit assumption that they could not be assigned to OH stretching vibrations or to vibrations of the phosphorus–oxygen anion, and in general this is not true. No use was made even of deuteration, which could have shown whether the hydrogen atom takes part in the vibration. Thirdly, even if it is considered that the band is due to vibrations in which the OH bond participates, and that the frequency of this band is in fact above 1670 cm^{-1}, we still do not have any foundation for making a definite interpretation. As will be shown below, the deformational vibrations of the hydroxonium ion are found in the region 1750–1670 cm^{-1}, and for some reason or other the presence of this ion was not considered. In view of the above, we shall not concern ourselves further with these bands.

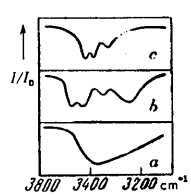


Fig. 4. Spectra of the stretching vibrations of the water of crystallisation of uranyl nitrate[207]: *a*) hexahydrate; *b*) trihydrate; *c*) dihydrate.

3. Absorption Spectra of Hydroxonium Ions (the OH_3^+ Group)

There have been seven investigations of the absorption spectrum of the *hydroxonium ion*. Infrared absorption and Raman methods, which give identical spectra for molecules of symmetry C_{3v}, give different results for the hydroxonium ion; there is no explanation of this in the literature. Since this review is concerned with the effects due to OH_n groups in the absorption spectrum, and the Raman spectrum of the hydroxonium ion is always less clear[265,266], we shall deal only with the frequencies obtained from the absorption spectra.

Studies of the hydroxonium ion in aqueous acid solutions at room temperature[210,267-269] and in crystal hydrates of acids and equimolar mixtures of water and acid[269-272] at -195° have given frequency values which are in good agreement; bands were always found in the ranges 3380–2650, 2150–2100, 1750–1670, and 1200–1130 cm^{-1}. The two high-frequency bands are always fairly weak and very broad; they were resolved only in two cases[270,271]. The band at about 1700 cm^{-1} is considerably narrower and stronger; it was always the most clearly developed in the absorption spectrum, and was therefore detected in all the investigations except one[272], in which it overlapped with two bands of higher frequency, forming a region of absorption at 2800–1650 cm^{-1}. The narrow band at about 1150 cm^{-1} ($\Delta S_{\frac{1}{2}}$ = 100 cm^{-1}) has a constant frequency but is of very low intensity.

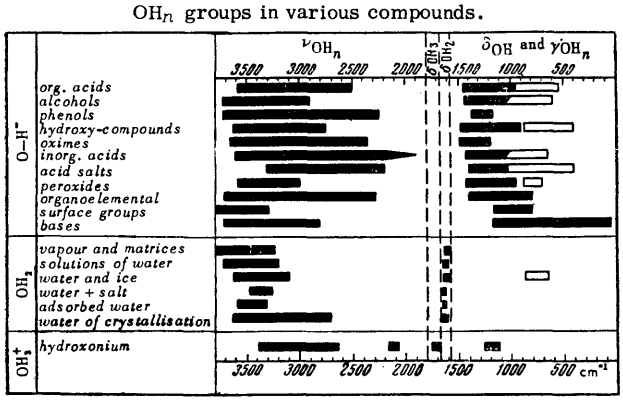
III. DEPENDENCE OF THE VIBRATIONAL SPECTRUM OF OH_n GROUPS ON THEIR STRUCTURE

We have been considering the spectroscopic characteristics of O–H⁻, O–O–H⁻, H–O–O–H, H–O–H, and



groups in 20 different classes of compounds and systems, and since we have included every published work at our disposal, any regularities we see must be considered to be of general application, and of use in molecular spectroscopic analysis. The collected data are shown visually in Table 4, in which the black strips represent the regions in which the fundamental planar vibrations of the OH_n groups appear, and the white strips the regions of non-planar vibrations of the OH group and H_2O molecules as a whole.

TABLE 4. Frequencies of the characteristic vibrations of OH_n groups in various compounds.



1. Determination of the Type of OH_n Group

The data lead to a result of great importance for spectroscopic studies, a result which enables definite establishment of the type of an OH_n group from its deformational vibrations. While the stretching frequencies of all OH_n groups appear in the same region, their deformational vibrations appear in completely different regions; they do not overlap under the influence of any intra- or inter-molecular interactions. Thus the frequencies of the deformational vibrations of water molecules and OH groups are always within the limits from 1680 to 1590 cm^{-1} and from 1500 to 600 cm^{-1} respectively. In all the systems studied, one of the frequencies of the deformational vibration of the OH_3^+ ion lies in the region from 1750 to 1670 cm^{-1}, which serves to distinguish it from the H_2O molecule and hydroxylic compounds‡.

This relationship is very useful analytically. In finding it we used all existing literature data, but these are purely experimental. For full confirmation of the relationship found experimentally we shall consider it in terms of the modern theory of molecular vibrations.

Let us consider to a first approximation the vibration of the angle R–O–H and follow the change of frequency of this vibration with change of its kinematic parameters. We shall consider the vibration to be characteristic in type and the angle to be constant and the same as in the free water molecule. In the water molecule the frequency of this vibration is 1595 cm^{-1}. If R is deuterium the frequency is lowered to 1402 cm^{-1}. In any real molecule the hydroxyl oxygen is attached to an even heavier atom R, and the R–O distance is usually greater than the value 0.96 Å characteristic of the O–H bond. Taking one of the lighter atoms, *e.g.* the boron atom, and taking the B–O distance as 1.2 Å,[273] these changes alone will reduce the frequency of the deformational vibration to 1180 cm^{-1}. Further increase in the mass of R will produce a further reduction in the frequency. Thus we see that changing only the kinematics of the R–O–H group must reduce the frequency of the deformational hydroxyl vibration by 300–400 cm^{-1} as compared with that of water. Clearly in the general case the effect will be more complex: there may be some increase in the bending force constant, and also participation of neighbouring bonds in the deformational OH vibration, and either may produce some increase in the frequency in comparison with the value of 1180 cm^{-1} which we have obtained. However, the factors which increase the frequency are slight, and it is therefore natural to expect the frequencies of the deformational vibrations of the OH groups to be always lower than those of the H–O–H molecules. Hydrogen bonding has very little effect on this frequency[101,274]. This is readily seen with Seignette salt (potassium sodium tartrate), in which four types of water molecule have been detected, distinguished by the strength of their interaction with neighbouring molecules, and having absorption bands in the range from 3537 to 3049 cm^{-1}; however, the frequency of the

‡ The band corresponding to the other deformational OH_3^+ vibration is of low intensity and its frequency coincides with that of OH vibrations; it cannot therefore serve as a basic analytical signpost.

deformational vibrations is 1650 cm^{-1} for molecules of all four types[252]. Thus we see that our relationship found experimentally is in full accord with theoretical views, which again confirms the correctness of our conclusion.

The difference between the frequencies of the deformational vibrations of the OH_3^+ and OH_2 groups is very much less. It has as yet no definite theoretical explanation, and so remains a purely experimental fact. However, it can be shown that within reasonable limits of the $H\overset{O}{\diagdown\diagup}H$ angle (115°–105°) and the O–H distance (1.09 to 0.96 Å) the diagonal term of the matrix of the kinematic coefficients of OH_3^+ ions derived by symmetry is always 6–18% greater than the corresponding coefficient for the water molecule; hence only the configuration of the OH_3^+ and OH_2 groups need be considered when explaining the observed difference in frequencies.

From all that has been said it follows that if, on the basis of any data, a band can be assigned to a deformational vibration of an OH_n group, then the frequency of the vibration will immediately indicate the type of group: OH_3^+, OH_2, or OH^-.

Having obtained a very simple and convenient analytical method for establishing the type of OH_n group, we must also consider the requirements of the method. We can readily establish, from the shift of the band on deuteration (the frequency decreases by a factor of 1.28–1.35), that it is caused by some vibration of one of the OH_n groups. The assignment of the band to a deformational vibration is only possible by analysing the whole spectrum, otherwise we cannot distinguish the bands due to deformational vibrations from the other bands, which we do not need, due to non-planar deformational vibrations of hydroxyls, vibrations of water molecules as a whole, and low-frequency deformational vibration of the OH_3^+ ion.

To establish the type of OH_n group, the band to be considered must have the highest frequency of all the bands in the range from 1800 to 400 cm^{-1} which is shifted on deuteration. It should also be remembered that all deformational vibration bands are of medium intensity and, in the case of OH^- and OH_2 groups, are as a rule weaker than stretching vibration bands. The band due to deformational vibration of the hydroxonium ion at about 1700 cm^{-1}, on the other hand, is usually stronger than both of its stretching vibration bands.

As stated earlier, neither hydrogen peroxide nor hydroperoxides exhibit any specific spectroscopic characteristics due to OH vibrations which distinguish them from other R–O–H compounds (Table 4).

Review of the spectroscopic characteristics of the various OH_n groups has shown that the type of group can only be established from the frequency of the deformational vibrations; no information of the type of OH_n group can be obtained from the OH stretching vibration spectrum. The tacit assumption of many investigators that hydroxy-groups have narrower OH stretching vibration bands than do water molecules is quite incorrect. As was shown in the appropriate subsections of Section II, when hydrogen bonding occurs alcohols, acids, phenols, oximes, etc., have absorption bands with half-widths of several hundred reciprocal centimetres (Fig. 1), while water molecules isolated in matrices or in low concentrations and in inert solvents have absorption bands narrower than 70 cm^{-1} (Fig. 2). It follows incontestably from these results that the half-width of a band due to an OH stretching vibration does not depend on the type of OH_n group and so cannot be used to establish the type. The half-width of such bands changes over very wide limits under the action of hydrogen bonding. This broadening has long interested investigators, but no regularity in it has yet been definitely established.

2. Hydrogen Bond Parameters from the OH Stretching Vibration Spectrum

The possibility of determining the type of OH_n group only from the frequency of its deformational vibration might create the impression that the study of stretching vibrations is worthless, but this is quite untrue, since it is just the OH stretching vibrations which are the most sensitive to intermolecular interaction.

Thus analysis of all the collected studies shows that the OH stretching frequencies appear in the range 3750–1900 cm^{-1}, and are independent of the type of OH_n group and of the type of compound in which it is present, but they are very sensitive to the condition of the OH_n groups: whether they are isolated, or disturbed by dispersion forces of molecules of inert solvent or by hydrogen bonding. The OH stretching frequencies for these cases fall within the ranges 3750–3600, 3600–3500, and 3500–1900 cm^{-1} respectively. Hence the OH stretching vibrations exhibit a characteristic frequency in relation to intramolecular influences, but the characterisation is lost if the group takes part in the formation of a hydrogen bond, however weak.

Since the type of OH stretching vibration remains characteristic in any system[275], the reduction in its frequency when hydrogen bonding occurs can only be due to a decrease in the force constant of the OH bond. Hence the study of OH stretching vibration spectra *cannot give information on the type of* OH_n *group, but can provide information on intermolecular interaction and the nature of the atom* R_2. Let us consider in more detail what parameters of the system can be found from the OH stretching vibration spectrum.

In any investigation the first thing noted is the number of bands. If we have a compound with only one OH group we should expect only one band in the OH stretching region, but, in fact, without considering fortuitous superimposition of frequencies, there are considerably more.

The number of bands observed in the OH stretching region is increased because of (*i*) the presence of various types of association[52,53,188,252], (*ii*) the appearance of overtones strengthened by Fermi resonance and of frequencies of type $\nu_{OH} \pm \omega$, where ω is the frequency of intermolecular vibrations[118,206,207,231,237,238,276,277], and (*iii*) splitting of a band because of tunnelling by the proton[37,38,131,154,155,234,277–284]. The interpretation of the spectrum in the region of OH stretching vibrations therefore presents immeasurably more difficulty than its interpretation in the region of OH deformational vibrations.

Such difficulties can usually be met by using a suitable method. The presence of various types of association can usually be established by investigating the variation of the intensities of the bands with temperature[55,284–286] or concentration[52,162,188]. The first overtone of the deformational vibration of the water molecule and the component frequencies of type $\nu_{OH} \pm \omega$ are easily distinguished by comparison with the spectra of the corresponding deuterated analogues. These bands are very often found in the spectra, and recent studies have shown that their number, frequencies, and intensities

depend markedly on the symmetry of the crystal rather than on its chemical composition[167,201,231,237] (Fig. 5).

To show proton tunnelling in the compound under investigation and to assign the observed doubling of the bands to this cause it is necessary to obtain the infrared and Raman spectra of the compound and its deuterated analogue[283]. The potential barrier between the two positions of the proton can then also be determined.

Thus in almost every case the combination of infrared spectroscopy with some other method can be used to interpret the bands due to OH stretching vibrations. If the type of OH_n group is already known, the number of different types of association present in the given system can be found from the number of bands due to purely stretching vibrations of the OH group.

When the corresponding OH stretching frequencies have been found for any OH_n group, the variation of the intensity of these bands with temperature can be used to evaulate the hydrogen bond energy. Measurements made on different compounds have shown this energy to vary from 0.9 to 9.0 kcal mole^{-1} [55,161,162,284,285,287-290]; it increases with the proton-donating strength of the compound. Thus in the series $Ca(OH)_2$, $Mg(OH)_2$, $Ni(OH)_2$, $Al(OH)_3$, $B(OH)_3$, AlOOH the energy increases from 2.35 to 6.85 kcal mole^{-1}.[287] If the hydrogen atom of the hydrogen bond is replaced by deuterium the energy of the bond is slightly less[291-293]; for ice at 0°K the difference is 0.3 ± 0.14 kcal mole^{-1}.[291]

Of no less interest are the second derivatives of the potential energy of the hydrogen bond with respect to the various vibrational coordinates, or in other words the force constants. These values are needed for calculations on the spectra of systems with hydrogen bonding; they can be calculated if the vibrational spectra of all the deuterated analogues of OH_n groups and their geometry are known. For organic acids[20,294], hydroperoxides[167], and water[250,295] they are respectively 0.42, 0.38, and 0.22×10^6 cm^{-2}. Comparison of the force constants with the energy values given above shows that with the hydrogen bond, as with other types of bond, the force constant varies in the same sense as the energy of the bond. The bending force constants of the hydrogen bond have been found to be: for formic acid dimers[20] 0.06, for ice[296] 0.05, and for halide hydrates[250] $(0.2-0.4) \times 10^6$ cm^{-2}. These values were obtained by assuming a linear hydrogen bond, but this is a very doubtful assumption for crystal hydrates, and a more correct value would be about 0.05×10^6 cm^{-2}. The non-diagonal force constants of the hydrogen bond are[20] less than 0.03×10^6 cm^{-2}.

In addition to the force parameters, the OH stretching frequency can provide a fairly accurate estimate of the distance between the oxygen atoms (R_{OO}) in the O–H · · · O system; this is possible because a large number of investigations have been made seeking the relationship between the shift of the OH stretching frequency from its position in the monomer and the length of the hydrogen bond (R_{OO})[25,78,91,151,287,297-301]. Most of the curves obtained coincide for the main part, but individual curves show slight variations (Fig. 6). There is no analogous relationship for OH deformational vibration bands, firstly because there is no single relationship[246] between the band shift δ_{OH} and the distance R_{OO}, and secondly because while such a relationship is observed for certain compounds, the change of frequency δ_{OH} is generally too slight. Simple relationships have been established between the shift of the OH stretching band and the ionisation constant, electronegativity of the proton acceptor, and the Hammett constant[50,61,127,290,302-305], but as a rule these only relate to a single class of compound, and therefore are not of great significance in the analytical application of infrared spectroscopy.

As has just been shown, the vibrational spectrum of OH_n groups can be used to find the energy of the hydrogen bond, its rigidity (force constant) and its length (R_{OO}); in each case we use only the frequencies and intensities of the corresponding absorption bands. In Section II it was stated several times that when hydrogen bonding occurs the OH stretching bands are considerably broadened; this has long been known, and for some reason is now considered to be necessarily so. The falseness of this assumption is shown by cases[112,201,306] where absorption bands shifted by 400–300 cm^{-1} have a half-width of less than 70 cm^{-1} (Figs. 3 and 7); the usual half-width of bands in this region is more than 200 cm^{-1}. A particularly good example is the case of ice[201], for which the spectrum obtained at -80° and a fixed water vapour pressure depends on the method of its production (Fig. 3): the different modifications of ice produced by the different conditions at the time of freezing have very different spectra. This result demonstrates clearly that under identical experimental conditions a given compound will exhibit different spectra even if only the mutual disposition of its molecules is changed. A slight rearrangement of the molecules changes the number of bands observed, their half-widths, and the positions of their maxima, which again demonstrates the complex nature of band half-widths, but brings us no nearer understanding them.

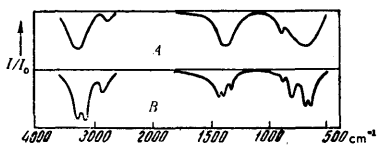


Fig. 5. Spectra of hydrogen peroxide[167] at 80°K: *A*) amorphous; *B*) crystalline.

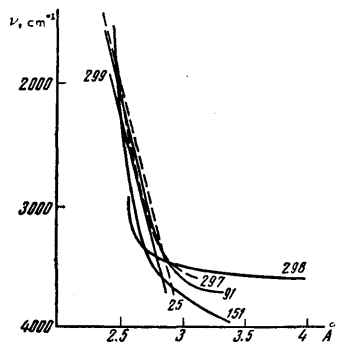


Fig. 6. Variation of the OH stretching frequency with the distance between the oxygen atoms, as obtained by different investigators: the numerals on the curves are the literature references.

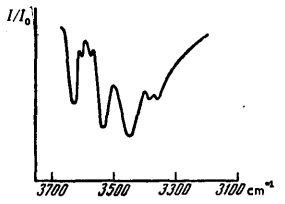
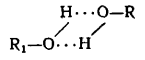


Fig. 7. Spectrum of aluminium hydroxide[112].

The spectroscopic study of compounds which form a hydrogen bond has established other relationships also. Thus it has been found that in most real systems the hydrogen bond is not linear; the O–H · · · O angle in these bonds[91,188,286,307-311], which are called conjugated, may reach 160°. Many investigators of the spectra of hydroxyl-containing compounds consider that two molecules of such a compound interact to form dimers with four-membered rings[52,55,162,188,286,289,296,312]:



Correct application of infrared spectroscopy is thus seen to provide considerable and varied information on the nature and interaction of the OH groups in the compound studied. The type of OH_n group can be found from the OH deformational frequency. The number of bands observed in the stretching frequency region can, in conjunction with information obtained by other methods, establish how many different OH^-, OH_2, and OH_3^+ groups are present in the given system. The OH stretching frequency can be used to find the length and energy of the hydrogen bond. All this information on the nature of the OH_n groups and their interaction is obtained from the number and frequencies of the observed absorption bands. Such important characteristics as the intensity and shape of the bands are not used at all, because no general relationship has yet been found between these properties and the intra- and inter-molecular parameters of the system under investigation. The finding of such a relationship will enable investigators to obtain new data on intermolecular effects.

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SYNTHESES AND REACTIONS IN THE CYCLOBUTANE SERIES

M. Yu. Lukina

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INTRODUCTION

A characteristic feature of the four-membered carbon ring is its instability, which is shown by the fact that in various reactions it readily undergoes isomerisation accompanied by a change in the carbon skeleton. This complicates syntheses in the cyclobutane series, since the preparation of even the simplest derivatives often requires complicated, roundabout routes in order to maintain the four-membered ring. Isomerisation of such a ring can involve not only enlargement and cleavage but also contraction to a three-membered ring.

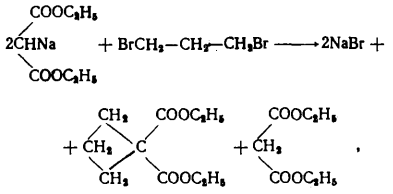
Isomeric changes in cyclobutane compounds have long attracted attention, and much work has been done on them. This field appears especially interesting in the light of recent work on the mechanism of isomerisation reactions. Such changes have been widely studied in cyclobutane compounds containing various functional groups, but very little work has been done on the hydrocarbons. This latter class of compounds has been altogether inadequately studied, probably owing to the difficulty of preparing cyclobutane hydrocarbons.

Several reviews have recently been published[1-5] on the synthesis and properties of various cyclobutane compounds, in which the hydrocarbons themselves do not receive much attention. Because of the abundance of miscellaneous information, it is not easy to obtain from these reviews an idea of the properties of the hydrocarbons, the difficulties in their preparation, or the advances which have recently been made in this direction. In the present review an attempt has been made to discuss in greater detail the chemistry of the cyclobutane hydrocarbons, and their synthesis, properties, and reactions. In order to give a more complete idea of the instability of the four-membered ring, the last section of the review will include an account of isomeric changes in cyclobutane derivatives covering the most recent work on this problem.

I. SYNTHESIS OF HYDROCARBONS OF THE CYCLOBUTANE SERIES

Hitherto most hydrocarbons of the cyclobutane series have been obtained from diethyl cyclobutane-1,1-dicarboxylate and its homologues, *via* the monocarboxylic acids, the alcohols, aldehydes, and ketones. The most difficult stage on the way to the hydrocarbons, usually involving low yields, is the first stage, the preparation of the initial ester.

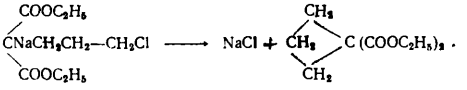
Diethyl cyclobutane-1,1-dicarboxylate was first obtained by Perkin[6] in 1887, by means of the reaction:



the yield of the ester being only 25%.

Many attempts have been described in the foreign literature to improve the yield in the Perkin's reaction, but they were unsuccessful, and the yield of the ester remained very low[7-11]. The authors of these papers were probably unacquainted with the published work of Russian scientists, who had succeeded in considerably improving the yields of the ester.

Thus Kizhner[12] modified Perkin's method as early as 1905, by replacing the 1,3-dibromopropane with 1-bromo--3-chloropropane. The different rates of reaction of the bromine and chlorine atoms in the latter compound with the sodium atom of the sodiomalonic ester result in the initial formation of 3-chloropropylmalonic ester, which then undergoes cyclisation:



By this method Kizhner obtained a 40% yield of diethyl cyclobutane-1,1-dicarboxylate.

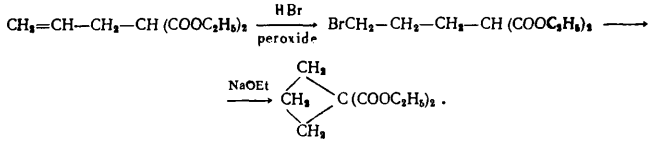
In 1941 Gol'mov and Kazanskii[13] undertook Kizhner's synthesis in two stages, and isolated the intermediate products. They found that, in the presence of sodium ethoxide, 3-chloropropylmalonic ester is readily converted (in 75–77% yield) into diethyl cyclobutanedicarboxylate. Consequently, the low yield in Kizhner's reaction is due, not to the difficulty of closing the four-membered ring, but to the great quantity of by-products obtained in the first stage of the reaction. Gol'mov and Kazanskii tried to find conditions which would increase the yield of the 3-chloropropylmalonic ester, and found that the use of 3 moles of malonic ester per mole of the bromochloropropane increases the yield of 3-chloropropylmalonic ester to 78.4% (compared with 52%). Thus carrying out the experiments in two stages raises the overall yield of diethyl cyclobutanedicarboxylate (based on the bromochloropropane) to 60%, which represents an increase by a factor of $1\frac{1}{2}$ compared with the yield in Kizhner's synthesis, and by a factor of $2\frac{1}{2}$ compared with Perkin's method.

Subsequently Gol'mov[14] studied the reaction of malonic ester with 1,3-dibromopropane, and found that varying the proportions of the reactants gave a considerable increase in yield. Thus he obtained a 70% yield of the ester by taking 4 moles of 1,3-dibromopropane and 4 moles of malonic ester per gramme-atom of sodium.

The last two methods, which show great improvements in the yield, have their disadvantages, since carrying out the reaction in two stages considerably lengthens the time required for the synthesis.

In 1949 Cason and Allen[15] described the preparation of cyclobutanedicarboxylic ester in 60% yield from malonic ester and 1,3-dibromopropane in one stage. In the opinion of Mariella and Raube[16], the ester obtained by this method contains about 14% of impurities, so they proposed a different method for its preparation, which gave a yield of about 55% of the unpurified ester or 43% of the pure ester[17]. This method hardly differs at all from that described by Kizhner.

An interesting process for obtaining the ester was suggested in 1949 by Walborsky[18]:



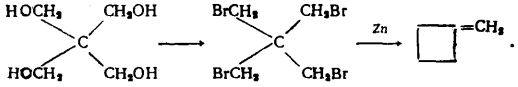
Diethyl allylmalonate was prepared in 80% yield by Linstead and Rydon's method[19], the overall yield of cyclobutanedicarboxylic ester being about 50% based on the diethyl allylmalonate.

Campbell and Rydon[20] suggested condensing the more reactive 1,3-diiodopropane with sodiomalonic ester, but the former substance must be synthesised specially, which considerably complicates the general method.

In conclusion we must consider the two-stage synthesis of diethyl cyclobutanedicarboxylate suggested in 1952 by Favorskaya and Yakovlev[21], the first stage of which takes place in absolute ether. The overall yield of the cyclic ester is here 80%, which far exceeds all the yields reported hitherto. The present reviewer, however, has been unable to reproduce this yield, and in many experiments carried out by this method the yield did not exceed 30%.

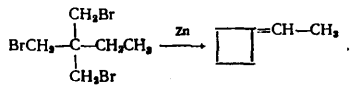
All the procedures reported above apply to reactions of malonic ester with dihalides in which both halogen atoms are attached to primary carbon atoms. The work of Ipat'ev[22] and of Kazanskii and Lukina[23] has shown that the course of the reaction is different when dibromides of different structure are used. The homologues of diethyl cyclobutanedicarboxylate can be used to prepare the corresponding disubstituted homologues of cyclobutane[24,25].

A great many investigations deal with another method of synthesising cyclobutane hydrocarbons, by the action of zinc dust on pentaerythritol tetrabromide[26]. This reaction, discovered by Gustavson[27], represents one of the simplest methods for obtained methylenecyclobutane from a readily available starting material:



The tetrabromide is usually obtained by the prolonged heating of pentaerythritol with a large excess of phosphorus tribromide[28]. Recently a new method has been suggested which considerably simplifies this synthesis[29].

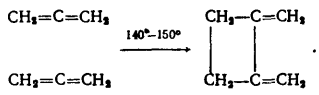
In a similar manner 1,1,1-trisbromomethylalkanes give good yields of alkenyl- and alkylidene-cyclobutanes[30,31]:



In all these syntheses, unfortunately, preparation of the initial polyhalogeno-compounds is associated with considerable difficulty.

In connection with this method of obtaining hydrocarbons, we must mention the work of Roberts and Sauer[32], who suggested many methods of converting methylenecyclobutane into cyclobutanol, cyclobutanone, and cyclobutane.

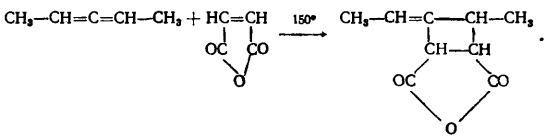
An interesting direction, in which new routes for the synthesis of cyclobutane hydrocarbons may be found, involves development of the dimerisation of allenes, discovered by Lebedev in 1911:[33,34]



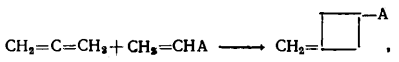
The low yields of the dimer reported by Lebedev and the difficulty of isolating it prevented this reaction from becoming in due course a preparative method for the synthesis of cyclobutane hydrocarbons.

In 1956 Blomquist and Verdol[35] succeeded in improving the method of dimerisation: they obtained an approximately 50% yield of the dimer, 1,2-dimethylenecyclobutane, by passing allene over glass beads heated to 500°–510°. The allene was prepared by the action of zinc dust on 2,3-dibromoprop-1-ene.

Another way of using allene was no less promising, consisting in its addition across a carbon–carbon double bond with the formation of cyclobutane and cyclobutene derivatives. In 1957 Alder and Ackermann[36] reported the addition of allenes to maleic anhydride. In the case of 1,3-dimethylallene a 60% yield of the adduct was obtained:

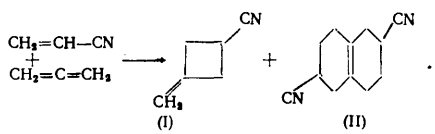


Shortly after this, Cripps *et al.*[37] published the first of a series of papers on the synthesis of substituted alkylidenecyclobutanes by the addition of allene to unsaturated compounds. They used this method to prepare methylenecyclobutanes containing a cyano, carboxy, alkoxycarbonyl, or aryl group in position 3:[38]



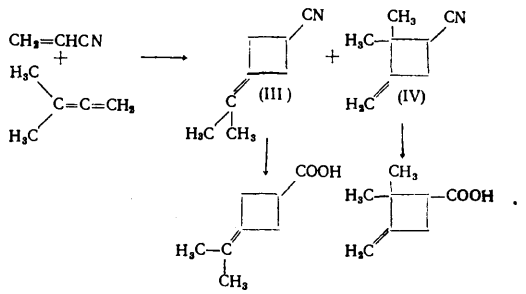
where A = CN, COOR, COOH, CHO, Ar.

Allene adds on especially smoothly to acrylonitrile, to give a cyclobutane derivative (I) and an octahydronaphthalene derivative (II):



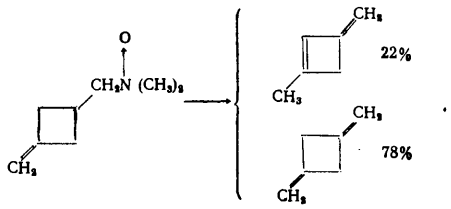
The reaction is carried out at 150°–250°, the maximum pressure during the reaction being about 4–4.5 atm. When a large excess of acrylonitrile is used, a 60% yield of I is obtained and a 15–20% yield of II. Under the conditions of the reaction the allene can undergo dimerisation to 1,2-dimethylenecyclobutane. The use of unsymmetrically substituted allenes in this reaction has shown that both double bonds can take part in addition with ring formation (cycloaddition).

Thus 1,1-dimethylallene reacts with acrylonitrile to give a 36% yield of 3-isopropylidenecyclobutyl cyanide (III) and 2,2-dimethyl-3-methylenecyclobutyl cyanide (IV). Alkaline hydrolysis of these compounds gives the corresponding acids, from which the hydrocarbons can be obtained:

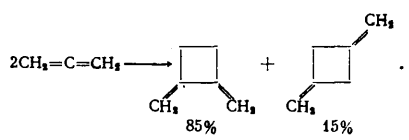


By using this method to obtain 3-methylenecyclobutyl cyanide, Caserio *et al.*[39] synthesised a series of 3-substituted methylenecyclobutanes.

At almost the same time, Williams and Sharkey[40] published the preparation of these same hydrocarbons by the pyrolysis of *NN*-dimethyl-3-methylenecyclobutylmethylamine oxide:



In the course of this work the interesting phenomenon was observed that heating the resulting mixture of hydrocarbons with a 10% solution of caustic potash in ethylene glycol produced a marked change in the relative proportions of the hydrocarbons. The product which was isolated consisted of 96% of 1-methyl-3-methylenecyclobutene and 4% of 1,3-dimethylenecyclobutane. Experiments which were then carried out on the dimerisation of allene showed that at 400° and atmospheric pressure the product is not pure 1,2-dimethylenecyclobutane, as would follow from the work of Lebedev[33] and of Blomquist and Verdol[35], but a mixture of 85% of this compound with 15% of the 1,3-isomer:

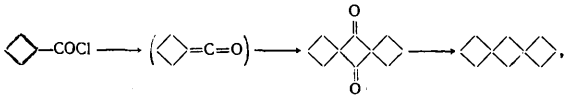


The process developed in this way permitted the preparation also of 3-isopropylidene-1-methylcyclobutene and 1,4,4-trimethyl-3-methylenecyclobutene.

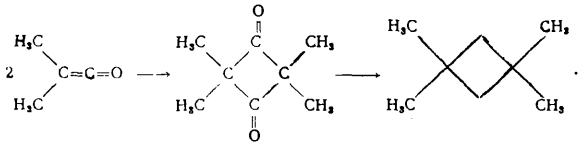
Migration of the double bond from the exocyclic position into the ring was observed also by Cripps *et al.*[41] in the action of excess of alkali on 3-methylenecyclobutane-1,2--dicarboxylic anhydride followed by acidification.

The above syntheses permitted for the first time familiarity to be gained with cyclobutane hydrocarbons containing double bonds in the side-chain or in the ring. It is easy to pass from these hydrocarbons to disubstituted saturated hydrocarbons.

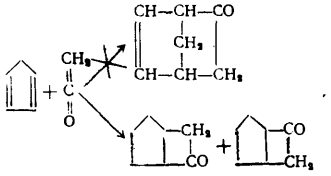
Another type of synthesis of hydrocarbons, which has been developed recently, appears to be of great interest. As early as 1912 Staudinger[42] found that ketoketens are able on standing to dimerise with the formation of substituted cyclobutane-1,3-diones. Buchman *et al.*[43] used this reaction to obtain a spiro-hydrocarbon according to the scheme:



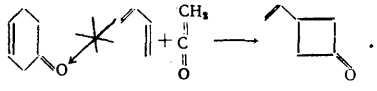
and also for the preparation of tetramethylcyclobutane[44]:



Staudinger also established that ketens are able to add on to a carbon–carbon double bond with the formation of cyclobutanones. Compounds containing conjugated double bonds can also undergo this reaction, diphenylketen being especially active in such reactions[45,46]. It was found that the addition of ketens to conjugated dienes never proceeds according to a diene synthesis mechanism:



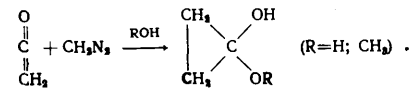
Vogel and Müller[47] have reported that keten reacts with butadiene to give a 66% yield of the 1,2-addition product, 3-vinylcyclobutanone:



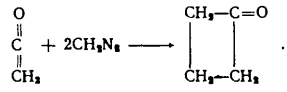
Reduction of the ketone by Kizhner's method gives vinylcyclobutane, from which ethylcyclobutane can be readily obtained. Application of this reaction to various dienes may provide wide opportunities for synthesising cyclobutane hydrocarbons of various structures.

Syntheses of cyclobutanone and its homologues (from which the hydrocarbons can be readily obtained) by the action of diazomethane on ketens are of great practical and theoretical interest. This reaction was discovered by Lipp and Köster[48] as long ago as 1931, but only recently have investigators paid more serious attention to it.

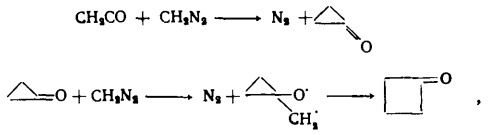
If keten is slowly run into an ethereal solution of diazomethane containing small amounts of methanol or of water, the hemiacetal or the hydrate of cyclopropanone is obtained in theoretical yield:



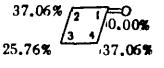
In the absence of water or alcohol, and with concentrated solutions of diazomethane at -70°, cyclobutanone is formed in 75% yield:



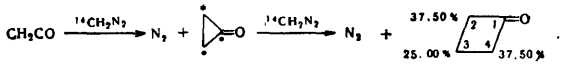
Lipp and Köster at first regarded this reaction as involving the intermediate formation of cyclopropanone:



but they later rejected this mechanism, since they considered it improbable that cyclopropanone would react smoothly with diazomethane in ether at -70°, while cyclobutanone would be stable under these conditions. In order to test the mechanism of this reaction, Semenow *et al.*[49] studied the reaction of keten with labelled diazomethane. The distribution of ^{14}C in the resulting cyclobutanone was

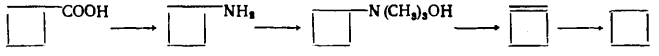


These results agree well with the hypothesis of the intermediate formation of cyclopropanone, from which cyclobutanone can be obtained equally probably by introducing a methylene group on either side of the carbonyl group:



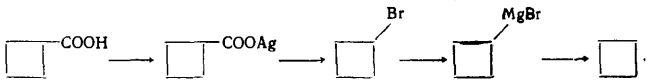
This equation gives the distribution of ^{14}C activity predicted for the intermediate formation of cyclopropanone. The high reactivity of this compound towards diazomethane may be associated, in the opinion of these workers, with the greater angular stress in a three-membered compared with a four-membered ring.

Kaarsemaker[50], using Lipp and Köster's method, obtained a 65% yield of cyclobutane by the Wolff–Kizhner reduction of cyclobutanone semicarbazone. Thus the overall yield of cyclobutane based on the diazomethane was 48%, which exceeded all yields of cyclobutane then available. Willstätter's method[51]

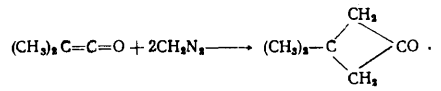


gives a 25% yield of cyclobutane based on cyclobutanemonocarboxylic acid, while the process more recently suggested

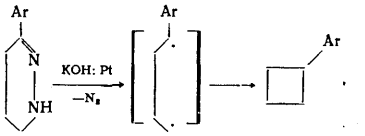
by Cason and Way gives a yield of about 40% based on the acid[52,53]:



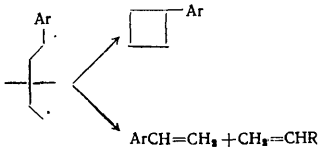
The reaction of substituted ketens with diazomethane may result in homologues of cyclobutane having the most varied structure. Thus Owen *et al.*[54] condensed diazomethane with dimethylketen and obtained 3,3-dimethylcyclobutanone:



A new method for the synthesis of arylcyclobutanes has been suggested by Levina *et al.*[55], who established that tetrahydropyridazines, the six-membered analogues of pyrazolines, on being heated in the presence of caustic potash and platinum to 250°–300°, decompose with the evolution of nitrogen and the formation of cyclobutane hydrocarbons:

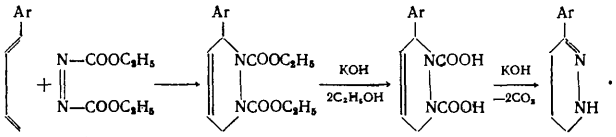


The intermediate diradicals undergo not only cyclisation to cyclobutane hydrocarbons but also cleavage with the formation of ethylenic hydrocarbons:

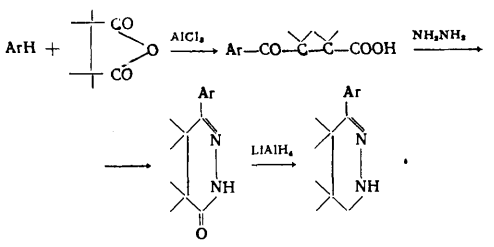


Sometimes the production of unsaturated hydrocarbons is the main reaction, and that of cyclobutane hydrocarbons a side-reaction. In the case of cyclobutylbenzene, its yield is 35%, while that of the styrene formed at the same time is 43%.

The applicability of the method was at first greatly restricted by the comparative difficulty of obtaining the starting materials for the synthesis, the tetrahydropyridazines. They were produced by hydrolysis accompanied by decarboxylation of adducts of diene hydrocarbons with diethyl azocarboxylate:



Recently Shabarov and his coworkers[56] have proposed a simpler method for synthesising 3-aryl-1,4,5,6-tetrahydropyridazines, from succinic anhydride:



By decomposing the corresponding tetrahydropyridazines they accomplished the first synthesis of *o*-, *m*-, and *p*-tolylcyclobutanes (in yields of 33.5, 20.5, and 32% respectively)[57], *o*- and *p*-methoxyphenylcyclobutanes (14.2 and 13.0%)[58], and also *p*-biphenylylcyclobutane (yield 41%)[56]. Unfortunately, this method cannot be used to obtain alkylcyclobutanes[59].

This brief survey of methods for synthesising hydrocarbons of the cyclobutane series shows that some progress has recently been made in this field. Comparatively simple routes for the synthesis of various hydrocarbons have already been developed. The chief difficulty is that at the present time the starting materials for these syntheses require special preparation, in several cases by a quite complicated path.

II. PROPERTIES OF HYDROCARBONS OF THE CYCLOBUTANE SERIES

I have given some information on the electronic structure of cyclobutane in a review of work on the structure of cyclopropane[60]. According to modern views, the four-membered carbon ring, like the three-membered ring, involves distortion of the valency angles with the accompanying change in bond hybridisation, which is, however, considerably less strongly marked in this case than in cyclopropane[61,62].

For a long time it was assumed that, like the three-membered ring, a four-membered ring is planar. In 1952 Dunitz and Schomaker[63] made an electron diffraction examination of cyclobutane, and found that the four-membered ring is not planar but represents either a dihedron with an angle of about 160° (Fig. 1), or an insufficiently rigid planar ring with oscillations of large amplitude out of the plane. It was found that the H–C–H angles in cyclobutane are 114° ± 8°, the length of the C–H bonds is 1.09 ± 0.04 Å, and the length of the C–C bonds 1.56 ± 0.02 Å, which exceeds that of the C–C bonds in cyclopropane and the mean carbon–carbon bond length in general.

A little later the non-planar structure of cyclobutane was confirmed by comparing entropy values obtained from experimental data (heat capacities and heats of transition) with those calculated for a planar model, and also by the infrared spectra and by the calculated energies of formation and of isomerisation[64].

Recently Bastiansen and his coworkers repeated the electron diffraction examination of cyclobutane and cyclopentane, and have published preliminary results[65]. Values obtained for internuclear distances in cyclobutane were C–C 1.548 ± 0.003 Å and C–H 1.092 ± 0.010 Å. Thus the C–C bond is shown to be longer in saturated four-membered rings than in open-chain alkanes (1.536 Å for ethane and 1.533 Å for butane), but substantially shorter than found by Dunitz and Schomaker[63]. The paper mentions that the



Fig. 1.

cyclic carbon skeleton of cyclobutane and that of cyclopentane are non-planar, but the deviations from planarity were not determined with sufficient accuracy in the preliminary stage of the investigation.

From Seubold's data the mean energy of dissociation of the C–C bonds in cyclobutane is estimated[66] to be 60 ± 3 kcal mole^{-1}.

Carter and Templeton[67] found that at 173°K cyclobutane has a body-centred cubic lattice with a unit cell containing two molecules, the lattice constant being $a = 6.06 \pm 0.03$ Å.

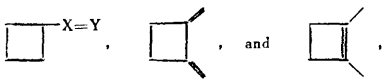
Several of the constants of pure cyclobutane have been determined accurately — vapour pressure[68], boiling point (285.7°K)[69], and melting point (182.43°K)[70].

Information on cyclobutadiene can be found in the recent review by Vol'pin[71], and therefore we shall not discuss it here.

Derfer *et al.*[72] studied the infrared spectra of several alkylcyclobutanes, and at the same time those of many cyclopropane hydrocarbons. Comparison of the spectra opened up the possibility of determining hydrocarbons of both types in mixtures.

Roberts and his coworkers[39] studied the infrared and ultraviolet spectra of 1,3-dimethylenecyclobutane and related compounds. Loeffler *et al.*[73] investigated the absorption spectra in the far ultraviolet of cyclobutene, 1-methylcyclobutene, and methylenecyclobutane. Lord and Rea[74] examined the infrared absorption spectra of liquid and gaseous cyclobutene and hexadeuterocyclobutene, as well as their Raman spectra.

In 1956 Wren[75] studied the ultraviolet spectra of several cyclobutane compounds of the types:



and compared them with those of derivatives of the type >–X=Y, in which, owing to the unsaturated character of the three-membered ring, the absorption bands are displaced to longer wavelengths (bathochromic effect) and the intensities of the characteristic frequencies are increased (hyperchromic effect). Wren did not observe these effects in five cyclobutane compounds, which were found to show an auxochromic effect, *i.e.* a diminution in intensity of the characteristic frequencies, which he attributed to the influence of the four-membered ring.

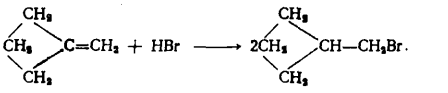
Aleksanyan and Sterin[76,77] examined the Raman spectra of sixteen alkylcyclobutanes and two unsaturated hydrocarbons of this series. The spectrum of isopropenylcyclobutane, a hydrocarbon having a double bond adjacent to the ring, showed no enhanced intensity of the characteristic frequencies such as was observed in the cases of isopropenyl- and vinyl-cyclopropanes. In other words, it would appear from the Raman spectra of isopropenylcyclobutane that there is no conjugation between the double bond and the four-membered ring, as in the cases reported by Wren.

Treshchova *et al.*[78] found that the intensities of the lines characteristic of the four-membered ring and of the benzene ring in the Raman spectra of several arylcyclobutanes are higher than in those of alkylbenzenes and alkylcyclobutanes. Hence it was concluded that conjugation exists between the two types of ring, although it is less strongly developed than in arylcyclopropanes.

As a result of advances in the synthesis of unsaturated hydrocarbons of the cyclobutane series, several papers have appeared on the behaviour of such hydrocarbons in various reactions. These investigations are comparatively rare, and are concerned mainly with the reactivity of the double bonds, not of the four-membered ring itself.

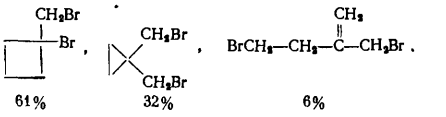
Thus Buchman and Howton[79] studied the Ziegler bromination of methylenecyclobutane, and found that reaction between *N*-bromosuccinimide and methylenecyclobutane in benzene in the presence of peroxides yielded a mixture of 14% of 2-bromomethylenecyclobutane and 56% of α-bromomethylcyclobutene. Cyclobutene under the same conditions gave 48% of 1,2-dibromocyclobutane and only 1% of 3-bromocyclobutene[80].

Krug *et al.*[81] reported the preparation of a 59% yield of bromomethylcyclobutane in the presence of a peroxide:

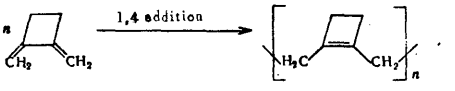


As was to be expected, this addition takes place contrary to Markovnikov's rule, and results in neither cleavage nor expansion of the ring.

Applequist and Roberts[82] obtained a mixture of dibromides by the reaction of methylenecyclobutane with bromine in carbon tetrachloride:



The properties of 1,2-dimethylenecyclobutane, studied by Blomquist and Verdol[83], proved to be of considerable interest. This hydrocarbon possesses two exocyclic double bonds conjugated through the cyclobutane ring, and very readily undergoes polymerisation. In this respect it resembles the previously investigated exocyclic dienes of the cyclohexane series[84]:

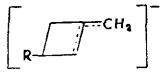


Emulsion polymerisation of dimethylenecyclobutane at 50° for 24 h gave a 100% yield of polymer. Analysis showed that the latter contained about 80% of the 1,4-addition product and 20% of the 1,2 product. The great readiness of 1,2-dimethylenecyclobutane to undergo polymerisation was confirmed by comparing its behaviour with that of 2,3-dimethylbuta-1,3-diene under these conditions. Dimethylenecyclobutane gave a 96% yield of polymer, while the open-chain diene gave only 13% under the same conditions. Furthermore, 1,2-dimethylenecyclobutane was very active in the Diels–Alder reaction, giving adducts with maleic anhydride and with *N*-phenylmaleimide.

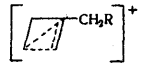
Applequist and Roberts[82] investigated the polymerisation of the compounds methylenecyclobutene (V), 3,3-dimethyl-4-methylenecyclobutene (VI), and 3′-methylenecyclobut-1′-enylbenzene (VII), which they had synthesised. Anionic polymerisation of all three hydrocarbons in the presence of sodamide and potassamide in liquid ammonia or of sodamide in benzene gives polymers of relatively low molecular weight. Radical polymerisation of V and VII takes place readily on standing in air, giving polymers of higher

molecular weight than in the first case. The compound VI shows less tendency to radical polymerisation. Cationic polymerisation of V under the influence of boron trifluoride goes extremely rapidly with formation of a polymer having the highest molecular weight.

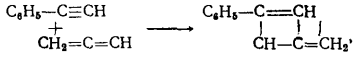
These investigators consider that anionic polymerisation involves the intermediate formation of an anion of the type



and cationic polymerisation that of a cation of the type



having a 1,3 π-bond. The possible existence of such a cation is supported by LCAO calculations. In this work 3′-methylenecyclobut-1′-enylbenzene was obtained in 1% yield by the reaction:



and 3,3-dimethyl-4-methylenecyclobutene from pinene *via* pinic acid.

Recently Shabarov *et al.*[85] have studied the behaviour of cyclobutylbenzene in several reactions, and have shown that, even under comparatively severe conditions, the four-membered ring of this hydrocarbon is stable in the presence of mercuric acetate (which readily cleaves a three-membered ring), and it also does not undergo alkylation in the presence of aluminium chloride.

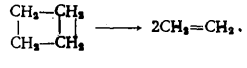
Nitration and acylation of cyclobutylbenzene resulted in substitution in the benzene ring, while the four-membered ring remained unchanged.

III. REACTIONS OF HYDROCARBONS OF THE CYCLOBUTANE SERIES

Cyclobutane and its homologues, like the alkanes, are inert towards most chemical reagents. The comparatively few papers which have been published on their reactivity are concerned mainly with thermal and catalytic reactions — decomposition, isomerisation, and hydrogenolysis.

(*a*) Thermal Decomposition and the Isomerisation of Hydrocarbons

Genaux *et al.*[86] in 1953 studied the thermal decomposition of cyclobutane, and found that at 420°–480° ethylene is formed:



Later Langrish and Pritchard[87] studied the kinetics of the thermal decomposition of equimolecular mixtures of $C_4H_8 + C_4D_8$ at 431°–485° and 0.7–36 mm Hg. Analyses were made with a mass spectrometer. No compounds of the type $C_2H_2D_2$ were detected among the decomposition products (ethylenes), which indicates that free radicals are not formed in the course of thermal decomposition. According to these workers, the latter is a purely unimolecular reaction. A similar conclusion concerning reaction order was reached by Srinivasan and Kellner[88] from a study of the thermal decomposition of 1,1,2,2-tetradeuterocyclobutane.

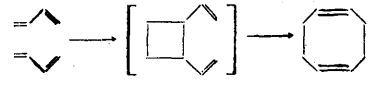
Cooper and Walters[89] showed that the four-membered ring is considerably less stable in cyclobutene than in cyclobutane. Thus they obtained buta-1,3-diene from cyclobutene at temperatures as low as 130°–175°. The reaction velocity was independent of the ratio of surface to volume of the reaction vessel and was unaffected by replacement of Pyrex glass by quartz, which indicates that the reaction is homogeneous in character. From the fact that additions of nitric oxide and propene have no inhibiting effect it was concluded that this reaction does not involve free radicals.

Subsequently Walters and his coworkers investigated the thermal decomposition of ethylcyclobutane[90], methylcyclobutane[91], propylcyclobutane[92], and *cis*-1,2-dimethylcyclobutane[93], and found that the rate of decomposition is increased by the introduction of methyl groups into cyclobutane. Thus at 430° methylcyclobutane decomposes more rapidly than cyclobutane by a factor of 1.5, and dimethylcyclobutane by a factor of 4.

The thermal decomposition of methylenecyclobutanes was studied by Drysdale *et al.*[94], who suggested that, since the weakest site in such compounds is the allyl bond, thermal cleavage may lead to the intermediate formation of one or two diradicals.

It can be concluded from the above work that the presence of a double bond in either the four-membered ring or a side-chain considerably diminishes the stability of the ring towards heat.

The thermal isomerisation of *cis*-1,2-divinylcyclobutane, accompanied by enlargement of the ring, was observed by Vogel[95] in an investigation of the mechanism of the formation of cycloocta-*cis*-1,*cis*-5-diene. He suggested that formation of this hydrocarbon by thermal dimerisation of butadiene in absence of a catalyst takes place by 1,2–1,2 addition with intermediate formation of *cis*-1,2-divinylcyclobutane:



Vogel assumed that, as a result of the interaction of the adjacent vinyl groups, divinylcyclobutane would be unstable, and pass into cycloocta-1,5-diene under the conditions of the reaction. In order to test this hypothesis, *cis*-1,2-divinylcyclobutane was synthesised, and was actually found to isomerise into cycloocta-*cis*-1,*cis*-5-diene at as low a temperature as 120°.

Little has been published on the catalytic isomerisation of hydrocarbons of the cyclobutane series. Ipat'ev and Tikhotskii[96] studied the isomerisation of methylenecyclobutane in the presence of alumina at 290°–300° and found that under these conditions the ring opened to form a diene, whose structure was not established.

Quite different results were obtained by Filipov[97] in experiments on methylenecyclobutane in the presence of aluminium oxide at 300°. According to his observations, almost complete isomerisation to methylcyclobutene took

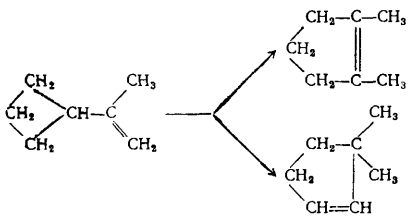
place. Doyarenko[98] studied the isomerisation of methylenecyclobutane over aluminium oxide at higher temperatures (400°–430°). Several reactions took place at the same time — isomerisation to isoprene, hydrogenation, dehydrogenation, and polymerisation. As a result, the reaction products were found to contain cymene, a rubberlike polymer, 2-methylbut-2-ene, propene, and gaseous products.

In 1929 Rozanov[99] investigated the isomerisation of methylcyclobutane in the presence of aluminium oxide and thorium oxide. The reaction products, identified solely by their boiling points, were pent-2-ene and 2- and 3-methylbut-1-enes.

The behaviour of hydrocarbons of the cyclobutane series under conditions favouring isomerisation was subsequently studied by Kazanskii, Lukina, and their coworkers[100,101]. All experiments were carried out in such a way that the stabilities of the four-membered and three-membered rings could be compared. It was found that, in the presence of all the catalysts producing isomerisation of the three-membered ring under comparatively mild conditions, the ring in alkylcyclobutanes was stable even at considerably higher reaction temperatures[100]. Even at 250° aluminium silicate produced no change in the constants of ethyl- and isopropyl-cyclobutanes, and kieselguhr caused no variation either at 150°, 300°, or 400°. It was only at 500° that the resulting product differed markedly in constants from the initial hydrocarbon, but such change can be attributed to the high temperature.

Under conditions of chromatographic adsorption analysis, even without additional cooling, the ring in alkylcyclobutanes, in contrast to that in alkylcyclopropanes, underwent no change. As a result, this method has been employed successfully for the purification of such hydrocarbons from contaminants[101].

The same workers found that cyclobutane hydrocarbons containing a double bond in a side-chain behave quite differently under isomerisation conditions[100]. Thus isopropenylcyclobutane on contact with silica gel at room temperature was completely isomerised with expansion to a five-membered ring:



These results agree well with the behaviour of pinene, which according to Arbuzov and Isaeva[102] isomerised to a mixture of bornane, *p*-mentha-1,8-diene, and *p*-mentha-1,4(8)-diene when an attempt was made to purify it by chromatographic adsorption on silica gel.

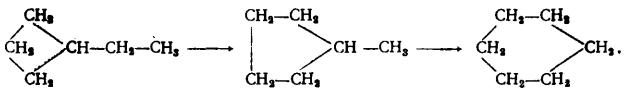
Subsequently Lukina, Kazanskii, and their collaborators showed[100] that, in the presence of kieselguhr at 200°, isopropenyl- and isopropylidene-cyclobutane are completely isomerised with the formation of the same mixture of unsaturated hydrocarbons of the cyclopentane series. The hydrogenated product of the isomerisation was a mixture of 1,2- and 1,1-dimethylcyclopentanes.

Both the catalysts investigated are able to cause migration of the double bond, and it can therefore be supposed that in both cases (isopropenyl- and isopropylidene-cyclobutane) the same unsaturated hydrocarbon had reacted.

It has thus been shown that the four-membered ring is considerably more stable than the three-membered ring under conditions of catalytic isomerisation. Only cyclobutane hydrocarbons containing a double bond in the substituent form an exception. In the presence of acidic catalysts, *i.e.* under conditions favourable to the formation of a carbonium ion, such hydrocarbons isomerise as readily as do alkylcyclopropanes.

Interesting results have been obtained from a study of the isomerisation of alkylcyclobutanes in the presence of more active catalysts. Turova-Polyak and Lukina[103] examined the isomerisation of ethylcyclobutane in the presence of aluminium chloride, the reaction conditions being chosen to permit comparison with the behaviour in this reaction of cyclopentane hydrocarbons, which had been studied earlier by Turova-Polyak and her coworkers[104–112]. The relative proportions of ethylcyclobutane and aluminium chloride were 3 : 1, and it was intended to carry out the reaction by prolonged boiling, as with cyclopentanes. However, the reactivity of the cyclobutane hydrocarbon was quite different: a vigorous exothermic reaction took place on contact with the aluminium chloride even at room temperature. Among the reaction products were detected methylcyclopentane and cyclohexane to the extent of 36–37% of the total. Isomerisation was accompanied by alkylation of the cyclohexane and polymerisation of the decomposition products of ethylcyclobutane with the formation of saturated hydrocarbon fractions of high boiling point.

In the view of these workers, the isomerisation of ethylcyclobutane takes place in stages:



Such a reaction mechanism is confirmed by the presence of methylcyclopentane among the reaction products, and this readily isomerises into cyclohexane, the most stable system under the experimental conditions. Thus it has been shown in this work that a four-membered ring is considerably less resistant to reaction with aluminium chloride than are five- and six-membered rings.

A little later this type of isomerisation was studied by Ipatieff† and his coworkers[113] with methyl-, ethyl-, and isopropyl-cyclobutane as examples.

Ipatieff *et al.*[114] described the reaction of methylcyclobutane with benzene in the presence of sulphuric acid, and found that here, as in the case of olefins and cyclopropanes[115,116], the benzene ring underwent alkylation. This was preceded by isomerisation of the four-membered ring under the influence of the sulphuric acid. However, these latter results are open to doubt, since the initial hydrocarbon used in the experiment was impure, the t-pentylbenzene (1.5 ml) which resulted from the reaction boiling over a range of 15°.

Summarising the little work which has been done on the reactions of cyclobutane hydrocarbons, we can conclude that cyclobutane and its homologues are quite stable towards

† Ipat'ev (Ed. of Translation).

heat and catalysts. The four-membered ring is considerably less stable in unsaturated hydrocarbons. In most cases the action of heat leads to cleavage of the ring, while the action of catalysts results in ring enlargement.

(*b*) Catalytic Hydrogenation of Hydrocarbons of the Cyclobutane Series

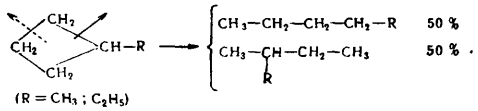
One of the most characteristic reactions of cyclobutane hydrocarbons is the catalytic addition of hydrogen with cleavage of the ring (hydrogenolysis). In 1907 Willstätter and Bruce [117] observed that, when cyclobutane is passed together with hydrogen over finely divided nickel at 180°, it is converted into n-butane. In 1911 Lebedev [118] showed that heating 1,2-diisopropylcyclobutane at 275° in hydrogen under a pressure of 100 atm results in opening of the four-membered ring. Later Rozanov [119] reported that, when methylcyclobutane is hydrogenated in the presence of freshly reduced nickel at 210°, isopentane is formed.

Raik [120,121] hydrogenated methyl-, ethyl-, and propyl-cyclobutane in the presence of platinised carbon, and found that fission of the C–C bonds of the four-membered ring starts at about 260°. In his view, the bond one carbon atom distant from that linked to the substituent undergoes rupture. As in all the previous work, quite primitive methods were used to analyse the reaction products in Raik's investigation. This casts doubt on his conclusions concerning the selective cleavage of the four-membered ring in this reaction.

The temperature limits of hydrogenolysis given by Raik are probably governed by the feeble activity of the catalyst, since the five-membered cyclopentane ring, which can be expected to be more stable, is already broken at 225° in the presence of platinised carbon [122].

Kazanskii, Lukina, and their collaborators [123-127] made a more detailed study of the hydrogenolysis of alkylcyclobutanes in the presence of platinised and palladised carbon. They established the temperature limits at which cleavage of the four-membered ring occurs with addition of hydrogen, and determined the way in which the ring breaks. They found that, in the presence of platinised carbon, hydrogenolysis begins at 150° and goes to completion at 250°. [123]

On palladised carbon a rather higher temperature (290°) is required for hydrogenolysis [127]. Cleavage of the four-membered ring on both catalysts takes place in all possible ways, with the formation of approximately equal quantities of isomeric alkanes:



In the case of isopropylcyclobutane, the bond farthest from the substituent was broken to a rather greater extent than the adjacent bond [125].

The hydrogenolysis of disubstituted homologues of cyclobutane — the 1,3-dimethyl and 1-ethyl-3-methyl derivatives — was also examined under comparable conditions [123]. They were found to undergo hydrogenolysis at approximately the same rate as the monosubstituted cyclobutane hydrocarbons.

The stabilities of the three-, four-, and five-membered rings to hydrogenolysis have been compared by hydrogenating ethylcyclopropane, methylcyclobutane, and cyclopentane in the presence of the same specimen of platinum catalyst [124].

The reactions of hydrocarbons of the cyclobutane series are of considerable interest because they provide an opportunity of assessing the stability of the four-membered ring in compounds containing no atoms other than carbon and hydrogen. Moreover, the investigations can be carried out with hydrocarbons which can be obtained comparatively easily in a high state of purity.

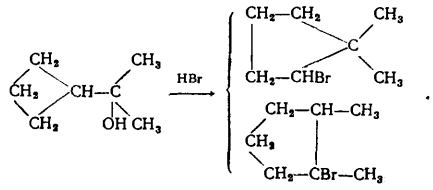
However, a study of the literature on a wider range of cyclobutane compounds shows that the information given here cannot completely characterise the stability of the four-membered ring and also give an idea of the changes in the carbon skeleton accompanying isomerisation. As already mentioned in the introduction, isomeric changes have been studied mainly with cyclobutane derivatives containing functional groups. The survey given below of work on this problem will enable a more correct idea to be obtained of the four-membered ring.

IV. ISOMERIC CHANGES IN SOME DERIVATIVES OF CYCLOBUTANE

(*a*) Isomerisation with Ring Enlargement

Among the early investigations in this field was Kizhner's work on isomeric changes in tertiary alcohols of the cyclobutane series. He first synthesised cyclobutyldimethylcarbinol as starting material for the preparation of cyclobutane hydrocarbons, but the properties of this compound at once attracted his attention, since under various conditions the alcohol is converted with exceptional ease into a cyclopentane derivative [128-130].

Thus heating cyclobutyldimethylcarbinol with excess of fuming hydrobromic acid gave a mixture of two bromocyclopentanes:



Gaseous hydrogen iodide already gave analogous derivatives at 0°, whereas at 200°–210° it produced more profound isomerisation, yielding 1,2-dimethylcyclopentane contaminated with a little methylcyclohexane.

The action on cyclobutyldimethylcarbinol of oxalic and dilute sulphuric acids [131], and also of acetic anhydride, produced isomerisation to 2,2-dimethylcyclopentanol. Similar isomerisation occurred with cyclobutyldiethylcarbinol [132]. It was only in the case of cyclobutyldiphenylcarbinol [133] that dehydration with oxalic acid was not accompanied by isomerisation, the product of the reaction being a cyclobutane hydrocarbon.

Chavanne and Chiurdoglu [134] used toluene-*p*-sulphonic and formic acids as dehydrating agents, and in both cases observed enlargement of the cyclobutyldimethylcarbinol ring to a five-membered ring.

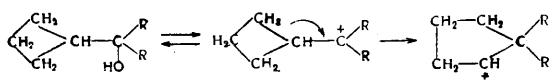
At a later date Favorskaya and Yakovlev published a series of papers[135-138] on the reaction of tertiary cyclobutane alcohols with dilute hydrochloric and sulphuric acids. They studied the behaviour in this reaction of cyclobutyldiisopropylcarbinol and of the corresponding ethyl-, methyl-, and isopropyl-phenyl derivatives. From a comparison of their results with those of Kizhner, they concluded that the tendency of the alcohol to isomerise is diminished on replacement of an alkyl by an aryl radical. Thus in the cases of cyclobutylethyl(and methyl)phenylcarbinols the four-membered ring was preserved on dehydration with hydrochloric and sulphuric acids.

With increase in size of the alkyl radical the direction of the reaction changed, and in the case of cyclobutylisopropylphenylcarbinol, as with cyclobutyldiisopropylcarbinol, isomerisation took place, with or without dehydration depending on the conditions of the reaction.

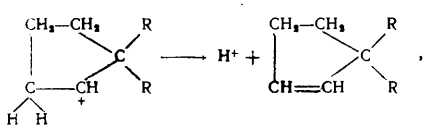
Not only tertiary but also primary and secondary alcohols of the cyclobutane series are characterised by a tendency to isomerise under the influence of acidic reagents. Dem'yanov[139] studied the changes undergone by cyclobutylcarbinol on treatment with oxalic and sulphuric acids, and Tatevosyan *et al.*[140] those undergone by the secondary alcohol, cyclobutylmethylcarbinol.

All these investigations show that acidic reagents are unsuitable for the conversion of cyclobutylcarbinols into the corresponding cyclobutane hydrocarbons, as in all these cases isomerisation with ring enlargement takes place to give cyclopentane derivatives.

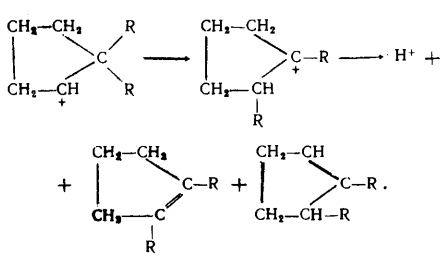
The changes undergone by cyclobutane alcohols under the influence of acidic reagents can be represented by the general formulae



Stabilisation can occur either by transfer of an electron pair to the electron-deficient carbon atom without migration of a proton:

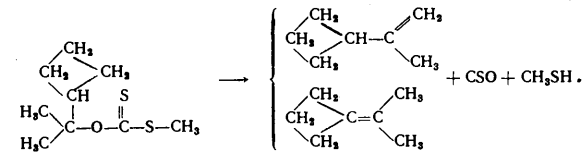


as a result of which a multiple bond is formed; or by capture of the electron pair together with the alkyl group from the adjacent carbon atom:



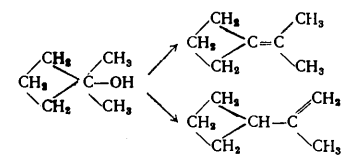
As early as 1936 Kazanskii[141] succeeded in dehydrating cyclobutyldimethylcarbinol without changing the carbon skeleton, by pyrolysis of the xanthate (Chugaev's method).

A low yield of a mixture of hydrocarbons was obtained as follows:



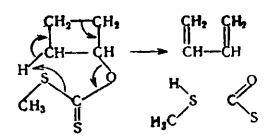
In 1953 Ipatieff and his coworkers[142] dehydrated the alcohol by heating it with phenyl isocyanate. A mixture of unsaturated hydrocarbons was obtained, hydrogenation of which gave isopropylcyclobutane. These workers assumed that the reaction involves the formation of phenylurethane, the mechanism of whose decomposition is similar to that suggested by Hückel *et al.*[143] for the Chugaev reaction.

Kazanskii *et al.*[144] obtained the corresponding unsaturated hydrocarbons of the cyclobutane series (in 75–90% yield) by boiling the alcohols with a few drops of concentrated sulphuric acid and simultaneously distilling off the products of dehydration:

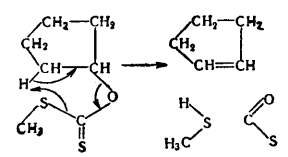


This method was used to dehydrate cyclobutyl-dimethyl-, -ethylmethyl-, and -diethyl-carbinols[145]. Under these conditions alcohols or hydrocarbons containing a five-membered ring are not formed at all.

Cyclobutanol behaves in a very interesting manner under conditions of dehydration. In an attempt to dehydrate it in the presence of aluminium oxide at 360°–390°, Doyarenko[146] obtained a mixture of propene and butadiene. Roberts and Sauer[32] tried to use the Chugaev method for the dehydration, but here, too, almost pure buta-1,3-diene was obtained:



On the other hand, when this method was applied to cyclopentanol, a 70% yield of cyclopentene was obtained:

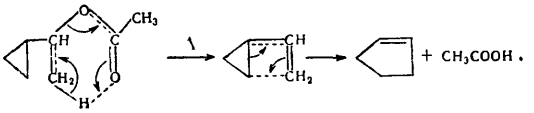


In the view of these workers[32], the cyclobutane ring undergoes fission during pyrolysis of the xanthates.

It is probable that pyrolysis does not always result in fission of the four-membered ring. Thus Overberger and Borchert[147] observed a new thermal rearrangement, accompanied not by fission but by enlargement of the ring, in the pyrolysis of acetates containing small rings. They showed that the main pyrolytic product of 1-cyclopropylethyl acetate was cyclopentene, and that 1-cyclobutylethyl acetate gave cyclohexene. It is interesting that in the case

of 1-cyclopentylethyl acetate enlargement of the ring was not observed, the normal reaction product, vinylcyclopentane, being obtained.

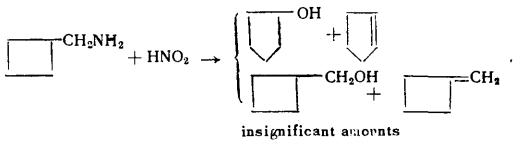
Pyrolysis was carried out at 500°–510°. It was assumed that, in the case of 1-cyclopropylethyl acetate, cyclopentene was formed mainly from vinylcyclopropane:



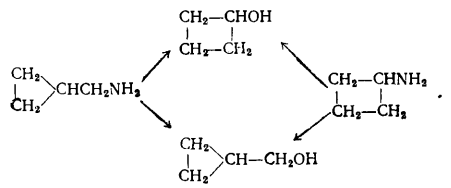
In order to test this hypothesis, vinylcyclopropane in acetic acid was subjected to pyrolysis under identical conditions, when 40% of it was converted into a mixture of 95% of cyclopentene and 5% of penta-1,4-diene. This rearrangement is especially interesting in that here the ring is enlarged by two carbon atoms instead of by only one.

(*b*) Isomerisation Accompanied by Ring Enlargement, Contraction, and Cleavage

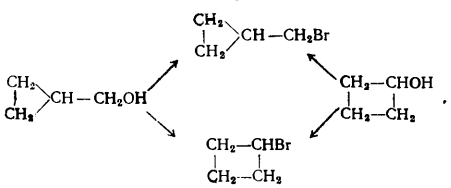
In 1903 Dem'yanov [148,149] found that the main product of the action of nitrous acid on cyclobutylmethylamine was a mixture of alcohols and hydrocarbons consisting predominantly of cyclopentane derivatives:



This remarkable discovery led Dem'yanov to make a broad study of the action of nitrous acid on cyclic amines [150]. In the course of this he disproved the results of Perkin [151] and of Dalle [152] on the synthesis of cyclobutanol and of cyclopropylcarbinol by the action of nitrous acid on the corresponding amines. He showed that in fact both cyclopropylmethylamine and cyclobutylamine yield a mixture of the above two alcohols on treatment with nitrous acid [153]:



Dem'yanov isolated both alcohols in the pure form, and made a thorough study of their properties. It was later found that a similar isomerisation of a three-membered into a four-membered ring, and conversely, takes place in other reactions as well. For example, cautious treatment of both alcohols with hydrobromic acid gives a mixture of cyclobutyl and cyclopropylmethyl bromides:



Dem'yanov concluded from this investigation that ring enlargement occurs when a CH_2NH_2 or CH_2OH side-chain is present. When the amino- and hydroxy-groups are attached directly to a cyclic carbon atom, the ring size is always maintained.

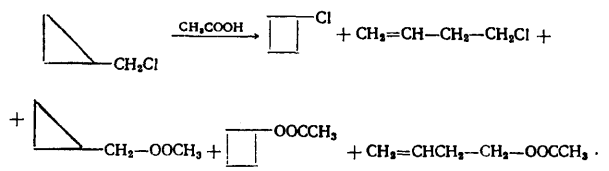
More recently, Smith and McKenzie extended these observations, and showed that treatment of cyclopropylcarbinol with phosphorus tribromide yields a bromide which reacts with magnesium and carbon dioxide to give pent-4--enoic acid [154]. According to the observations of Bruylants [155] and also of Favorskaya and Fridman [156], cyclopropyldimethylcarbinol reacts with hydrogen chloride to form 5-chloro-2-methylpent-2-ene, which passes back into the carbinol on hydrolysis.

A systematic study of this most interesting phenomenon was begun by Roberts and his coworkers in 1945, and has continued to the present time [157–165].

Studying the synthesis and properties of compounds having small rings, Roberts found that most reactions of cyclopropylmethyl‡ and of cyclobutyl derivatives having a carbonium ion type of mechanism yield the same mixtures of reaction products, independently of whether the starting material contains a three-membered or a four-membered ring. In his opinion this is due to the astonishing ease of intramolecular changes in cyclobutyl and cyclopropylmethyl derivatives which is observed in reactions of a certain type. Roberts and his collaborators observed such changes in the vapour-phase chlorination of methylcyclopropane, in reactions of cyclopropylcarbinol with thionyl chloride and Lucas's reagent, in the reactions of cyclopropylmethylamine, cyclobutylamine, and but-3-enylamine with nitrous acid [161,164], in the hydrolysis and acetolysis of cyclopropylmethyl and cyclobutyl chlorides, and in Grignard reactions with cyclopropylmethyl halides [157,158]. Among all the reactions investigated, it was only in the reaction of but-3-enol with thionyl chloride, the vapour-phase chlorination of cyclobutane in the light, and Grignard reactions of but-3--enyl and cyclobutyl halides that internal rearrangement was not observed.

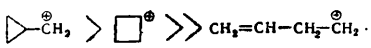
Roberts and Mazur's investigation [157,159] of the solvolysis of cyclopropylmethyl chloride was especially interesting. They prepared it by the photochemical chlorination of methylcyclopropane. Solvolysis of the chloride with acetic acid and several other solvents showed it to be extremely reactive. Thus the rate constant for the solvolysis of cyclopropylmethyl chloride in 50% aqueous ethanol exceeds the constant for cyclobutyl chloride by a factor of 27, and the constant for methylallyl chloride by a factor of 40 (allyl chloride itself did not react at all at this temperature).

These results were unexpected, since secondary halides usually undergo solvolytic reactions more readily than primary halides. It was also observed that solvolysis was accompanied by internal rearrangement of the cyclopropylmethyl chloride to form a 1.7 : 1 mixture of the less reactive cyclobutyl and but-3-enyl chlorides (on acetolysis). The products of acetolysis were cyclopropylmethyl and cyclobutyl acetates in the proportions 2.6 : 1, perhaps contaminated with small amounts of but-3-enyl acetate:



‡ The Russian reviewer felt it desirable to retain Roberts' "carbinyl" nomenclature, but in the translation this has been replaced by standard nomenclature (Ed. of Translation).

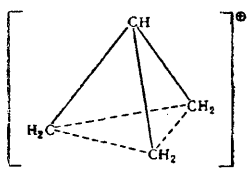
From the comparative solvolytic reactivity of cyclobutyl, cyclopropylmethyl, and but-3-enyl halides, the stability sequence of the corresponding carbonium ions is probably



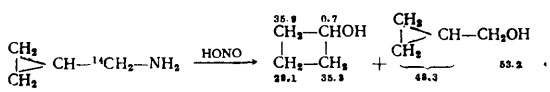
The composition of the products of carbonium-ion reactions accompanied by interconversions could have been expected on the assumption that classical cyclopropyl and cyclobutyl cations were formed as intermediates, between which equilibrium was established very rapidly. However, this hypothesis cannot explain the unusual tendency to solvolysis of both cyclopropylmethyl and cyclobutyl derivatives. Indeed, although the reactivity of compounds containing a three-membered ring can be explained by the diminution in stress in the transition state of solvolysis due to the direct formation of a cyclobutyl cation, this explanation cannot be applied to the reactivity of compounds containing a four-membered ring if they do not directly form but-3-enyl cations. This possibility is excluded by the fact that but-3-enyl derivatives have been observed only in small quantities as products of an irreversible reaction.

The ease of interconversion of cyclobutyl, cyclopropylmethyl, and but-3-enyl derivatives, together with the abnormal tendency of cyclopropylmethyl chloride to undergo solvolysis, to rearrange into isomeric chlorides, and to form rearranged solvolysis products, led these investigators to the view that such reactions involve the formation not of classical carbonium ions but of a common cationic intermediate compound [159,160].

Such an intermediate compound should embody the structural features of cyclopropylmethyl, cyclobutyl, and but-3-enyl cations, and was at first assumed to be a non-classical symmetrical cation of the following structure



the so-called "tricyclobutonium" ion, in which all three methylene groups are completely equivalent. In such a cation all the carbon atoms employ ordinary sp^3 orbitals for bonding. The three special sp^3 orbitals of each methylene group are arranged so that they overlap, as shown above, forming a stable molecular orbital (Fig. 2). The equivalence of the methylene groups in the intermediate cation must inevitably result in an equal probability of isotopic distribution when the reactions are carried out with labelled atoms. In order to demonstrate the mechanism of these reactions, therefore, labelled cyclopropylmethylamine was deaminated. Analysis of the reaction products showed that, although the degree of isotopic redistribution was very large, the methylene groups did not achieve complete equivalence:



In later papers, Roberts and his coworkers [161,162] therefore suggest that the intermediate product in such reactions

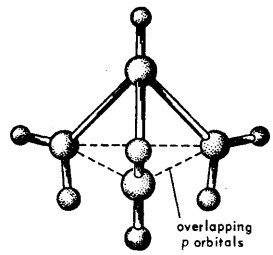
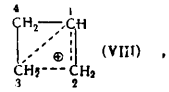


Fig. 2.

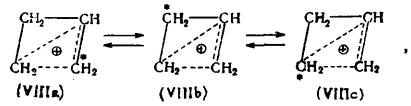
may be an unsymmetrical dicyclic cation of the type VIII, the so-called bicyclobutonium ion



(VIII),

which can be represented geometrically as in Fig. 3.

If the reaction is carried out with a compound containing a labelled methylene group, the existence of three possible labelled bicyclobutonium ions can be represented as follows:



(VIIIa) (VIIIb) (VIIIc),

equilibrium between which is established rapidly but not instantaneously. The less uniform isotopic distribution when the reaction between cyclobutanol and thionyl chloride is carried out in the presence of butylamine in ethereal solution shows that this medium does not favour the establishment of equilibrium. Under better ionisation conditions, equilibrium is reached more rapidly, and this is shown in a more uniform isotopic distribution.

Closer consideration of these structures showed that VIIIa and VIIIb can readily change one into the other, whereas the reversible conversion of VIIIa and VIIIb into VIIIc is difficult. It is possible that the reversible interconversion of the ions VIIIb and VIIIc involves the intermediate formation of the pyramidal tricyclobutonium cation.

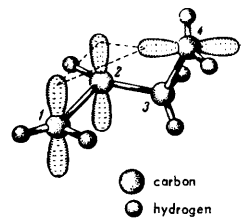
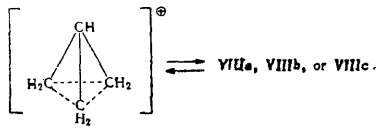


Fig. 3.

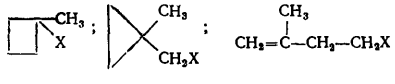
Since this is symmetrical, it can pass with equal ease into VIIIa, VIIIb, or VIIIc:



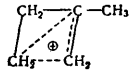
Thus the tricyclobutonium cation can be regarded as a possible intermediate in internal rearrangements.

Roberts' work agrees well with the views of Winstein and his coworkers on intramolecular rearrangements in allyl derivatives [166,167]. Thus the latter workers postulate the possibility of a common intermediate compound in the solvolysis and intramolecular rearrangement of 1,2-dimethylallyl chloride.

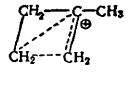
In the bicyclobutonium ion (VIII) the positive charge is distributed among the positions 1–3. On attack by a nucleophilic reagent in these positions, cyclobutyl, cyclopropylmethyl, and but-3-enyl compounds are formed respectively. The proportions of these products in irreversible carbonium-ion reactions led Roberts and his coworkers to the conclusion that the positive charge in VIII is equally distributed among $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$. It was assumed, however, that any disturbance of this balance, produced, for example, by substitution of a methyl group in one of these positions, might lead to profound changes [163–165]. Examination of systems of the type



showed that in this case the intermediate compound is no longer a cation of the type



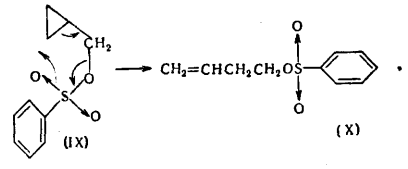
but the non-classical cation



in which the positive charge is no longer completely delocalised, the ion being preferentially located at the tertiary carbon atom. Work on these lines is still being continued by the same investigators.

Several other workers, besides Roberts and his collaborators, have investigated the mechanism of isomerisation, and the views held by the various investigators have not always coincided with those discussed above. Thus in 1952 Brown and Borkowski [168] prepared cyclopropylmethyl chloride by the liquid-phase chlorination of methylcyclopropane, and determined its rate of solvolysis in 80% ethanol. The products thus obtained were not examined, and the reaction was classified as of the first order. These workers cast doubt on the possibility of solvolysis being accompanied by other reactions, as had been found earlier by Roberts.

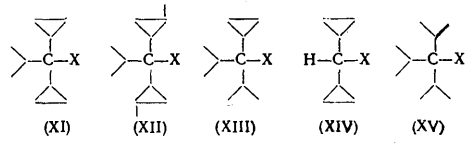
Almost simultaneously Bergstrom and Siegel [169] found that pure cyclopropylmethyl ethyl ether is formed in the solvolysis of cyclopropylmethyl benzenesulphonate (IX) in absolute alcohol. They also found that, on treatment with anhydrous potassium carbonate at 20° for 24 h, the sulphonate is 90% isomerised into a mixture comprising mainly but-3-enyl benzenesulphonate (X). These workers assumed that X can be formed by intramolecular rearrangement as follows:



On the basis of these results, which agreed well with Brown's observations quoted above, the latter completely rejected [170] the mechanism of solvolysis suggested by Roberts and Mazur. In his opinion the solvolysis of cyclopropylmethyl derivatives is not accompanied by rearrangement with intermediate formation of a classical carbonium ion. The products of rearrangement isolated by Roberts and Mazur [157] arose, in Brown's view, because the chloride used was impure.

The isomerisation of cyclopropylmethyl benzenesulphonate (IX) has recently been examined afresh by Denney and Kupchik [171] using ^{18}O, and these workers completely reject Bergstrom and Siegel's mechanism.

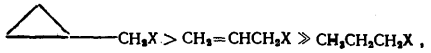
In connection with Brown's work, Caserio *et al.* [162] repeated in 1960 the earlier experiments of Roberts and Mazur [157], using nuclear magnetic resonance spectra to study isotopic distribution, and gas–liquid chromatography to analyse the products of solvolysis. The earlier results were fully confirmed, which casts doubt on Brown's data, and gives grounds for concluding that the mechanism of carbonium-ion reactions suggested by Roberts is the most plausible.



where X represents (a) OH, (b) p-$OCOC_6H_4NO_2$, (c) OCH_3.

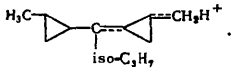
Hart and Sandri [172] published an interesting paper on the solvolysis of the p-nitrobenzoates of various cyclopropylcarbinols, their aim being to find out why the rate of solvolysis of cyclopropylmethyl derivatives is greater than that of the corresponding allyl compounds. They were also interested in the behaviour of tertiary systems in this reaction, since until then solvolysis had been studied only with primary and secondary compounds. For this purpose they synthesised the p-nitrobenzoates of the series of carbinols XIa–XVa, and subjected them to solvolysis in aqueous or methanolic dioxan solution at various temperatures. The rate of solvolysis was determined by titration of the p-nitrobenzoic acid liberated. For solvolysis in 80% aqueous dioxan at 60° the following relative rates were obtained: XVb 1, XIVb 60.7, XIIIb 246, XIb 23 500, and XIIb 124 000.

These workers consider that the reason for the greater rate of solvolysis of cyclopropylmethyl compared with the corresponding allyl derivatives:

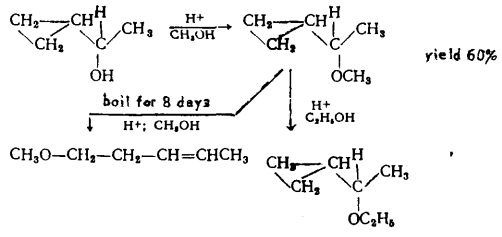


is that the positive charge remaining on the carbon when X is ionised is retained better by the cyclopropyl than by the vinyl group. According to their results, the rate of solvolysis increases on replacement of an isopropyl by a cyclopropyl group, a second three-membered ring increasing the rate to almost the same extent as the first.

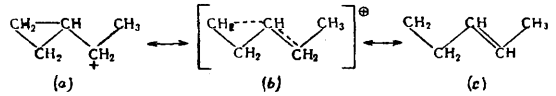
Two methyl substituents in the cyclopropyl group increase the rate of solvolysis fivefold. This increase is too great to be an inductive effect transmitted through the saturated bonds to the tertiary carbon atom in XIIb. Hart and Sandri therefore explain this effect by hyperconjugation involving the three-membered ring, and represent the transmission of the induction effect through the ring thus:



The behaviour of cyclopropylmethylcarbinol in carbonium-ion reactions has been described by Pearson and Langer[173], who carried out a series of reactions based on the scheme:



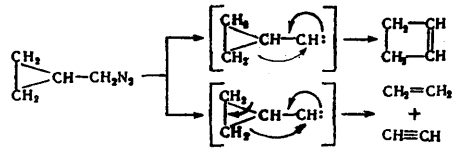
and found that no rearrangement occurred in cyclobutane derivatives. Formation of the allyl derivative required quite severe conditions. These workers explain their results, and also those reported earlier by Dem'yanov[174] and by Bruylants[155], by the intermediate formation of a carbonium ion (*b*):



The severe conditions required for the conversion of a cyclopropylmethyl into an allyl derivative indicate, in the opinion of Pearson and Langer, that the resonance form (*b*) is present to only a small extent, because the positive charge in (*b*) is located on a primary carbon atom.

New rearrangements, leading to the interconversion of cyclopropane and cyclobutane derivatives, have been reported quite recently by Friedman and Shechter[175], who studied the decomposition of diazohydrocarbons to carbenes. These workers[176] had previously found, as had also Powell and Whiting[177], that tosylhydrazones of aliphatic aldehydes and ketones react with alkalis in aprotic solvents to form diazo-compounds, which are able to undergo thermal decomposition to carbenes with loss of nitrogen and formation of olefinic and cyclopropane compounds.

On application of this reaction to cyclopropanal tosylhydrazone (*p*-tolylsulphonylhydrazone), the cyclopropyldiazomethane resulting from reaction of this substance with sodium methoxide in diethyl Carbitol (3,6,9-trioxaundecane) or *N*-methylpyrrolidine at 180° is converted with ring enlargement into cyclobutene (60 or 67%), with disruption of the carbon skeleton into ethylene (13 or 10%) and acetylene (13 or 10%), and with opening of the ring into buta-1,3-diene (4.5 or 7%):

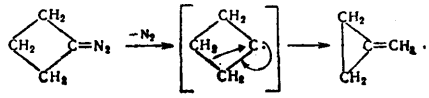


Whether the butadiene is formed directly by decomposition of the tosylhydrazone or as a result of decomposition of the cyclobutene was not established. According to these observations, methylenecyclopropane is not formed at all.

The formation of cyclobutene in this reaction is the first example of rearrangement of a carbon skeleton involving expansion of the ring in a simple carbene system.

The ability of cyclopropylcarbene systems to undergo rearrangement with ring enlargement was confirmed in the reaction of the tosylhydrazone of cyclopropyl methyl ketone in diethyl Carbitol in the presence of alkali, when the products were 1-methylcyclobutene (in 92% yield), vinylcyclopropane (1%), isoprene (2%), propyne (2%), and ethylene (3%).

The decomposition of cyclobutanone tosylhydrazone in diethyl Carbitol or in *N*-methylpyrrolidine to give a carbene involves contraction of the ring, giving methylenecyclopropane (79 or 80%), migration of hydrogen forming cyclobutene (18 or 20%), and also buta-1,3-diene (2–1%):



The decomposition of cyclopentanone tosylhydrazone gives a 94% yield of the normal reaction product, cyclopentene.

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The published information surveyed above is evidence of the extreme instability in many chemical reactions of a cyclobutane ring containing functional groups.

The interest of these isomeric changes lies especially in the fact that the strained four-membered ring passes easily not only into the unstrained five- and six-membered rings but also into the more strained three-membered ring as well as into open-chain derivatives. Thus various reactions described above are often common to cyclopropane and cyclobutane derivatives. It is for this reason that in most cases investigators are interested in both series of compounds, *i.e.* in the whole field of small rings.

From a comparison of the information on the isomeric changes in hydrocarbons and in derivatives of the cyclobutane series, it can be concluded that, in the case of the hydrocarbons, by no means all questions have been exhausted whose solution could shed additional light on isomeric changes in three- and four-membered rings.

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MODERN VIEWS ON THE MECHANISM OF THE CATIONIC POLYMERISATION OF VINYL MONOMERS

B. L. Erusalimskii

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I. INTRODUCTION

Since the basic principles of the theory of cationic polymerisation were laid down in monographs dealing with the general chemistry of polymers [1-5] and in review articles [6-8], in particular Pepper's outstanding review [6], there have been many new publications which have barely found mention in the more recent review literature [9,10]. Moreover, many recent investigations have broadened the earlier concepts and make it necessary to review the existing theories on the mechanism of formation, propagation, and termination of chains in cationic polymerisation. The present review is intended to focus attention on these studies. The existence of the earlier sources (especially Pepper and Plesch [6,8,9]) covering the literature extremely fully makes a long introduction unnecessary here, and we limit ourselves to the following brief notes.

Because of the considerable individuality of each polymerisation system, it is impossible to set out a universal mechanism for cationic polymerisation such as is possible for polymerisation by a radical mechanism. Nevertheless, there are some features of cationic polymerisation which are general. The initiation step can be formulated in terms of equations:

for acid catalysis

$$HX + \overset{|}{C}{=}\overset{|}{C} \rightarrow H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C^+}} + X^-, \qquad (1)$$

for catalytic complexes of the proton-donor–Lewis acid type such as $BF_3.H_2O$

$$H^+[AB]^- + \overset{|}{C}{=}\overset{|}{C} \rightarrow H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C^+}} + [AB]^-. \qquad (2)$$

and for catalytic complexes of the carbonium ion-donor–Lewis acid type such as $SnCl_4.C_4H_9Cl$

$$R^+[AX^-] + \overset{|}{C}{=}\overset{|}{C} \rightarrow R{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C^+}} + [AX]^-. \qquad (3)$$

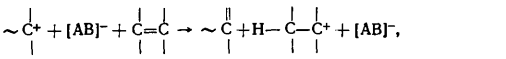
The most widely held view is that the monomeric cations formed by one of these reactions and the growing macrocations are not kinetically independent entities, but exist as ion–counterion pairs held together by electrostatic forces. The growth of the chain is then considered as the entry of a monomer molecule into the interaction zone of the components of such pairs:

$$\sim\overset{|}{C^+} + [AB]^- + \overset{|}{C}{=}\overset{|}{C} \rightarrow \sim\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C^+}} + [AB]^-.$$

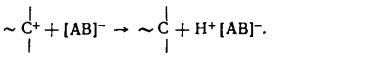
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The universality of this theory was open to doubt[6] and was disproved by later work which showed that free macrocations could exist under certain conditions[11-13]. However, the concept of the growing chain as an ion pair is more general, particularly with media of moderate polarity.

The most important feature of the process under review is the absence of kinetic termination as a necessary and unavoidable step in the reaction. In the overwhelming majority of cases the growing chains are terminated either by transfer of the chain to the monomer:

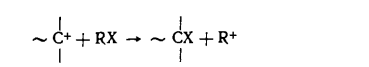


or by regeneration of the catalytic complex:

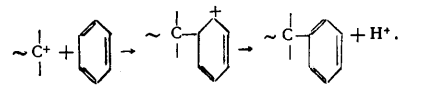


The role played by these reactions at the normal temperatures for radical polymerisation, *i.e.* 20°–30° above room temperature, is so great that the production of high-molecular-weight polymers by cationic polymerisation under these conditions is practically excluded. A substantial reduction of temperature causes, in Pepper's phrase[6], "freezing out" of these processes, and so increases the degree of polymerisation. In radical polymerisation lowering the temperature increases the chain length only in the limited temperature range where a reduction in the contribution of the reaction involving chain transfer to the monomer predominates. Transition to a lower temperature necessarily decreases the molecular weight of the polymer because of increased chain termination in comparison with chain propagation, as is clearly shown, for example, in the radical polymerisation of vinyl acetate[14].

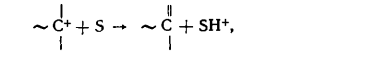
In the presence of a solvent or other additive other types of chain transfer are possible (see Plesch[8] for more detail), of which the most important are apparently anion capture[15]:



and alkylation of an aromatic nucleus by the growing chain[16,17]:



Chain transfer by proton transfer:



the low probability of which was noted by Plesch[8], must be considered, for example, in systems such as $SnCl_4$–styrene–vinyl acetate, where the known transfer of the chain to vinyl acetate[18] can hardly be explained by any other mechanism.

Suppression of chain termination and transfer steps in cationic polymerisation by lowering the temperature sometimes increases the overall rate of the process as well as the degree of polymerisation. In some systems the rate constant for chain propagation in cationic polymerisation has comparatively little temperature dependence[19], but may vary considerably with the nature of the reaction medium[20-22]. In a polar medium a marked increase in the dielectric constant together with a reduction in temperature can even make the rate constant of the propagation reaction vary inversely with temperature[19], which is apparently one of the reasons for the often observed negative value of the overall activation energy of the low-temperature cationic polymerisation of various monomers[2,6,23].

In this review we shall consider mainly work relating to the fundamental steps of cationic polymerisation, generally of isobutene, monomers of the styrene series, and vinyl ethers, on which most of the fundamental investigations have been made.

II. FORMATION AND NATURE OF ACTIVE CENTRES

For a long time the greatest problem in the mechanism of initiation of cationic polymerisation, if initiation by protic acids is ignored, was the problem of co-catalysis. After the discovery of co-catalysis in the polymerisation of isobutene in the presence of boron fluoride and traces of water[24,25], there was a tendency to extend this type of mechanism to other systems, where, however, it cannot always be proved. It was long thought that with certain monomer–catalyst pairs the presence of a co-catalyst is not essential for cationic polymerisation, but work is still being published which proves the opposite. An example is the styrene–aluminium chloride system, for which the co-catalytic action of water and the absence of polymerisation in absolutely dry conditions have been very recently established by Jordan[26], who had previously assumed that initiation took place in this case through a monomer–catalyst complex without the participation of a co-catalyst[27]. Sinn and coworkers[28] have recently shown that H_2O or HCl must be present as co-catalysts in the polymerisation of various monomers under the influence of alkyl aluminium halides†. Particular difficulties arise with a process carried out in a polar medium, where the observed acceleration effects can be ascribed to the increase in the dielectric constant as well as to the co-catalytic action of the solvent. Closely related to this is the question of the actual nature of the catalytic complexes, and hence of the initiating ions, which is often in doubt.

The known cases of initiation of cationic polymerisation can be divided into the following types, distinguished by the components of the primary initiating ions: (a) the catalyst (without participation of the monomer); (b) a catalytic complex of catalyst and co-catalyst (without participation of the monomer); (c) catalyst + monomer; and (d) a catalytic complex of catalyst and co-catalyst + monomer.

Initiation by protic acids (1) belongs to the first type, and initiation by complexes of Lewis acids with proton donors (2) or (if the process takes place in media of sufficiently high polarity) with alkyl halides (3) to the second. The third type includes the polymerisation of monomers which can act as co-catalyst, that is vinyl ethers and oxygen- and nitrogen-containing compounds which are not vinylic: oxides, carbonyl derivatives, cyclic imines, etc. Polymerisation under the influence of catalyst–monomer π-complexes also belongs to this type. The fourth type is characteristic of polymerisation in media of low dielectric constant, in which ionisation of the catalytic complexes is only possible with participation of the monomer as well. Polymerisation under the influence of iodine in polar media where, according to Eley and Richards[29], I^+ ions are produced by the bimolecular reaction

$$2I_2 \rightleftarrows I_3^- + I^+, \qquad (4)$$

† It has also been established that these monomers (isoprene, styrene, etc.) do not polymerise under the influence of complex Ziegler catalysts if all traces of moisture are excluded[28].

in which one of the iodine molecules fulfils the function of co-catalyst, can be related to the second type. In non-polar media the possibility of formation of primary ions *via* iodine–monomer π-complexes must be considered, as suggested by Gantmakher and Medvedev[30]:

$$2MI_2 \rightleftarrows MI^+ + I_3^- + M.$$

This classification has been made possible mainly by recent investigations, amongst which those of Colclough and Dainton[31–35] on the polymerisation of styrene in various media under the influence of stannic chloride deserve mention. They were able to distinguish clearly between the effects of co-catalysis and acceleration of polymerisation due to the polarity of the medium. Using highly purified monomer and solvents, they showed that in CCl_4 and nitrobenzene, which have very different dielectric constants (2.2 and 36.0 respectively‡), reaction proceeds only in the presence of added co-catalysts. Water and alkyl halides are suitable in nitrobenzene, and only water in CCl_4. The reason for this difference must be that the complexes formed between the catalyst and an alkyl halide, *i.e.* compounds of the type $RSnCl_5$, require a certain minimum dielectric constant for their ionisation, and they remain unionised in CCl_4 solution. On the other hand the catalytic complex formed in the presence of water, which is thought to be trichlorostannic acid monohydrate, is able to ionise in CCl_4. From the order of the rate of polymerisation with respect to the monomer, it follows that in the latter case the monomer takes part in the formation of the initial active centres, *i.e.* in the ionisation of the catalytic complex (5), while in nitrobenzene the ionisation proceeds without the participation of the monomer (6):

$$\text{rate of polymerisation in carbon tetrachloride } K[M]^2[C], \quad (5)$$

$$\text{rate of polymerisation in nitrobenzene } K[M][C]. \quad (6)$$

Thus the large difference in the rates of polymerisation in these two media is wholly explained by the difference in their polarities.

The absence of co-catalytic influence in nitrobenzene makes it useful as a medium for evaluating the relative activities of certain alkyl halides as co-catalysts: dichloroethane was found to have an activity of only 0.007 of that of t-butyl chloride[35]. Despite this, in the absence of nitrobenzene and any specially introduced co-catalysts, polymerisation in dichloroethane proceeds at a definite, reproducible rate, which is of second order with respect to the monomer. Hence a high concentration of a polar agent, even if its dielectric constant is relatively low (ϵ of dichloroethane is 10.4), ensures ionisation of the catalytic complex formed from it; the monomer must, however, participate in the ionisation step. Comparison of the polymerisation of styrene under the influence of the $SnCl_4$–t-C_4H_9Cl system in nitrobenzene and dichloroethane shows the overall rate of the process to be lower in the second case by a factor of 70, which was thought to be due to a lower rate of initiation. This cannot be considered an incontrovertible conclusion, however, since recent data indicate that the polarity of the medium has a very considerable influence on the rate constant of the propagation reaction in cationic polymerisation[20–22]. The corresponding values will be given below.

‡ Here and later the values of ϵ are taken from Ref. 23 if no other reference is given.

The features of the process proceeding under the influence of RCl–$SnCl_4$ complexes in the various media, as established by Colclough and Dainton, can be represented by the following equations:

in nitrobenzene

$$RCl + SnCl_4 \rightarrow R^+SnCl_5^- \xrightarrow{M} RM^+ + SnCl_5^-.$$

in dichloroethane

$$RCl + SnCl_4 \rightarrow RSnCl_5 \xrightarrow{M} RM^+\ SnCl_5^-.$$

These results confirm Pepper's earlier suggestions[6,36] of the possible co-catalytic action of alkyl halides and the associated deduction that polymerisation is initiated by the carbonium ion of the catalytic complex (as by the proton produced from complexes incorporating the hydroxyl-containing co-catalysts water, alcohols, and acids). Direct proof of this mechanism of initiation was obtained by Kennedy and Thomas[37], who established the presence of labelled carbon in polyisobutylene formed under the influence of aluminium chloride in labelled methyl chloride. Since in cationic polymerisation the chain transfer and termination processes can occur only by capture of an anion by the growing chain or by expulsion of a proton from it, the appearance of labelled carbon in the polymer can only occur in the initiation step. The formation of the primary ions is formulated as follows[37]:

$$^{14}CH_3Cl + AlCl_3 \rightleftarrows {}^{14}CH_3^+[AlCl_4]^- \rightleftarrows {}^{14}CH_3^+ + [AlCl_4]^-.$$

These workers later suggested[15] that the labelled carbonium ion might be produced by the reaction

$$\sim\overset{|}{\underset{|}{C}}{}^+[AlCl_4]^- + {}^{14}CH_3Cl \rightleftarrows \sim\overset{|}{\underset{|}{C}}Cl + {}^{14}CH_3^+[AlCl_4]^-,$$

but from the point of view with which we are here concerned this does not affect the essential features of the mechanism.

Initiation by a carbonium ion is also possible in another type of system, in which polymerisation takes place under the influence of Lewis acid etherates. Eley[38] showed that when boron trifluoride etherate is used, the initiating agent is the $C_2H_5^+$ ion; this was also demonstrated later[39], using labelled atoms, in the polymerisation of vinyl ethers with $BF_3.O(^{14}C_2H_5)_2$. The detection of labelled carbon in the polymer indicates that the initiation process is

$$^{14}C_2H_5^+[BF_3.O^{14}C_2H_5]^- + CH_2{=}CH(OR) \rightarrow {}^{14}C_2H_5CH_2{-}\overset{+}{C}H(OR)[BF_3.O^{14}C_2H_5]^-.$$

It may be assumed that in the absence of added co-catalysts the initiation of polymerisation of vinyl ethers proceeds in an analogous manner, *i.e.* by way of the etherate formed by the monomer itself:

$$BF_3O(R)CH{=}CH_2 \rightarrow R^+ + [BF_3{\cdot}OCH{=}CH_2]^-. \quad (7)$$

It has also been suggested that with vinyl ethers the sources of the initial active centres are catalyst–monomer π-complexes[40] and not the coordination complexes (7). There is no doubt that such π-complexes can be formed; their existence has been proved experimentally in systems containing iodine[20,21,41], stannic chloride[41,42], and trichloroacetic acid[43] as catalysts for the polymerisation of vinyl ethers and styrene monomers. However, most workers have rejected the idea of initiation by π-complexes, which has been considered for the systems iodine–vinyl ethers[44], titanium tetrachloride–styrene[19,45] and isobutene[46], and aluminium chloride-styrene[26]. In a recent study Okamura and coworkers[20] dealt with this question in the iodine-catalysed polymerisation of various monomers, and suggested that the formation of a π-complex should be

included as a separate fundamental stage in the usual mechanism of cationic polymerisation. They established the existence of π-complexes in the systems which they studied: they investigated the possible types of initiation, and found that the observed kinetics would fit mechanisms in which monomer–catalyst π-complexes either did or did not participate in the initiation. In calculating the rate constant for chain propagation, however, they took the second alternative, clearly considering it the more probable. It must be emphasised that iodine-containing systems can hardly be considered suitable for evaluating the role played by π-complexes, since the co-catalytic effect produced by the catalyst itself (4) very probably occurs in such systems, and this could mask the weaker effect due to π-complexes. For this reason, the initiating action of the latter can only become evident in systems where other catalytic effects are precluded.

The concept that cationic polymerisation can occur with a particular type of initiation involving monomer–catalyst π-complexes is due to Gantmakher, Medvedev, and co-workers[47,48], who studied the stannic chloride polymerisation of various monomers[47,49-51]. From the donor–acceptor properties of catalyst and monomer, they concluded that the catalyst in solution in the monomer is present as a π-complex, and that initiation occurs by reaction of this complex with another molecule of monomer, which produces an ion pair[47,48]. The kinetics of the separate polymerisation of styrene[30] and isoprene[49] and of the polymerisation of styrene in the presence of small amounts of more active monomers in the $SnCl_4$–C_2H_5Cl system[40,51-53] have been considered on the basis of initiation mechanisms involving a π-complex. The observed sharp increase in the rate of initiation when small amounts of isoprene, isobutene, or α-methylstyrene are added to the styrene is ascribed to the formation of π-complexes of various compositions and hence of varying activity. This is in agreement with the absence of accelerated polymerisation when small amounts of H_2O or HCl are added, since these are more active than the monomers in their complexing action on the catalyst. Higashimura and Okamura[54] assume the formation of active centres by direct reaction between catalyst and monomer in the stannic chloride polymerisation of styrene in benzene solution; they have shown the existence of an induction period even when the reagents are very pure. It is significant that the induction period is less in the presence of a previously polymerised reaction mixture, but the rate and degree of polymerisation are the same as in its absence. The participation of the π-complex $SnCl_3OH.H_2O.CH_2{=}CHC_6H_5$ in the initiation has been used[35] to explain the observed third order kinetics (with respect to monomer) of styrene polymerisation in the $SnCl_4$–H_2O–CCl_4 system, where the monomer is thought to participate in the ionisation

$$M\cdot SnCl_3OH\cdot H_2O + M \rightarrow HM_2^+[SnCl_3(OH)_2]^-.$$

Zlámal and Kazda[55] have said that aromatic monomers can act as co-catalysts in cationic polymerisation.

Pepper has remarked[9] that in systems containing ethyl chloride the formation of a catalytic complex with the solvent cannot be excluded, since the activity of ethyl chloride, despite its low dielectric constant, may be sufficient to produce ionised complexes§.

The difficulties associated with theories of the mechanism of initiation of cationic polymerisation in the presence of alkyl halides become apparent when several systems of this type are compared. Thus the papers previously cited[32-35] indicate that the stannic chloride polymerisation of styrene in alkyl halides proceeds at dielectric constants as low as 7, as demonstrated for reaction in CCl_4–$C_2H_4Cl_2$ mixtures. On the other hand, the titanium tetrachloride polymerisation of styrene[19] or even such an active monomer as isobutene[46] in methylene chloride solution will only proceed in the presence of water, *i.e.* the alkyl halide, of dielectric constant 8.9, cannot here act as co-catalyst. The possibility of initiation of cationic polymerisation in alkyl halides without these acting as co-catalysts must therefore be borne in mind. The effect of the properties of the medium on the influence of various agents which might act as co-catalysts has also been noted[56]; thus the addition of HCl increases the rate of polymerisation of styrene in the $SnCl_4$–C_2H_5Cl system, but reduces it if the reaction is carried out in a less polar solvent (cyclohexane).

When we come to consider initiation of polymerisation by complexes involving water and other oxygen-containing compounds, we find that these can form a number of adducts with metal halides, unlike alkyl halides, which usually give 1:1 complexes¶. These adducts may differ considerably in their catalytic activity, as was shown long ago for BF_3[6] and more recently for $SnCl_4$,[35] $AlCl_3$,[11] and $TiCl_4$.[12] As we noted above, Colclough's studies[32,35] show that the actual catalytic agent in the styrene–$SnCl_4$–H_2O–CCl_4 system is trichlorostannic acid monohydrate, while the stannic chloride mono- and di-hydrates, which are also present, are almost inactive. This is shown by the existence of a maximum on the curve relating the rate of polymerisation to the concentration of water in the region corresponding to the ratio $H_2O:SnCl_4 = 2$, and by the gradual increase in the rate before it reaches the maximum value.

It is assumed that the reaction

$$SnCl_4\cdot 2H_2O \rightarrow SnCl_3OH\cdot H_2O + HCl$$

takes place during this period, and that the reduced rate of polymerisation is due to formation of HCl†. The initiation process yields the unionised monomer complex $M.SnCl_3OH.H_2O$, which forms with a second monomer molecule the first active centre capable of further propagation, $HM_2^+[SnCl_3(OH)_2]^-$. From the absence of an induction period with the same system in dichloroethane, it is thought that initiation is here accomplished by the dihydrate, but with participation of the monomer in the formation of the primary polymerisation centres:

$$SnCl_4\cdot 2H_2O + M \rightarrow HM^+ + [SnCl_4OH]^- + H_2O.$$

Overberger and coworkers showed[58] that in the same system in the presence of nitrobenzene the maximum rate in a solvent consisting of 30% nitrobenzene and 70% CCl_4 corresponds to $H_2O:SnCl_4 = 1$. They take the initiating agent here to be stannic chloride monohydrate.

Zlâmal[11] has established the presence of four catalytic complexes of different compositions, with the general formula $nAlCl_3.mROH$, where R is an alkyl (from methyl

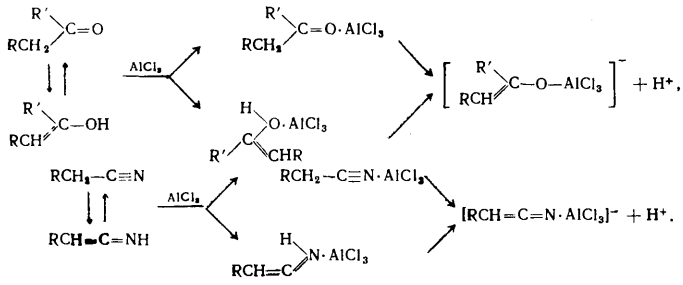
§ Pepper[9] quoted a value for the dielectric constant of C_2H_5Cl which was low, it was later shown[22] to be 10.

¶ Zlâmal and Ambrož showed[57] that higher complexes such as RAl_2Cl_7 may be formed in Lewis acid–alkyl halide systems.

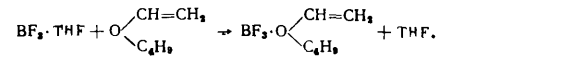
† Under the given conditions HCl as initiator gives only low-molecular-weight products, and this effect is almost unobservable dilatometrically.

to butyl). In each instance the 1:1 complexes were the most active in the polymerisation of isobutene dissolved in ethyl chloride. Zlámal and Ambrož[57] found a similar effect with a large number of different oxygen-, sulphur-, and nitrogen-containing compounds: in the polymerisation of isobutene under the influence of complexes of aluminium chloride with aldehydes, ketones, esters, water, hydrogen sulphide, acetonitrile, and other compounds the 1:1 complexes showed the greatest catalytic effect. The difficulty in interpreting these data is that in such systems a change in the co-catalyst:catalyst ratio not only yields a complex of new composition, but also permits an actual change in the role of the co-catalyst. Beyond a certain ratio, usually 2 or 3, the latter becomes a termination agent, as is particularly well known for water and alcohols. The same is said to be the case with the above-mentioned compounds[57]. The double action of agents of this type (methanol, organic acids) was noted by Higashimura and Okamura[59] in the stannic polymerisation of styrene. The dependence of the efficiency of a system on the concentration of one component of the catalytic complex does not always therefore have a unique interpretation. This is particularly clearly seen when considering the relationship between the composition of the complex and the degree of polymerisation, which will be dealt with in the following section.

The nature of the ions produced from these complexes was not considered, but the ionisation is more readily visualised as due to the expulsion of a proton than of a carbonium ion:



These mechanisms have not been verified experimentally, and are based solely on the observed initiation of cationic polymerisation by the catalyst–co-catalyst pairs. On the other hand, the absence of styrene polymerisation in the presence of the complex formed between boron fluoride and tetrahydrofuran (THF)[60] shows just as clearly that the BF_3.THF complex does not ionise under the conditions used (30° in benzene solution). Since this complex does produce polymerisation of vinyl butyl ether, it is concluded that the initiation is preceded by an exchange reaction between the initial complex and the monomer:



It is a curious fact that tetrahydrofuran can itself be polymerised under the influence of BF_3.THF to a polymer of molecular weight up to 400 000, but this requires a catalyst concentration at least 5% of the monomer[61].

In addition to the well-known arguments in favour of these polymerisation processes proceeding through cations as intermediates (nature of the catalysts, the nucleophilic character of the monomers, inhibition by anions, etc.), there have recently been direct proofs of their existence. Previously ions could only be identified in certain model systems, such as the $(C_6H_5)_2C=CH_2-BF_3.H_2O$ pair[2], but not under polymerisation conditions, so that the actual nature of the monomeric ions had not been confirmed by direct experimental facts. Jordan and Treloar[62,63] used a spectroscopic method to establish the presence of $\sim CH_2\overset{+}{C}HC_6H_5$ ions in the aluminium chloride or stannic chloride polymerisation of styrene in dichloroethane and carbon tetrachloride. They also concluded that in the sulphuric acid polymerisation of styrene the primary monomeric ions $CH_3\overset{+}{C}HC_6H_5$ are converted, because of the presence of water, into $CH_3(C_6H_5)CHOH_2^+$ ions, the basis for their conclusion being the proximity of the absorption bands of a solution of styrene in sulphuric acid to those obtained with 1-phenylethyl alcohol, which ionises in accordance with the equation

$$CH_3(C_6H_5)CHOH + H_2SO_4 \rightleftarrows CH_3(C_6H_5)CHOH_2^+ + HSO_4^-.$$

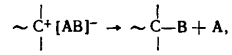
Metz[64] studied the conductivity of the styrene–$SnCl_4$–$C_2H_4Cl_2$–CCl_4 system and established the presence of ions only when catalyst and monomer are both present. This effect illustrates the kinetic results[35] referred to above regarding the participation of the monomer in the ionisation of the catalytic complex in media of low polarity.

The results investigated indicate that the study of the mechanism of initiation of cationic polymerisation should be considered not so much from the point of view of establishing a general approach to any system, but rather of establishing the limits within which a given type of excitation applies, to the case under investigation.

III. PROPAGATION AND LIMITATION OF CHAIN GROWTH

Most of the questions which arise when considering the propagation and termination of chains in cationic polymerisation are associated with the question of the actual nature of the growing chain, which may take the form of a free ion, an ion pair, or an undissociated complex capable of reversible ionisation. The probable coexistence of these states and their mutual overlap is one cause of the complicated kinetics and the difficulty of their elucidation.

A characteristic feature of termination reactions in cationic polymerisation, as we noted in the Introduction, is that they are only extremely rarely associated with irreversible disappearance of the active centres. In most chain growth limitation reactions either the active centres themselves are regenerated or the catalytic complexes from which they are obtained. In this sense such steps should be considered as chain transfer to the counterion rather than as kinetic termination. Of all the possible types of reaction leading to cessation of chain growth (for more detail, see Pepper[9]), excluding direct inhibition by added materials, only one can be classed as a kinetic termination, namely capture of an anion combined with decomposition of the catalytic complex:



where B is a hydroxy-group or an acid residue. Such instances are rather rare, but are observed, for example, in the polymerisation of isobutene under the influence of the complexes $SnCl_4.H_2O$, $TiCl_4.CCl_3COOH$,[6] and $TiCl_4.H_2O$ [13] and in the polymerisation of vinyl phenyl ether under the influence of $SnCl_4.C_6H_5OH$,[65] as is shown by the presence of the corresponding groups in the polymer. Termination of

this type is also possible when protic acids are used as catalysts; the effect in non-polar media is then so great that the polymerisation is practically completely suppressed[23,66]. The most frequent type of termination — regeneration of the active centre — in systems which do not contain additional ion sources is predominantly due to reaction of the growing ion with the counterion. The usual assumption that the growing chain–counterion ion pair is held together by electrostatic interaction implies that the reaction between them is monomolecular, and this is confirmed by results which show that the degree of polymerisation is independent of the catalyst concentration[6,8]. However, as Zlámal, Ambrož, and Veselý have shown[11,12,57,67], in some instances the molecular weight of the polymer depends on the concentration of the catalytic complex, although there are wide ranges over which the degree of polymerisation remains almost constant when the catalyst concentration is varied[67]. From this it was concluded[11] that the concept of monomolecular termination arose simply because the process had been studied in just these specific regions, and had been generalised rather prematurely. The correctness of this view is shown by the results obtained in the polymerisation of isobutene under the influence of various complexes nROH.mAlCl$_3$ in ethyl chloride[11]. The effect of varying the ROH : AlCl$_3$ ratio on the molecular weight of the polymer and the conductivity of the system showed the maximum molecular weight to correspond with the minimum conductivity, the latter occurring with an equimolar ratio of the components. However, as already mentioned, a number of complexes of different compositions exist in this system, namely 4ROH.AlCl$_3$, 2ROH.AlCl$_3$, ROH.AlCl$_3$, and ROH.2AlCl$_3$, so that with ROH : AlCl$_3$ > 1 there is no free co-catalyst present, since any excess over the 1 : 1 ratio will lead to the formation of other complexes having other degrees of ionisation. It was therefore concluded[11] that the lower molecular weight of the polymer formed at higher alcohol concentrations is due to the increased concentration of anions from a more ionised complex. From this viewpoint the termination is considered to be the direct consequence of the formation of free anions:

$$ROH\cdot AlCl_3 + ROH \rightarrow 2ROH\cdot AlCl_3 \rightleftarrows [ROH_2]^+ + [AlCl_3OR]^-,$$

and not the result of interaction between the growing chain and the co-catalyst:

$$\sim\overset{|}{C}^+ + ROH \rightarrow \sim\overset{|}{C} + [ROH_2]^+.$$

By maintaining the relative proportions of the components of the catalytic complex constant and allowing for the effects of very small amounts of impurities which can act as terminating agents, Zlámal[11] demonstrated the inverse proportionality between the concentration of the complex and the molecular weight of the polymer, showing that termination proceeds by a bimolecular mechanism, *i.e.* by reaction of the growing cation with free anions. In laying the foundations for his concept of the growth of free macrocations, Veselý[12] shows that the main arguments in favour of the growth of ion pairs (their low degree of dissociation and the absence of a fractional order in the dependence of the rate and degree of polymerisation on the catalyst concentration) are open to objection. According to his calculations[12], there should be considerable ionisation under the normal conditions of cationic polymerisation, *i.e.* a catalyst concentration 0.0001–0.001 M and a dielectric constant of about 9 or higher. Secondly, kinetic data in the literature occasionally indicate deviations in the rate and degree of polymerisation from first order dependence on the catalyst; these are usually ignored. He cites the work of Norrish[68] and Brown[69] on the polymerisation of isobutene who respectively obtained reaction orders of 0.8 and 1–3.5 with respect to the co-catalyst. Deviations of this type have also been noted in other instances, for example in the polymerisation of styrene[60,70].

Clearly this concept, which is based on the experimental results of Czech workers, could be extended to other systems, and would require observance of the conditions indicated above, *i.e.* a constant catalyst–co-catalyst ratio and exclusion of chain-terminating agents. It is as yet difficult to estimate how far this type of treatment can be applied to different examples of cationic polymerisation, because even quite similar systems show substantial differences, as Veselý himself remarked[12]. Thus in the polymerisation of isobutene in ethyl chloride solution under the influence of titanium tetrachloride etherate, a change in the ratio of the catalyst components only affects the molecular weight of the polymer if $Et_2O : TiCl_4 > 1$. With excess $TiCl_4$ the conductivity of the system does not vary and so the number of ions remains constant; therefore the molecular weight of the polymer is independent of the $TiCl_4$ concentration under these conditions. On the other hand, in isobutene polymerisation under the influence of aluminium chloride monoetherate, which is very little ionised, excess of either component leads to the formation of more highly dissociated complexes, as shown by conductivity data, and to a sharp decrease in the molecular weight of the polymer (Fig. 1).

A qualitatively similar situation is observed in the isobutene–ethyl chloride–AlCl$_3$–benzene system studied by Zlámal and Kazda[55]. Here the specific conductivity passes through a maximum and the molecular weight of the polymer through a minimum at a C_6H_6 : AlCl$_3$ ratio of about 400; no such relationships are observed if the aluminium chloride is replaced by its complex with ethanol, when the conductivity of the reaction mixture and the molecular weight of the polymer decrease with increasing benzene concentration. This difference was shown to be due to the relative basicity and polarity of the polymerisation components. The increased conductivity of the catalytic complex in the absence of ethanol can be explained by the reaction

$$C_6H_6 + EtAlCl_4 \rightleftarrows \left[\bigcirc\!\!-Et\right]^+ + [AlCl_4]^-,$$

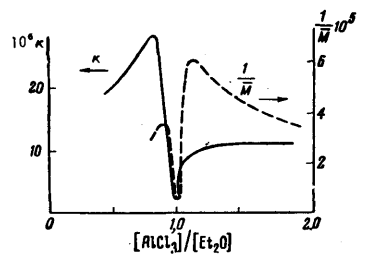


Fig. 1. Dependence on the AlCl$_3$/Et$_2$O ratio of the specific conductance at 25° of the solution and of the molecular weight of the polyisobutylene (polymerised at -78.5°); solvent – ethyl chloride.

in which benzene acts as an electron donor. However, benzene cannot displace ethanol from the $AlCl_3$.EtOH complex; the addition of benzene only reduces the dielectric constant. This conclusion is confirmed by the effect of hexane under analogous conditions: hexane does not form complexes, and its presence reduces the conductivity of the system for each complex. An interesting fact is that the molecular weight of the polymer is affected differently in each case: dilution of the isobutene–ethyl chloride–$AlCl_3$ system with hexane increases the molecular weight of the polymer, which can be explained as chain termination by free anions, the concentration of which falls with decreasing polarity of the medium. This is not found with the $AlCl_3$.EtOH complex.

It thus becomes clear that the suggestion of Veselý and coworkers provides a termination mechanism which may predominate under certain conditions. This is particularly probable for catalyst–co-catalyst systems which can form several catalytic complexes of markedly different degrees of ionisation.

The related studies by Kennedy and Thomas [15,37,71-74] of the polymerisation of isobutene, are of particular interest because of the unusual kinetic relationships found and their interpretation. Aluminium chloride in various media [73,74] gave a degree of polymerisation which varied inversely with the concentration of monomer. Only at low concentrations was there a direct relationship (Fig. 2).

The explanation given was that propagation, like initiation, only occurs when the ion pair is dissociated [Eqns. (8) and (9)], while transfer to the monomer proceeds by reaction of the latter with an undissociated ion pair [Eqn. (10)]:

$$M_n^+A^- \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} M_n^+ + A^- \text{ (slow)}, \qquad (8)$$

$$M_n^+ + A^- + M \xrightarrow{k_2} M_{n+1}^+A^- \text{ (very fast)}, \qquad (9)$$

$$M_n^+A^- + M \xrightarrow{k_4} P + M^+A^-, \qquad (10)$$

where K_1 is the dissociation constant, k_2 the rate constant of propagation, k_4 the rate constant of chain transfer to the monomer, and P the polymer. The inclusion of these steps in the usual kinetic treatment of the steady state in cationic polymerisation gives the relationship

$$\bar{P} = \frac{K_1 k_2 [M]}{(k_2[M] + K_{-1})(k_3[X] + k_4[M])},$$

where k_3 is the rate constant of the termination reaction and X the termination agent. If $K_{-1} \ll k_2[M]$, it agrees with the experimental data described.

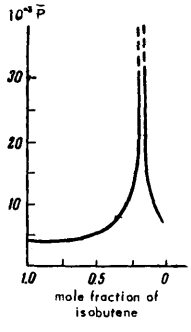


Fig. 2. Influence of monomer concentration on the degree of polymerisation of isobutene at -78°; catalyst — $AlCl_3$; solvent — methyl chloride.

From this point of view the reason for the inverse dependence of $\bar{P}$ on [M] is that at relatively large monomer concentrations an increase in the concentration increases only the rate of chain transfer to the monomer but does not affect the propagation reaction, since the rate of the latter is determined by the slow ionisation of the complex M^+A^-. With low [M], $k_2[M] \ll K_1$ and $\bar{P}$ varies directly with [M].

There are certain objections to this suggested mechanism. Even if it is allowed that there is a distinction between the steps of propagation and transfer to the monomer (8) and (10), it still does not follow that transfer is excluded for the dissociated ion pair, and it is even more difficult to consider that transfer according to Eqn. (10) predominates. Nevertheless there is no other satisfactory explanation of the fact established by Kennedy and Thomas. For example, the role of the dielectric constant in cationic polymerisation, where it usually affects the separation of the ion pair, *i.e.* the rate and degree of polymerisation, suggests a different interpretation of the above results, for when the process is conducted in a polar medium a decrease in the monomer concentration necessarily increases the dielectric constant. However, this idea must be rejected in view of the results of the same investigators for the polymerisation of isobutene in ternary mixtures of monomer, alkyl halide, and CS_2 [73] where the similar dielectric constants of CS_2 and isobutene make it possible to hold the solution at a given dielectric constant while varying the monomer concentration. In this system the degree of polymerisation varied with the monomer concentration in the same way as before. Decreasing [M] from 3 to 1 mole per litre produced a substantial increase in the degree of polymerisation, while further decrease of [M] reduced it. To reconcile the contradictions between literature data on the influence of the dielectric constant and their own results, they introduced the concept of "effective dielectric constant". The process is treated in a specific topochemical fashion, according to which it is assumed that a difference exists between the overall dielectric constant throughout the reaction volume and that in the solvate sheets surrounding discrete sectors in which the fundamental steps of the polymerisation occur. It can then be further assumed that even a small amount of a polar solvent is sufficient to produce a high dielectric constant around the growing centre. Further increase in the concentration of the polar material will then increase the dielectric constant in the main bulk of the solution without affecting the "effective dielectric constant". This approach explains why there is no increase in the molecular weight of polyisobutylene when the dielectric constant of the medium is increased by increasing the concentration of methyl chloride [72]. According to Kennedy and Thomas [73], the amount added with the catalyst (aluminium chloride in solution in methyl chloride was used) creates the necessary "effective dielectric constant".

Another very important conclusion reached by Kennedy and Thomas in their investigation of isobutene polymerisation relates to the temperature variation of the dependence of the degree of polymerisation on the monomer concentration. They found [15] that plots of the degree of polymerisation

against the reciprocal of the temperature have different slopes with different monomer concentrations, and intersect in a single point. Special experiments at the temperature corresponding to this point of intersection showed that the degree of polymerisation is in fact independent of monomer concentration under these conditions. When the degree of polymerisation is plotted against monomer concentration at different temperatures, distinct regions occur in which $\bar{P}$ is independent of [M] over approximately the same concentration range at the various temperatures. The further course of the curves depends on the polymerisation temperature: a lower temperature gives an inverse relationship, and a higher temperature a direct relationship (Fig. 3). On this basis the concept of the inversion temperature is introduced, *i.e.* the temperature at which the dependence of $\bar{P}$ on [M] changes sign. The inversion temperature depends on the medium: in methyl chloride, vinyl chloride, and ethyl chloride it is -42°, -52°, and -55° respectively.

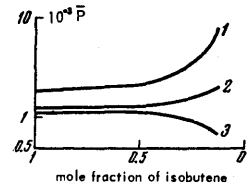


Fig. 3. Degree of polymerisation of isobutene as a function of monomer concentration at various temperatures: 1) -78°; 2) -50°; 3) 30°; catalyst — $AlCl_3$; solvent — methyl chloride.

The existence of the inversion temperature demonstrates the existence of a region in which there is a balance between the two tendencies — the direct ("normal") and inverse ("anomalous") dependence of the degree of polymerisation on the monomer concentration. This novel and extremely interesting fact is closely related to the dependence of the chain limitation reactions on the experimental conditions, mainly temperature and monomer concentration. Clearly, the key role is played by transfer and not termination reactions; this follows from the invariance of the extent of conversion in the polymerisation of isobutene over the temperature range -35° to -180°: a reduction in temperature only increases the degree of polymerisation[15,71] ‡.

Similar effects, namely the existence of a maximum on the plot of $\bar{P}$ against temperature, the invariance of $\bar{P}$ with [M] at low temperatures, and the increase of $\bar{P}$ with decreasing [M] in a definite concentration range had been observed previously[77-79], but in most cases the workers had restricted themselves to a statement of the facts. However, Biddulph and Plesch[78] also concluded that chain transfer to the monomer plays the decisive role in the titanium tetrachloride polymerisation of isobutene with various co-catalysts. They observed no variation of $\bar{P}$ with [M] in ethyl chloride at -70° and in ethyl bromide below -60°, the co-catalyst being trifluoroacetic acid in the first case and water in the second. The mechanism of the isobutene polymerisation in both systems is thus seen to be the same.

For other initiating systems or other monomers under the same polymerisation conditions there is often a considerable change in the specific contribution of a particular step in the process. In this respect it is relevant here to compare the above results[78] with those of Norrish and Russel[23,68] for the polymerisation of isobutene under the influence of $SnCl_4$–H_2O complexes at -78°, which differ greatly: the latter workers found $\bar{P}$ to vary directly with [M], with the process proceeding at an incomparably lower rate and the molecular weights of the polymers being much lower. It is perfectly clear that in this case transfer to the monomer is not the determining factor. From an analysis of the differences, it was concluded[78] that here the main reaction limiting the chains is termination by stannic chloride monohydrate. This fact and the low rate of initiation give relationships which are different in principle from those occurring in polymerisation under the influence of titanium or aluminium halides, where initiation is rapid and termination is slow§.

Of great interest are the differences established by Plesch and coworkers in the polymerisation of isobutene and styrene by the $TiCl_4$–H_2O system in methylene chloride under comparable conditions. With isobutene[46] 100% conversion is only attained in the presence of a certain quantity of water which is fixed for each temperature and each concentration of monomer. A process which has stopped because of a deficiency of co-catalyst can be restarted by adding further water. If $[H_2O]_C$ is the amount of water required for 100% conversion, it has been shown that when $[H_2O] < [H_2O]_C$ the initial rate of the process increases with the amount of water present, but when $[H_2O] > [H_2O]_C$ it is independent of it. For a monomer concentration of 0.1 M, $[H_2O]_C$ lies within the limits 1×10^{-5}–3×10^{-4} M in the temperature range -90° to +25°. The dependence of the initial rate on the monomer concentration is of first order above -30° and of zero order below -60°. A full interpretation of these facts is difficult, but there is no doubt that a fast termination reaction involving water occurs. The study of the polymerisation of styrene between -90° and -30° has established[19] that $\bar{P}$ is independent of [M], that the initial rate is of second order with respect to the monomer, and, most important, that there is no kinetic termination reaction such as was observed with isobutene. Moreover, the active centres do not disappear when the reaction ceases because of exhaustion of the monomer; if more monomer is added, the reaction starts up again, and this was considered to be the first instance in which "live" polymers had been shown to exist in cationic polymerisation. On this basis Plesch supposes that whereas with isobutene, in the polymers of which hydroxy as well as

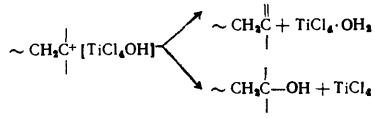
‡ Further development of these investigations has shown[75,76] that an inversion temperature is only observed in polar media. A more complete interpretation of the effects described is given. The expression for the degree of polymerisation is converted into the form

$$\bar{P} = \frac{K_1}{(k_4 - k_3)NS - k_3 L},$$

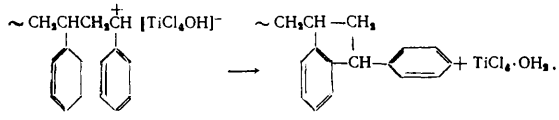
where N and S are the mole fractions of monomer and solvent respectively and L is the total number of moles of monomer and solvent. From this expression it is possible to find the boundary conditions corresponding to the experimental results referred to above, and to explain the different form of the variation of $\bar{P}$ with [M] in polar and non-polar media.

§ Biddulph and Plesch[46] also give previously unpublished results obtained by Russel.

vinylidene end-groups have been detected[46], both the termination reactions



occur, with styrene[19] the most probable termination reaction is cyclisation, with regeneration of the catalytic complex:



The formation of indane rings in the cationic polymerisation of styrene, α-methylstyrene, and stilbene is well established[6,23], but according to Pepper's results[80-82] this type of chain limitation reaction is not the predominant one. It was shown very recently[82] that in styrene polymerisation the indane rings arise as a result of transfer of the chain to the monomer; termination with regeneration of the catalyst leads to the formation of unsaturated end-groups.

Analogous differences — the presence and absence of irreversible kinetic termination — have been established by Pepper in the polymerisation of a single monomer, styrene, under the influence of different protic acids. With sulphuric acid[83,84] the rapid reaction may be broken off before exhaustion of the monomer, because of the insufficiency of catalyst. Addition of acid allows the process to go to completion. This leads to the suggestion that the reaction

$$\sim CH_2\overset{+}{C}H(C_6H_5)[H_2SO_4]^- \rightarrow \sim CH_2CH(C_6H_5)OSO_3H,$$

occurs. In the $HClO_4$ polymerisation of styrene[22] the effect found by Plesch in the styrene–$TiCl_4$ system[19] is observed, *i.e.* the reaction is not broken off. We shall return later to Pepper's studies of the polymerisation of styrene by protic acids.

Although the process continues when further monomer is added to the reaction mixture, it still does not follow that we are dealing with "live" polymers in the sense in which this term is used in anionic polymerisation. In the latter the retention of the activity by the reaction mixture after complete monomer consumption is associated with the theoretical continuity of the process, and is the result of the existence of "live" macroanions or polymers with end-groups of the type $C^- - M^+$ which are able to dissociate. In cationic polymerisation the activity of the system can also be retained in the absence of "live" macrocations, since here the absence of kinetic termination does not preclude the existence of chain limitation reactions involving regeneration of the active complex; it is clear that the renewal of the reaction on addition of extra monomer may be due to the presence in the system of the catalytic complex recovered from this process. In the general case, allowance must be made for the possibility of equilibrium between the polymer chain and the catalytic complex after all the monomer has been consumed. If there is no isomerisation of the macrocations into less active forms, this equilibrium would result in "indestructibility" of the live chains. A direct indication of the existence of "live" macrocations would be an increase in the molecular weight of the polymer after adding a further portion of monomer, or the synthesis of block copolymers such as has been achieved in anionic polymerisation using "live" polymers.

However, such evidence has as yet not been obtained in cationic polymerisation. In addition to the studies referred to above, certain indications of the existence of "live" macrocations have been obtained by Asami and Tokura[85,86] in their investigation of styrene polymerisation in the systems $SnCl_4-SO_2$ and $BF_3.OEt_2-SO_2$ at temperatures from 0° to 25°. They found a linear relationship between the degree of polymerisation and the monomer : catalyst ratio; this had not previously been observed in cationic polymerisation, and could not be explained by the usual mechanisms postulated for the process. It was further shown that liquid sulphur dioxide, which in this instance acts as the co-catalyst, can, because of its polar nature (ϵ = 15.6 and 13.7 at 0° and 25° respectively), strongly solvate the growing cations and counterions, which virtually prevents the termination reaction, as is shown by the rapid and quantitative polymerisation, producing polystyrene of unusually high molecular weight for a cationic process, reaching, in the case of $SnCl_4$, 90 000¶. All this supports the propagation of polymerisation by "live" chains. The following mechanism was suggested for the formation of the initial active centres:

$$2SO_2 \rightleftarrows SO_2^{2-} + SO_2^{2+},$$

$$2SnCl_4 + 2SO_2 \rightarrow 2[SnCl_4{}^{1}/_{2}SO_2]^{2-} + SO^{2+}.$$

The important part played by solvation of the growing chains in cationic polymerisation had previously been convincingly demonstrated by Szwarc and coworkers[66] in the polymerisation of styrene in the presence of trifluoroacetic acid, where the order of adding the reaction components play a key role. Adding the acid to the monomer gives only the product of addition of the elements of the acid to the double bond of the styrene, since the low polarity of the medium completely excludes the possibility of polymerisation. When the styrene is added to the acid, it polymerises immediately and quantitatively to give a polymer of molecular weight above 20 000.

The unusual kinetic features of cationic polymerisation often throw doubt on the correctness of the interpretation of a particular case from the point of view of the quasi-steady state. The vigorous development of the reaction and its rapid completion in many cationic systems have led to the process being regarded, as non-steady state, as was originally suggested by Pepper[6,9] who, together with his school, later developed this idea[21,83,84,88-90]. The first point to be considered in resolving this question is the relative rate constants of the separate stages, especially that of the initiation reaction. Polymerisation may be said to take place under steady-state conditions if the rate constant for initiation is small compared with that of the propagation reaction (with the termination reaction also occurring, of course), as in radical polymerisation, where these rate constants differ by 6 or 7 powers of ten. However, in the actual examples investigated by Pepper, *i.e.* the polymerisation of styrene by strong acids in polar media, the relative values are clearly quite different: thus the reaction is explosive in the styrene–sulphuric acid–dichloroethane system[82]. Reduction of the rate of polymerisation by decreasing the monomer concentration to $[M] \leqslant 0.35$ M and the catalyst concentration to $[C] \leqslant 3 \times 10^{-3}$ M

¶ High-molecular-weight polystyrene can also be obtained in other systems, but this requires a low temperature. Thus the sulphuric acid polymerisation of styrene in methylene chloride solution at -78° produces a polymer with M = 85 000; at 0° the molecular weight of the polymer is 4500.[87]

enabled the process to be studied under isothermal conditions, when it was found that the reaction breaks off sharply before complete consumption of the monomer (Fig. 4). This effect is a consequence of the non-steady-state nature of the polymerisation of styrene in the given system, which, it is thought, is due to the exceptionally high rate of initiation, with $k_1 \gg k_2$ (where k_1 is the rate constant of the initiation reaction) and a relatively fast termination reaction† determining the duration of the overall process, the half-life at 25° being about 2 min. Analogous effects were observed in the polymerisation of styrene in dichloroethane in the presence of several other acids[83]. There was a substantial difference with perchloric acid[22], where, while the inequality $k_1 \gg k_2$ is retained, there is no irreversible termination reaction and the reaction taking place before the complete disappearance of the monomer is (up to a degree of conversion of 95% or more) of first order with respect to monomer and has a rate constant proportional to the initial acid concentration. In this system there is instantaneous appearance of the absorption bands at 4100 Å observed in the polymerisation of styrene under the influence of $AlCl_3$ and $SnCl_4$ [62] and ascribed to a carbonium ion, the intensity of the bands not changing with time. In the given case, therefore, the rapid initiation and the absence of termination produce an immediate constant concentration of active centres equal to the initial acid concentration, and in this sense the process is a steady-state one. As Pepper and Reilly remark[22], the main conclusion from this investigation is in agreement with the results obtained by Okamura and coworkers[20,21], who showed, for quite different systems, namely iodine–vinyl ethers and iodine–*p*-methoxystyrene, that the concentration of active centres is 30–90% of the total catalyst content. Hence even with this catalyst whose activity is fairly low, the initiation must be very rapid.

The results discussed serve as a basis for considering certain other processes from the same point of view, for instance the low-temperature polymerisation of isobutene, which under certain conditions shows features similar to those of the polymerisation of styrene under the influence of protic acids. For isobutene polymerisation we could also take $k_1 \gg k_2$, which would mean that steady-state conditions are only possible in the absence of kinetic termination. This approach seems more applicable to this process than does Kennedy's mechanism[73], with propagation represented by a two-stage reaction the rate of which is determined by the slow dissociation of an ion pair, each successive addition of a monomer molecule again producing an undissociated species [see Eqns. (8) and (9)]. This question clearly requires further study.

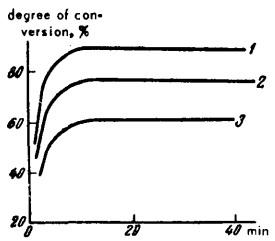


Fig. 4. Kinetics of the H_2SO_4 polymerisation of styrene at 25° in dichloroethane. Concentration of catalyst (10^{-3} M): 1) 3.4; 2) 1.7; 3) 0.81.

The investigations of Pepper and his collaborators have paved the way for a reappraisal of the energetics of cationic polymerisation. Until recently before the absolute rate constants were available for the separate stages of the process, the predominant view was that the rate constant of propagation in cationic polymerisation must be considerably higher than the corresponding value in radical polymerisation, because of the lower activation energy of the propagation reaction in the former, and this was apparently supported by the known negative temperature variation of the overall rate of the process. In the $HClO_4$ polymerisation of styrene, the absence of termination and the existence of the inequality $k_1 \gg k_2$ enabled Pepper[22] to take the experimental overall rate constants of the polymerisation to be the absolute rate constants of the propagation reaction, and the overall energy of activation to be the energy of activation of the propagation reaction: for the temperature range -30° to +25° and with dielectric constant ~ 10 this value was 8.3 kcal mole^{-1}. Reduction of the dielectric constant by changing the concentration of monomer or by using different reaction media led to an increase in the energy of activation, which with $\epsilon = 5.16$ reaches 13.0 kcal × × mole^{-1}. Taking the energy of activation for propagation in the H_2SO_4 polymerisation of styrene as 8.5 kcal mole^{-1}, on the basis of the results obtained with $HClO_4$, Pepper[84] obtained the following values for the activation energies (in kcal mole^{-1}) of the various stages for the styrene–H_2SO_4–dichloroethane system; irreversible termination 13.5, reversible termination with regeneration of catalyst 12.5, and transfer to monomer 16.0‡. The values found were quite different from what had been expected on the basis of the corresponding values for radical polymerisation. For the propagation reaction in cationic polymerisation a slightly higher rather than lower activation energy was obtained (in the radical polymerisation of styrene the activation energy for propagation is 6.9–7.8 kcal mole^{-1} [91,92]), while for the other reactions the activation energy was considerably higher than was expected. These results are also of interest in that they provide a simple explanation of the negative overall energy of activation and the high overall rates of the process, which had earlier often been related to a low activation energy for propagation. With $k_1 \gg k_2$ the concentration of active centres is close to the initial concentration of catalyst, and in the absence of irreversible termination is equal to it, *i.e.* it is of the order of 10^{-3} M, while in radical polymerisation the usual concentration of active centres is only 10^{-8} M. Thus even when the rate constants of the propagation of these processes are similar the difference in the total rates of polymerisation should be very large.

It is very desirable to estimate the extent to which the quantitative data given and the conclusions drawn from

† Irreversible termination is intended.

‡ For the rate constants of the corresponding reactions at 25°, the following values were obtained[84]: propagation 7.6 litre mole^{-1} × × sec^{-1}, irreversible termination 6.7 × 10^{-3} sec^{-1}, reversible termination 0.049 sec^{-1}, and transfer to monomer 0.12 litre mole^{-1} × × sec^{-1}.

them are applicable to other systems. The idea that the values obtained by Pepper may be reasonably accurate for other cases is also supported by the similarity between the quantity $E_3 - E_2 = 4.2$ kcal mole^{-1} found by him in the work cited and the values obtained by Imanishi and coworkers[93] for isobutene polymerisation under the influence of $TiCl_4$ and $SnCl_4$ (4.0 and 4.3 kcal mole^{-1} respectively, in hexane and 4.0 and 3.4 kcal mole^{-1} in chloroform). In an attempt to generalise these results, we may regard it as probable that when the overall activation energy of a cationic polymerisation process is negative (or positive but very small), the relationship between the activation energies of the separate stages will be about the same as was found for the H_2SO_4–styrene system. On the other hand, with cationic polymerisation in systems characterised by a relatively high positive overall activation energy, it is probable that the activation energy of the initiation reaction makes a substantial contribution. Of course, this throws no light on the absolute values of the activation energies of the other fundamental stages in the reaction.

TABLE 1. Absolute constants for the propagation reaction in cationic polymerisation.

Monomer	Catalyst	Solvent	t, °C	k_2, litre × × mole^{-1} × × sec^{-1}	References
Isobutene*	$TiCl_4 \cdot H_2O$	CH_2Cl_2	−30	14.3	20
	$TiCl_4 \cdot H_2O$	CH_2Cl_2	−60	11.3	20
	$TiCl_4 \cdot H_2O$	CH_2Cl_2	−90	12.8	20
p-Methoxystyrene	I_2	$C_2H_4Cl_2$	30	15.66	21
	I_2	CCl_4	30	0.13	21
Isobutyl vinyl ether	I_2	$C_2H_4Cl_2$	30	6.50	21
	I_2	CCl_4	30	0.04	21
Styrene	$HClO_4$	$C_2H_4Cl_2$	25	17.0	22
	$HClO_4$	$C_2H_4Cl_2$	−30	0.7	22
	$HClO_4$	$C_2H_4Cl_2+CCl_4$ (55 : 40)	25	0.4	22
	H_2SO_4	$C_2H_4Cl_2$	25	6.7	22
	$SnCl_4$	$C_2H_4Cl_2$	30	0.4	41
	I_2	$C_2H_4Cl_2$	30	0.003	41

* Plesch[17] has recently reported preliminary results in which k_2 for isobutene is of the order of 10^4 litre mole^{-1} sec^{-1}. The experimental conditions are not given.

IV. ROLE OF THE COUNTERION

The concept of the growing chain as an ion pair must be considered from yet another viewpoint, namely the influence of the counterion on the rate of growth of the chain and its microstructure. This question is of great interest for at least two reasons. Firstly, it is associated with the problem of regulating the rate of the reaction and the structure of the elementary units of the polymer chain, and, secondly, it is an approach to the investigation of the true nature of the growing chain in the sense referred to at the beginning of this section, since the parameters indicated should be independent of the nature of the catalyst when the active centres are the free macrocations. Despite the large amount of information on the relationship between the nature of the catalyst and the features of cationic polymerisation, only in a limited number of cases can it be used for quantitative evaluation of these effects. In dealing with the influence of the counterion on the rate of the propagation reaction (we shall deal first with this side of the process), it is necessary to consider the high sensitivity of cationic polymerisation to changes in the polarity of the medium, and particularly the fact that it can affect the various fundamental stages to different extents. It is thus extremely difficult to maintain the other conditions constant when passing from one counterion to another, especially when using cationic catalysts of different types (for instance Lewis acids and protic acids) for which the comparison would be particularly valuable. These considerations are based on recent data on the rate constant for propagation in cationic polymerisation in certain systems and its variation with the polarity of the medium. The temperature does not always affect this constant to any substantial extent (Table 1).

Okamura and coworkers[93-96] carried out special investigations of the effect of the counterion on the kinetics of polymerisation of styrene, α-methylstyrene, isobutene, and methyl vinyl ether, in which the ratios of the rate constants k_3/k_2 and k_4/k_2 for different catalytic complexes were compared. The results (some of which are given in Table 2) show that there are distinct differences between these ratios for different catalysts, especially with isobutene. This is an important finding, which demonstrates that the characteristics of a counterion may be clearly expressed in terms of kinetic data. However, no general

TABLE 2. Influence of the catalyst and solvent on the ratios of the constants for the fundamental reactions in the polymerisation of various monomers.

Monomer	Catalyst	Co-catalyst	Solvent	t, °C	$10^4(k_3/k_2)$	$10^4(k_4/k_2)$	References
Styrene	$TiCl_4$	H_2O	C_6H_6 + 30% by vol. of $C_2H_4Cl_2$	30	32	150	94
	$SnCl_4$	H_2O		30	62	108	94
	BF_3	$(C_2H_5)_2O$		30	78	80	94
α-Methylstyrene	BF_3	$(C_2H_5)_2O$	n-C_6H_{14}	−50	6.4	91.0	95
	BF_3	$(C_2H_5)_2O$	CH_3Cl_2	−50	35.5	25.9	95
Isobutene	$TiCl_4$	CCl_3COOH	n-C_6H_{14}	−50	0.8	2.0	93
	$SnCl_4$	CCl_3COOH	n-C_6H_{14}	−50	10.5	17.0	93
	$TiCl_4$	CCl_3COOH	CH_2Cl_2	−50	0.56	5.68	93
	$SnCl_4$	CCl_3COOH	CH_2Cl_2	−50	9.0	36.0	93
	$TiCl_4$	CCl_3COOH	CH_2Cl_2	−20	1.3	26.9	93
	$SnCl_4$	CCl_3COOH	CH_2Cl_2	−20	54.0	60.0	93
Methyl vinyl ether	$SnCl_4$	CCl_3COOH	CH_2Cl_2	−50	29.2	15.2	96
	$SnCl_4$	CCl_3COOH	CH_2Cl_2	−20	44.0	32.0	96
	BF_3	$(C_2H_5)_2O$	CH_2Cl_2	−50	12.4	6.4	96
	BF_3	$(C_2H_5)_2O$	CH_2Cl_2	−20	14.4	31.2	96

regularities could be established. For instance, the ratio k_3/k_2 is very sensitive to a change from hexane to methylene chloride with the system $BF_3 \cdot Et_2O$–α-methylstyrene, but is very little different when isobutene is polymerised in the same media under the influence of $TiCl_4$ or $SnCl_4$.

An unexpected feature is that differences in the values of k_3/k_2 for different catalysts are not evened out as the polarity of the medium is increased. An increase in the dielectric constant would be expected to suppress the effect of the counterion characteristics, because the ion–counterion bond is weakened, and so levels off the values of k_3/k_2 when the other experimental conditions are maintained constant. However, the ratio changes to approximately the same extent with both the above initiators in the case

of isobutene polymerisation in solution in hexane and in methylene chloride. Working with ratios of rate constants and not with their absolute values introduces substantial difficulties into the interpretation of these results. It is natural to suppose that a difference in the nature of the counterion may become evident in chain propagation and termination reactions to very different extents, and this will apply both to data for different catalysts under the same conditions, and to the results for a single catalyst in different media or at different temperatures. This is well illustrated by the complex relationships established in the polymerisation of α-methylstyrene under the influence of $BF_3.Et_2O$ (Fig. 5)[95]. Table 3 gives the polarities of the reaction media corresponding to the curves of Fig. 5.

It is no less difficult to explain the direction and extent of the changes in the rate constant of chain transfer to the monomer k_4/k_2 on passing from one medium to another but with the same catalyst in each case (Table 3). Irrespective of the temperature, the rate constant of chain transfer to the monomer during polymerisation in the system α-methylstyrene–$BF_3.Et_2O$–solvent passes through a minimum at a dielectric constant of 5 to 7; [95] this only indicates the substantial difference between the ways in which k_4 and k_2 change when the polarity of the medium is varied.

The possible existence of a connection between the microstructure of the polymer and the nature of the catalyst in cationic polymerisation was pointed out by Flory[2] in his discussion of certain consequences of the concept of propagation by ion pairs. He dealt only with differences in the structure of the unit in polymers of diene hydrocarbons by analogy with the polymerisation of dienes under the influence of alkali metals or their organic derivatives, where the proportions of the different types of elementary unit in the polymer are determined by the nature of the metal. This question has been very little studied in the field of cationic polymerisation, apparently because the polymerised diene hydrocarbons produced in this case are not of practical interest. In the only published work on this subject, Ferington and Tobolsky[97] compared the structure of the polybutadienes obtained at -78° in the presence of various cationic catalysts. For catalysts such as aluminium chloride or bromide in ethyl chloride solution, and boron trifluoride etherate in the absence of solvent, the ratio of 1,4-*trans*/1,2-units is 4.0–4.6, irrespective of the nature of the catalyst, over a wide range of reagent concentrations and for different degrees of conversion (in no case were 1,4-*cis*-units observed). There was some deviation with titanium tetrachloride, which in ethyl chloride solution gave a value of 3.1–3.4, and somewhat larger deviations on passing to the highly polar media nitroethane and nitrobenzene, where for aluminium chloride the ratio of 1,4-*trans*/1,2-units is 2.8 and 2.0 respectively.

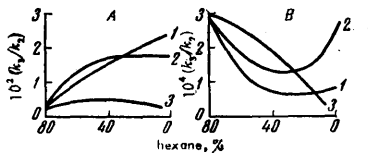


Fig. 5. Influence of the polarity of the medium on the ratio k_2/k_3 in the $BF_3.Et_2O$ polymerisation of methylstyrene: *A*) at -20°; *B*) at -70°; monomer concentration 20 vol.%. Reaction media: 1) chloroform–hexane; 2) methylene chloride–hexane; 3) toluene–hexane.

TABLE 3. Dielectric constant of solutions of α-methylstyrene in various media[95].

Components, vol.%					Dielectric constant	
α-methylstyrene	n-hexane	toluene	chloroform	methylene chloride	-20°	-70°
100	—	—	—	—	2.65	2.77
20	80	—	—	—	2.09	2.17
20	—	80	—	—	2.50	2.62
20	—	—	80	—	5.03	6.27
20	—	—	—	80	9.30	12.31

In general the normal tendency of cationic catalysts to produce diene polymers of predominantly 1,4-*trans*-structure is retained in all cases. In the investigation cited, the content of such units lies within the fairly narrow limits 66–82%, which creates the impression that the structural differences in the polymerisation of dienes by the cationic mechanism are considerably less than in their polymerisation by alkali metals and their derivatives, where the microstructure of the diene polymers is considerably affected by altering the metal or the medium. There are no real grounds, however, for making far-reaching conclusions on this basis, as to the difference in principle between the roles of the counterions in the propagation by the ion pairs $\sim \overset{|}{\underset{|}{C}}{}^{+}X^{-}$ and $\sim \overset{|}{\underset{|}{C}}{}^{-}M^{+}$. The results for the polymerisation of isoprene by alkali metals indicate that true stereospecificity has been established only for lithium, which can give a polymer constructed wholly of 1,4-*cis*-units. All the other alkali metals give polyisoprenes composed mainly of 1,4-*trans*- and 3,4-units, the ratio of these varying little with the metal used[98] (Table 4).

It is thus possible to refer only to a substantial difference between lithium and the other alkali metals in this respect§. The variations in the microstructure of the polyisoprene obtained with the metals sodium to caesium are fully comparable with those established by Ferington and Tobolsky[97] in the polymerisation of butadiene by various cationic catalysts. It is also necessary to point out that a high stereospecificity can be attained in the cationic polymerisation of diene hydrocarbons: thus Rinehart[100] obtained polybutadiene with up to 99% of 1,4-*trans*-units by using rhodium salts [$Rh(NO_3)_3.2H_2O$ and $RhCl_3.3H_2O$] as catalysts. There are also reports of the production of stereoregular poly(tetramethylbutadiene) using cationic catalysts[101]. It is difficult to compare these results with Ferington's[97], since the polymerisation was effected under quite different conditions, but it can be said that it is not by any means futile to consider the possibility of controlling

§ Organolithium compounds occupy a similar unique position in the stereospecific polymerisation of methyl methacrylate[99].

TABLE 4. Microstructure of polyisoprene produced under the influence of alkali metals in pentane solution[98].

Metal	Units, %			
	1,4-		3,4-	1,2-
	cis-	trans-		
Li	94.4	0	5.6	0
Na	0	43	51	6
K	0	52	40	8
Rb	5	47	39	8
Cs	4	51	36	8

the microstructure of diene polymers in cationic polymerisation and to discuss the role of the counterion in the propagation of the macrocation.

It is very tempting to correlate the nature of the counterion with another distinguishing feature of the unit structure of the polymer chain, namely the differences in tacticity in vinyl polymers. As with diene hydrocarbons, the number of facts at our disposal in this field is small, although the first isotactic polymers [poly(alkyl vinyl ethers) and polystyrene] were in fact obtained by cationic polymerisation, long before the idea of the stereoregularity of vinyl polymers was introduced. The data on the production of stereoregular polymers by cationic polymerisation and views on the possible nature of this effect have recently been compiled in a monograph by Gaylord and Mark[102]. Several new publications have recently appeared in this field, dealing mainly with vinyl ethers[103-113]; in these, as in the earlier investigations, the dependence of stereoregularity in polymers on the experimental conditions has been treated mainly from the viewpoint of the phase state of the system, the order of introduction of the components, and the polymerisation temperature. Only in some of these studies is there an indication that the nature of the catalyst has a substantial influence on the stereospecificity of the process. For example, in the polymerisation of vinyl isobutyl ether by $BF_3.Et_2O$ or $SnCl_4.CCl_3COOH$ the former catalyst gives the more stereoregular polymer[105]. It must be emphasised that the formation of stereoregular poly(alkyl vinyl ethers) under the influence of boron trifluoride etherate has been noted especially often. It has been thought[102] that the stereospecificity of this catalyst is due to the propagation process involving the formation of a coordination complex:

$$BF_3 \cdot O(C_2H_5)_2 \xrightarrow{CH_2=CHOR} BF_3 \cdot O(R)CH=CH_2,$$

which precedes the addition of the next monomer unit to the growing chain. It has recently been shown[108] that polymers of vinyl isobutyl ether which are more stereoregular than those obtained at low temperatures by boron trifluoride etherate can be prepared by using other cationic catalysts, which are complexes of sulphuric acid with aluminium, magnesium, or chromium sulphates. A selective stereospecificity in the polymerisation of vinyl ethers has been established for certain alkyl aluminium halides[104,110]. Polymers with a high degree of stereoregularity can be obtained by the cationic polymerisation of α-methylstyrene[112] and 3-methylbut-1-ene[113].

The limited data available and the high sensitivity of chain formation to various influences have so far prevented the determination of the actual part played by the counterion in the steps determining the microstructure of the polymer. The possible existence of such a connection has been touched upon when introducing this question.

While noting a connection between the effects considered in this section and the problem of the propagation of ion pairs and the role of the counterion, it must be said that the creation of an objective picture of cationic polymerisation would be much helped by an evaluation not only of the characteristics of a given ion pair, but of the macrocation also. It is relevant to recall here Szwarc's remark[114] about the useful information which may be gleaned from a systematic investigation of cationic polymerisation initiated by radiation, since ion pairs are apparently then absent, and it is free macrocations which grow. In this sense radiation-initiated cationic polymerisation is a very valuable method for investigating the mechanism of the process, since it should promote the appearance of features specific to the monomeric cations in the free state. Strictly speaking, the study of the reactivity of the growing chains in cationic polymerisation requires the macrocation to be in just this state, since the presence of the counterion substantially modifies the process, as the data given above (Tables 2 and 3) indicate. From this point of view, it is convenient to return to the problem of cationic copolymerisation. It had earlier been assumed that the counterion and the polarity of the medium were factors which could affect the copolymerisation constants, but until recently there were very few data on this point. It was known[115] that there were marked variations in the copolymerisation constants in the case of the pair styrene–3,4-dichlorostyrene when different catalysts were used, but with the pair styrene–*p*-chlorostyrene different cationic catalysts and variation of the dielectric constant from 2.2 to 29.7 hardly affected the copolymerisation constants[116,117]. Among more recent studies of the copolymerisation of various pairs of monomers by cationic catalysts[118-124], only a few deal specifically with this point[118,120,122,126]. Table 5 gives some results illustrating the substantial parts played by the catalyst and the medium.

As Overberger points out[126], the possibility of selective solvation of the active centres by one of the monomers

TABLE 5. Influence of catalyst and polarity of medium on the copolymerisation constants in cationic copolymerisation at 0°.

M_1	M_2	Catalyst	Solvent	r_1	r_2	References
Styrene	3,4-dichlorostyrene	$AlCl_3$	CCl_4	2.8	0.45	115
		$BF_3.Et_2O$	CCl_4	5.9	0.27	115
Isobutene	*p*-chlorostyrene	$AlBr_3$	*n*-hexane	1.01	1.02	120
			nitrobenzene	14.7	0.15	120
			nitromethane	22.5	0.7	120
Styrene	*p*-methoxystyrene	$SnCl_4$	nitrobenzene – CCl_4 (1 : 1)	0.04	19	124
		$AlCl_3$		0.34	11	124
		$TiCl_4$		0.12	14	124
		$TiCl_4$	CCl_4	0.05	46	124
		$TiCl_4$	nitrobenzene	0.48	5.6	124
Styrene	chloroprene	$AlBr_3$	benzene	6.9	0.04	126
		$AlBr_3$	nitrobenzene	16.0	0.06	126

must also be considered in cationic copolymerisation. For example, conditions may be more favourable for chain propagation by the more polar monomer even if it is less reactive than the other. Of course, such an effect would be more likely in the absence of stable solvation shells, *i.e.* in non-polar media. In particular, this view finds confirmation in the results obtained for the pair isobutene–*p*-chlorostyrene.

Results of studies on cationic polymerisation under the influence of γ-radiation began to appear in 1957. The results for copolymerisation obtained in this way, mainly by Abkin and coworkers[127-133], do not yet allow us to decide whether deviations from the values known for ordinary cationic polymerisation occur¶. Of course, differences in the copolymerisation constants determined by the presence, absence, or nature of the counterion are only possible with relatively similar monomers; in other cases, the possible effects of this type will always be hidden by differences in the polarities of the double bonds, which must occur not only with such pairs as styrene–methyl methacrylate, but also in less extreme cases.

It is thus clear that the whole problem of explaining the connection between the nature of the counterion in cationic polymerisation and the effects associated with it — the kinetics of the process, the relative contributions of the fundamental steps, and changes in the microstructure of the polymer chain — is in a very early stage of development. All these questions merit further study.

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CHELATE POLYMERS

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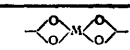
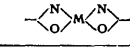
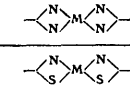
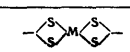
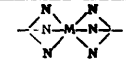
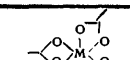
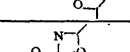
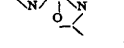
I. INTRODUCTION. SOME PROBLEMS OF TERMINOLOGY

Interest in macromolecular compounds containing metals has grown considerably during recent years. Such compounds are often termed "chelate polymers", and several reviews of work on their synthesis and properties have appeared in the Soviet and foreign literature[1-5]. Most of these, however, either do not cover the whole of the literature or else are already considerably out of date. The aim of the present review is to survey the literature on the preparation and properties of chelate polymers up to May 1962.

We must consider briefly some problems of the terminology of these compounds. The name "chelate compound" which we use is based on the term "chelate" ($\chi\eta\lambda\eta$), a claw or talon, proposed by Morgan and Drew[6]. The expressions "inner complex" and "clawlike compound" also are often employed in Soviet chemical literature. In several cases we use the nomenclature recommended by the International Union of Pure and Applied Chemistry[7].

The term "chelatophore" has been proposed[3] for a group which is capable of forming chelate rings. In our view, however, it is more appropriate to use the term "chelate ligand". Terent'ev and Rukhadze[8] proposed the name "analytical loops" for the cyclic groups formed by the addition of chelate ligands to a central atom. Later we suggested calling such cyclic chelate groups "chelate loops"[9]. The accompanying Table lists some possible chelate loops and the names and symbols which we employ for them.

Some possible chelate loops.

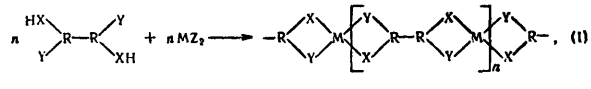
Coordination No. of metal (M)	Name of chelate	Schematic formula of chelate*	Shortened formula of chelate
4	**bisdioxa**		2(O, O) — M
4	**bisazaoxa**		2(N,O) — M
4	**bisdiaza**		2(N, N) — M
4	**bisazathia**		2(N, S) — M
4	**bisdithia**		2(S, S) — M
6	bistriaza		2(N, N, N)—M
6	trisdioxa		3(O, O) — M
6	trisazaoxa		3(N, O) — M

* In several actual cases the schematic formula can be still further simplified by representing N, O, and S atoms as points.

II. METHODS OF PREPARATION AND STRUCTURE

Chelate polymers can be synthesised in three fundamentally different ways.

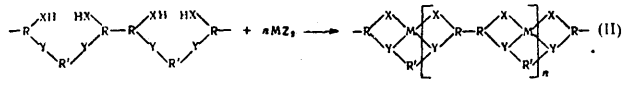
Firstly, by the metal forming donor–acceptor bonds with donor atoms in molecules which usually† contain at least two pairs of donor groups:



(I)

where X and Y are donor groups, and M is a metal.

Secondly, by entry of a metallic ion into an existing polymer chain in which the monomeric unit contains at least two pairs of donor groups:

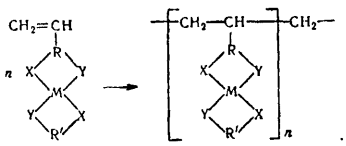


(II)

Polymers of types (I) and (II) can be formed also by the method of nascent reagents[10,11].

† In some rare cases polychelates may be formed when a chelate ligand possesses less than two pairs of donor groups, an example being provided by the hydroxo-bridged compounds. This question will be discussed in greater detail later.

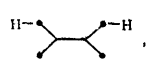
Finally, the third method of synthesis consists in the polymerisation of chelate compounds containing groups which themselves are able to undergo polymerisation:



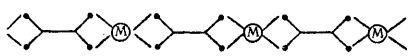
The formation of chelate polymers by the polycondensation of monomeric compounds containing chelate groups must evidently be included in this method.

The second and third methods of synthesising polychelates are usually linked with common methods for obtaining high polymers. The first method, however, is distinctive, and is applicable only to the production of coordinate-chain polymers. Such a reaction is often termed "polycoordination"[3]. Korshak *et al.*[12,13] have recently shown the similarity between the mechanism of this reaction and that of polycondensation.

Polycoordination can yield polymers with different spatial structures, both linear polychelates and planar and three-dimensional networks being possible. The structure of a given polymer is, of course, determined separately in each individual case. In particular, both the metal ion and the structure of the ligands influence the structure of a chelate polymer. In many cases the structure of the macromolecule is determined by that of the chelate loop formed. Confining ourselves to chelate polymers formed by four-coordinate metals, we can represent a bisbidentate ligand by the symbol

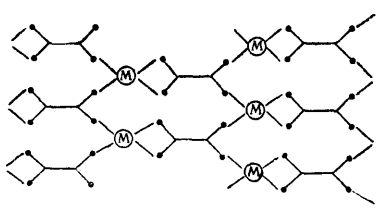


and write a linear polychelate formed by this ligand as



(III)

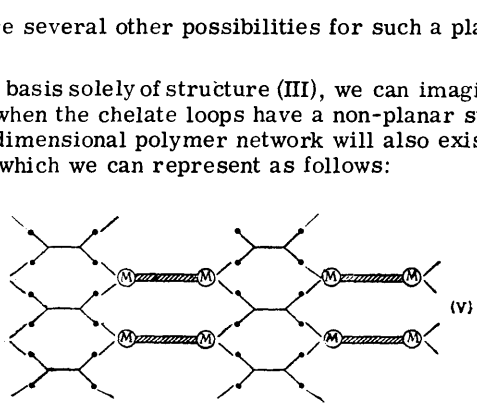
where M is a doubly charged metal ion. However, such a polymer can also have a different structure:



(IV)

There are several other possibilities for such a planar network.

On the basis solely of structure (III), we can imagine that, at least when the chelate loops have a non-planar structure, a three-dimensional polymer network will also exist, one layer of which we can represent as follows:



(V)

where ▭ denotes a ligand molecule "in profile". Here, of course, each chelate loop can form the basis of a new network layer of the polymer.

Each of the structures (III)–(V) clearly represents in some measure an "extreme case". Actually, there probably exists a definite combination of all three structures. Moreover, polychelates of any particular structure have their own rules for the building up of complete macromolecules, and it is difficult to regard chelate polymers as being completely analogous to one another. Nevertheless, in considering the various properties of polychelates it is probably necessary to start from the hypothesis that they have a network structure.

Few experimental results are available on the structure of chelate macromolecules. Terent'ev *et al.*[14,15] concluded, on the basis of a series of physicochemical properties of a large number of polychelates of differing structure, that chelate polymers are mainly two-dimensional and three-dimensional network structures. They assume that linear macromolecules are also present, although relatively few in number.

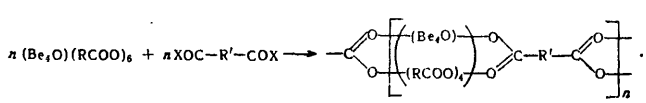
III. SYNTHESIS OF CHELATE POLYMERS

Published results show that the composition, structure, and constitution of the chelate loop have an important influence on the properties of chelate polymers. It will therefore be useful to discuss the literature on polychelates in the first place from the point of view of the composition of the chelate loop. In several cases such an approach enables the existing regularities to be revealed more clearly.

1. Polybisdioxachelates

One of the first polybisdioxachelates to be prepared was obtained in 1907 by the Russian chemists Tanator and Kurovskii[16]. In an attempt to isolate basic beryllium succinate, they obtained an infusible, transparent, vitreous product containing beryllium. Fifteen years later Meyer and Mantell[17] tried to isolate beryllium malonate, but failed to achieve satisfactory results. Neither the Russian nor the German chemists identified as polychelates the compounds which they had synthesised. A year later[18] X-ray examination of basic beryllium carboxylates showed them to be tetrahedra with the beryllium atoms at the corners and the oxygen atom in the centre, the six edges being occupied by the carboxylate groups.

Much more recently Marvel and Martin[19] established that formation of a chelate polymer required two carboxyl groups of a monobasic acid to be replaced by the carboxyl groups of a dibasic acid in the reaction

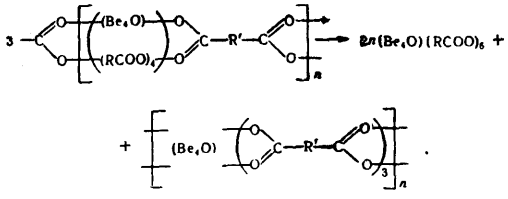


They prepared the polychelates from the basic beryllium salts of acetic, propionic, and benzoic acids, the second component of the reaction being adipoyl, sebacoyl, 3-ethyladipoyl, terephthaloyl, and isophthaloyl chlorides.

The polymers were in the form of powders, but some of them, containing only aliphatic acid radicals, could be drawn out into short filaments on plasticisation with a small quantity of solvent. Viscosity measurements showed a

very low degree of polymerisation, 4 or 5, carboxylic acid radicals obviously being located at the ends of the chains.

The polymers were thermostable right up to 350°–400°. However, even raising the temperature to only 110°–140° caused disproportionation to start, resulting in an insoluble and infusible network polychelate:



The disproportionation of beryllium carboxylates was known still earlier. Thus beryllium oxide acetate undergoes intramolecular rearrangement in boiling methanol or ethanol with the formation of the polychelate [20,21]

$$(Be_4O)(CH_3COO)_6 \rightarrow [(Be_4O_m)(CH_3COO)_{6-2m}]_n,$$

where $m = 2, 4$ and $n \gg m$. A similar transformation takes place even more rapidly at higher temperatures, for example in boiling butanol or decanol [22] and also in pyridine [23].

Marvel and Martin [19] also carried out the radical polymerisation of basic beryllium carboxylates containing acrylic acid radicals. In the presence of benzoyl peroxide, insoluble network polychelates were obtained. A network polymer was formed even when the basic beryllium carboxylate contained only one acrylate group. This phenomenon was explained in terms of the disproportionation reaction, which these workers had discovered. The polymers thus obtained already decomposed vigorously at 200°.

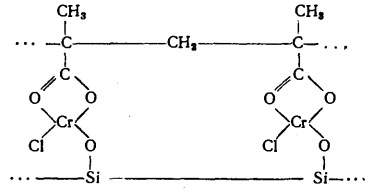
Macromolecular compounds based on acrylic acid have been known for a long time, and have been well investigated. Such polymers contain repeating carboxyl groups, which in some cases can form polychelates with various metal ions. A chelate loop of the type 2(O, O)–M is also formed. Several papers have been published on the synthesis and some of the properties of these compounds.

Wall and Gill [24] investigated the interaction of copper(II) ions with polyacrylic acid, and established from the infrared spectra and polarographic studies that a copper complex is formed: the titration curves show that each copper(II) ion replaces two hydrogen atoms to form a chelate compound. The copper polychelate differs from the compounds formed by the alkaline earth metals with polyacrylic acid, in which electrostatic interaction predominates [25]. It is interesting that nickel, zinc, and cobalt ions exhibit only a feeble tendency to form polychelates with polyacrylic acid.

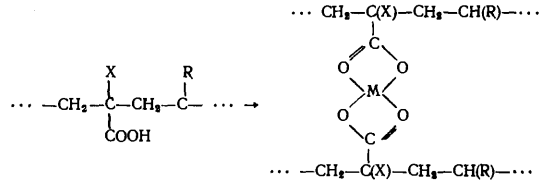
Morawetz [26] and Kotliar and Morawetz [27] investigated the tendency of copper acetate to form complexes with polyacrylic and polymethacrylic acids. From the results of titration, dialysis, and spectroscopic examination they established that each copper ion is linked with four oxygen atoms of these polymeric acids. The number of chelate loops formed depends on electrostatic factors and the concentration of the polymer. Gregor and his coworkers showed, in an examination of the complexing properties of polyacrylic acid, that the copper(II) polymers are extremely stable [28]. They remark [29] that the formation of copper polychelates is more difficult with cross-linked polyacrylic and polymethacrylic acids (1–9% of divinylbenzene in the copolymer) than with the linear polymers. Alkaline earth metals form [30] far less stable chelate polymers than does copper(II). After copper, the manganese and zinc polychelates were the most stable.

The barium salt of isotactic polyacrylic acid of molecular weight 60 000 has been described recently [31]. The electron micrographs indicate that the macromolecules have a compact globular structure, and remain unchanged over the pH range 4.2–10.7. Consolidation of the initial ball of isotactic polyacrylic acid is associated with the formation of stable bonds between the barium counterions and the carboxyl groups of the acid.

A noteworthy du Pont patent [32] reports the preparation of a polychelate of chromium with polyacrylic acid of low molecular weight on an ordinary silicate glass surface. In this case the chromium ion probably forms a link between the silicon atoms in the glass and the organic polymer:

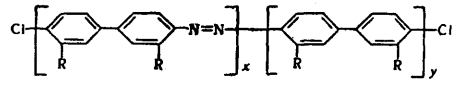


Interesting work has also been done on the synthesis of polychelates based on polymers and copolymers of several other unsaturated acids with metals. The possibility of the formation and industrial application of polymers of this type was noted by Berlin [33] as early as 1947. Copolymers of unsaturated acids with some unsaturated monomers contain systems of carboxyl groups. When such copolymers are compressed with salts or oxides of metals at 120°–140°, it is possible to obtain insoluble, heat-resistant, three-dimensional polychelates:



Morawetz *et al.* [34] prepared chelate polymers of alkaline earth metals with hydrolysed copolymers of maleic anhydride with styrene and ethyl vinyl ether.

The preparation and properties of some aromatic polymers having a conjugated bond system have been described more recently by Berlin *et al.* [35] Compounds of general structure



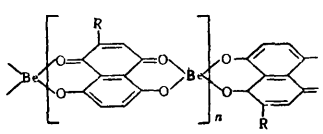
where R = H or COOH, were obtained by the decomposition of bisdiazotised derivatives of benzidine and of benzidine-3,3′-dicarboxylic acid. The macromolecular compound obtained from the acid was found to react with copper salts to form a three-dimensional chelate polymer, as was confirmed by the electron paramagnetic resonance spectra of this compound.

Compounds formed by reaction of various metal derivatives with bis-β-diketones represent a large and distinctive group of chelate polymers. The peculiarity of this

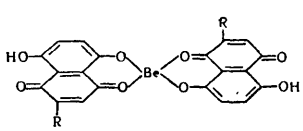
group is that the metal atoms form part of the main chain of the polymer, and have a substantial influence on the properties of the resulting macromolecular compounds.

Among the first workers to obtain chelate polymers based on bis-β-diketones were Bailes and Calvin[36], who, in a research on compounds which might act as artificial oxygen-carriers, turned to some peculiar compounds of cobalt. Among the huge number of substances which they examined, two were chelate polymers having the structure 2(O, O)–Co. The starting materials for the synthesis of such polymers were 4,6-dihydroxybenzene-1,3-dialdehyde and naphthazarin respectively. The products were yellow powders, which on being heated each lost two molecules of water of crystallisation per chain unit.

Underwood and his collaborators suggested naphthazarin and alkannin as reagents for the colorimetric determination of beryllium[37,38], the compounds thus formed obviously being chelate polymers. However, the composition of the products could not be established. A separate investigation showed that beryllium reacts with naphthazarin and alkannin to form two pairs of complexes depending on the proportions of the starting materials[39]. These workers consider that, when the ratio of beryllium to naphthazarin is 1 : 1, the product is a polychelate of the structure



where R represents H in the case of naphthazarin, and $-CH(OH).CH_2.CH:C(CH_3)_2$ in the case of alkannin. When the ratio of beryllium salt to ligand is 1 : 2, the product has the constitution

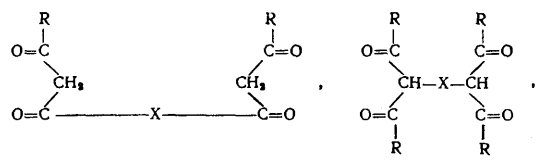


Still earlier a polymer of quinizarin with copper had probably been obtained by Flumiani and Bajić[40,41], but they did not identify their product as polymeric.

In 1953 Wilkins and Wittbecker patented[42] the preparation of chelate polymers by the reaction of various bis-β-diketones with acetylacetonates of bivalent metals. The bis-β-diketones used were terephthaloyldiacetone, bis-*p*-acetoacetylphenyl ether, 1,8-bisbenzoylacetyloctane, and *p*-bis-2,2-diacetylethylbenzene. Polychelates were obtained with the following four-coordinate bivalent metals: Be, Cu, Ni, Zn, Co, Fe, Pd, Mn, Ca, Sr, Ba, and Cd. The reaction was carried out by heating a mixture of the metal acetylacetonate and the bis-β-diketone in a vacuum, the acetylacetone distilling off. The patentees varied the reaction conditions, the metal ions, and the tetraketones, and prepared polymers suitable for the production of coatings, moulded articles, filaments, and films.

Glukhov[43] reported the preparation of a series of chelate polymers of Be, Mg, Ca, Zn, Cu, Co, and Fe with various bis-β-diketone derivatives of acetylacetone. He found that the polybisdioxachelates of beryllium were the most stable to heat, for they decomposed only at 350°. Polychelates were prepared[44] by emulsion polymerisation of the tetraketones and water-soluble salts of the above metals in aqueous chloroform at 40°–60° for 2 h. The products were powders: white in the cases of Be, Mg, and Ca, dark blue with Cu, green with Fe, and red with Co. The chelate polymers were soluble in pyridine and in dimethylformamide, with $[\eta] \simeq 0.1$. In this series of tetraketones, too, the beryllium polychelates were the most stable to heat.

During the past three years, Korshak and his coworkers have published a series of papers[12,13,45–54] on the synthesis and properties of the chelate polymers of metals with various tetraketones. A series of polychelates was described, formed by bivalent metals (Be, Cu, Ni, Zn, Co, Cd, and Mn) with bis-β-diketones having the structure



where X = $[CH_2]_3$, $(CH_2)_6$, $C_6H_4.CH_2.C_6H_4$, *p*-C_6H_4, *m*-C_6H_4, *p*-$C_6H_4.C_6H_4$-*p*′, $CH_2.C_6H_4.C_6H_4.CH_2$, $C_6H_4.O.C_6H_4$, etc., and R = CH_3, C_6H_5, OH, OCH_3.

The overwhelming majority of chelate polymers have been obtained as coloured amorphous powders, sparingly soluble or else completely insoluble in the usual organic solvents. The beryllium compounds are more soluble than others.

The thermal stability of the polychelates increases with increase in the number of phenyl groups in the initial tetraketone. The thermal properties of the polymers also depend on the metal ion, the stability diminishing in the sequence: Cu > Be > Ni > Co > Zn > Mn > Cd. Degradation of the polymers starts at 250°–400° with the various specimens.

Molecular weights were determined ebullioscopically in chloroform in the case of soluble polymers, and by approximate calculation from analytical results in the case of insoluble compounds. From these calculations the degree of polymerisation did not exceed 25, and had a value of 52 only for the chelate polymer of copper with *pp*′-diacetoacetylbiphenyl.

More recently, Korshak and Vinogradova[12,54] have reported the osmometric determination of the molecular weight of the polychelate formed by beryllium with *pp*′-bisacetoacetylphenyl ether; one of the chloroform-soluble fractions of this polymer had a molecular weight of 126 000.

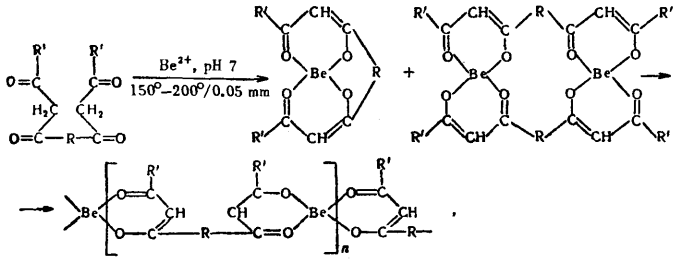
It has also been shown[48] that the thermal stability of chelate polymers based on bis-β-diketones is more clearly linked with the flexibility of the macromolecular chain than with solubility. X-Ray examination established[46] that a decrease in molecular weight is accompanied by an increased degree of order in the molecular structure.

Chelate polymers have also been obtained of the bivalent metals Cu, Ni, Zn, Co, Cd, and Mn with quinizarin[46]. They are infusible coloured powders which are stable up to 350°–400°.

A noteworthy paper by Knobloch and Rauscher[55] describes the original use of interfacial polycondensation for the preparation of chelate polymers, the components being 3-hydroxy-2-enones (tetraacetylethane and quinizarin), which are soluble in benzene or in ethylene dichloride, and aqueous cuprammonium solution. These workers emphasise that such interfacial polycondensation can be accomplished only if the copper is present as an unstable complex in the aqueous solution. Polychelates are still formed when the ammonia is replaced by pyridine, but the bis-ethylenediamine and glycine complexes of copper no longer give chelate polymers. Similar results were obtained with nickel(II) ions.

In order to produce thermostable plastics, Kenney[56] prepared polybisdioxachelates of Be, Cu, Ni, Zn, Co, and Fe and polytrisdioxachelates of Al. The polymers were synthesised by fusing the corresponding metal acetylacetonates with the bis-β-diketone in a vacuum, when several of the resulting compounds could be isolated as brittle films. The molecular weight of these compounds did not exceed 4000. On being heated in air at 300° for 3 h, the chelate polymers lost 16–46% of their weight.

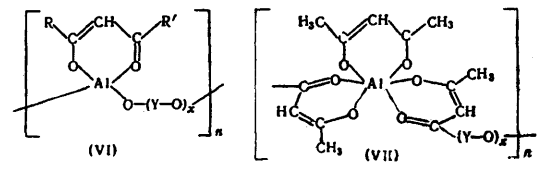
Kluiber and Lewis[57] prepared macromolecular chelate compounds with various bis-β-diketones according to the scheme



the intermediate products being isolated and characterised. They regard this as a new method for synthesising polychelates. In fact, this is the first work to show the possibility of formation of a macromolecular complex by ring cleavage. However, the authors themselves comment that aliphatic bis-β-diketones were used in which R = $[CH_2]_x$ (x = 6–12), and rearrangement of the macrocyclic rings into polychelates was found to take place more readily the longer the carbon chain (*i.e.* the higher the value of x). The presence of aromatic or conjugated systems in the macrocycle will obviously modify the rearrangement, or even lead to the direct formation of a polychelate. Kluiber and Lewis also consider, on the basis of viscosity measurements in benzene and of fluidities at moderate temperatures, that the final products have a high molecular weight. This hypothesis is supported also by the amorphous character of such compounds, as shown by the X-ray powder diagrams.

An interesting paper by Kugler[58] on the preparation of chelate polymers of aluminium shows that reaction between aluminium alkoxides and acetoacetic ester yields a compound in which a keto-ester grouping is combined with the aluminium atom in a chelate ring. On hydrolysis, such systems split off ethyl alcohol, and at high temperatures rearrangement takes place, with loss of water and formation of a polychelate.

Two years later Patterson *et al.*[59] described a series of chelate polymers of aluminium similar in structure to those obtained by Kugler[58]. They investigated the properties of polycondensates containing aluminium atoms in the chain, and attempted to increase the stability of such compounds by linking the aluminium in a chelate ring. Polymers of two types of structure were obtained

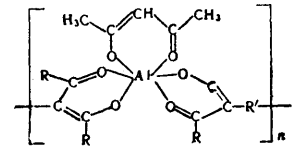


where normally R = R′ = CH_3 and Y is the radical of the diols HO.Y.OH. Polychelates having the structure (VI) are unstable to hydrolysis. They have low melting points, are soluble, and are thermally unstable. On being heated, however, they can disproportionate to give thermally stable, infusible, network polymers.

Chelate polymers having the structure (VII) are infusible powders, stable up to 360°. Their molecular weights were determined cryoscopically in benzene, in which several of the polymers were soluble, and lie within the range 400–2620.

The diols used were mono-, di-, and tri-ethylene glycols, butane-1,3(and 1,4)-diols, and also pentane-1,5--diol. An especially interesting diol was 2,2-diphenylpropane-*pp*′-diol, the polychelate of which was soluble in methanol. From it could be isolated hard, brittle, transparent, colourless films which were stable in air.

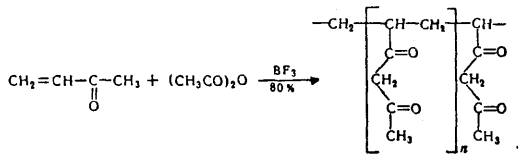
The polycondensation polymers thus obtained should have a linear structure. In order to obtain polychelates having a different spatial arrangement of the macromolecular chains, these workers turned to tetraketones, and synthesised more than a hundred chelate polymers of aluminium having the general formula:



where R = CH_3, C_6H_5, or OC_2H_5; R′ = C_6H_4 or $[CH_2]_x$, with x = 0–5. It is seen from the formula that four coordination positions in these compounds are occupied by the oxygen atoms of the tetraketones, and two by the acetylacetone grouping. These compounds were infusible and stable to heat, and probably represent polymers having a three--dimensional network structure.

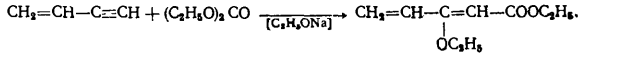
Formation of a network polymer can be expected also when the β-diketone radical forms part of the monomer unit of a carbon-chain or heterochain polymer. At the same time, formation of a network polymer in the synthesis of a polychelate having this type of structure makes it difficult to coordinate the metal ions with all the β-diketone groupings.

The preparation of chelate polymers in this way has been described by Hoeschele *et al.*[60], who were able to synthesise polyacetoacetylethylene by the ionic polymerisation of methyl vinyl ketone in acetic anhydride:

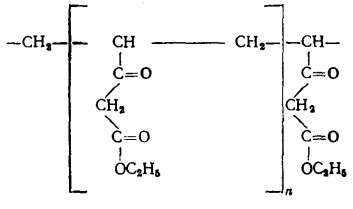


Comparison of the stability of these polychelates with that of the corresponding acetylacetonate complexes showed approximate equality in the copper, neodymium, and praseodymium chelate compounds, while the uranyl chelate polymer was about three times as stable as the corresponding acetylacetonate.

Cairns *et al.*[61] described the synthesis of ethyl 3-ethoxypenta-2,4-dienoate from but-1-en-3-yne:



The resulting compound readily polymerises both on standing in air and under the influence of compounds containing oxygen or nitrogen. The polymer thus formed can be hydrolysed to the corresponding keto-ester:



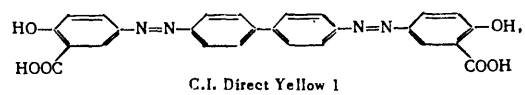
The latter can in turn yield chelate polymers. These workers described a copper polychelate of this type in which, from the analytical results, copper appeared to have entered 23% of the keto-ester groupings. This substance was an infusible and non-softening dark green powder, most probably a network polymer.

In 1958 a du Pont patent[62] claimed the production of solutions for the preparation of insoluble, hard polymeric coatings. On evaporation of the solvent, polychelates were formed of beryllium, aluminium, and other metals with various polymeric chelate ligands. The latter could include poly(allyl acetoacetate), copolymers of vinyl acetate and salicylaldehyde and of styrene and acryloylacetone, and other polymers and copolymers having donor atoms.

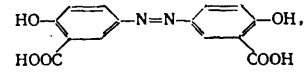
Several bis-*o*-hydroxycarboxylic and bis-*o*-dicarboxylic acids, as well as bis-β-diketones, are able to form polybisdioxachelates. Thus chelate polymers have been obtained from bivalent beryllium and iron with tetrasalicoylferrocene[63]. The electrical conductivity of such polychelates[64] is several orders of magnitude greater than that of the usual organic dielectrics, and approaches the conductivity of some organic semiconductors[65,66].

Terent'ev *et al.* have described[67] the synthesis and properties of polychelates of copper, nickel, iron, and cobalt with methylene-5,5'-bissalicylaldehyde, the products all being coloured amorphous powders of network structure. Magnetochemical measurements showed the chelate loops of all the polymers to have a tetrahedral structure.

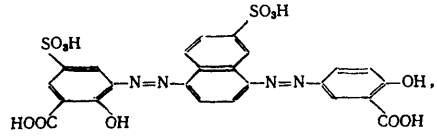
Several lakes formed by the interaction of a series of dyes and metal salts are regarded by Berlin and Matveeva[3] as chelate polymers. For example, the following three compounds



C.I. Direct Yellow 1



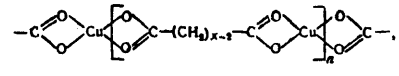
C.I. Mordant Yellow 5



C.I. Mordant Brown 51

give stable chelate compounds with salts of copper, chromium, aluminium, and iron[68]. From the structure of such dyes it must be assumed that their metal complexes are polymers.

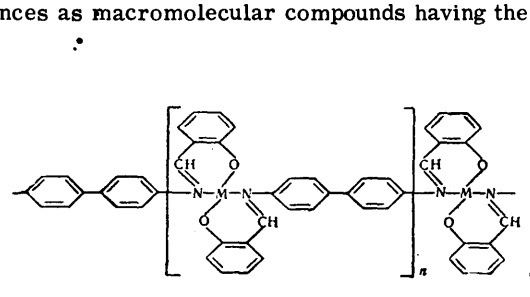
Interesting work has also been done by Kubo *et al.*[69] on the structure of the chelate polymers formed by copper with various dicarboxylic acids, their general formula being



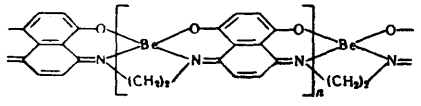
where $x = 2-10$. From measurements of magnetic moments they conclude that a network structure is most probable for $\alpha\omega$-dicarboxylic acids having an even number of carbon atoms. This conclusion is supported by results for infrared spectra, especially the C=O stretching vibrations and the rotational oscillations of the CH_2 groups.

2. Polybisazaoxachelates

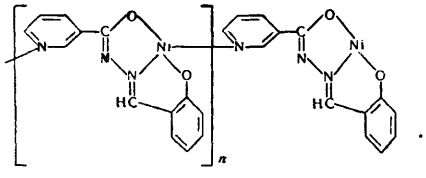
Among the earliest investigators to obtain polybisazaoxachelates were Pfeiffer and Pfitzner[70], who as long ago as 1936 described the preparation of copper complexes of Schiff bases formed by salicylaldehyde with *m*- and *p*-phenylenediamines and also with benzidine. All these substances were only very difficultly and sparingly soluble in chloroform. These insoluble internal complexes were assumed to be cyclic dimers. On the basis of present-day chemical knowledge, however, such a conclusion seems debatable. It is evidently more correct to represent these substances as macromolecular compounds having the structure:



Dubsky *et al.*[71] investigated the products formed by solutions of beryllium salts with naphthazarin in the presence of ethylenediamine, and found that the latter two compounds interact, forming a ketimine compound with the beryllium. It can be assumed that the products were chelate polymers

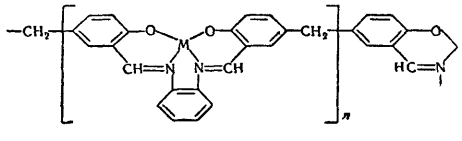


Sacconi[72] prepared Schiff bases from pyridine-3-carbohydrazide and salicylaldehyde, 5-bromosalicylaldehyde, *o*-hydroxyacetophenone, and *o*-hydroxynaphthaldehyde. These compounds reacted with nickel acetate to form amorphous substances, insoluble in water and in organic solvents, having the polymeric structure:



All the compounds were stable up to 350°, and possessed remarkable chemical resistance.

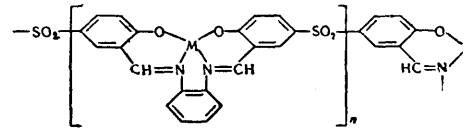
Marvel and Tarköy[73] prepared and examined the thermal stability of the chelate polymers of bivalent Cu, Ni, Zn, Fe, Co, and Cd with Schiff bases formed from methylene-5,5'--bissalicylaldehyde and *o*-phenylenediamine. A polymeric Schiff base was isolated which was an orange substance soluble in tetrahydrofuran. The viscosity of this compound indicated its degree of polymerisation to be 45. On treatment of this polymer in air with solutions of metal acetates at room temperature for 6 days, polychelates



were isolated as infusible coloured powders, which were also regarded as having a degree of polymerisation of 45. They showed considerable thermal stability: on being heated in air at 250° for 3 h, the losses in weight were 11–26%.

Somewhat later Terent'ev and his coworkers[9,74] prepared chelate polymers of Cu, Ni, Zn, Fe, Co, and Cd with Schiff bases formed by methylene-5,5'-bissalicylaldehyde with ammonia, ethylenediamine, hexamethylenediamine, and *o*-phenylenediamine. Polychelates of this type can readily be synthesised by the nascent reagent method. A comparative magnetochemical study of the products showed several structural regularities in the chelate loops of such polymers. It has also been established[14] that all the polychelates are amorphous substances having an appreciable predominance of network structures. Some of the compounds synthesised had semiconducting properties[75], and others found application in the rubber industry[15].

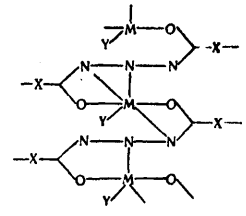
Marvel and Tarköy[76] also synthesised chelate polymers of the same metals with Schiff bases of sulphonyl-5,5'-bissalicylaldehyde and *o*-phenylenediamine



the products being infusible, insoluble, and coloured. The nickel and cadmium compounds were thermally the most stable.

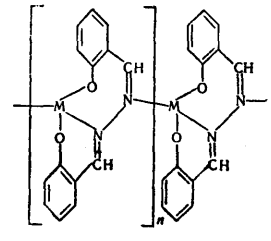
Spitsyn and his coworkers[77] reached the same conclusions from an examination of the properties of chlorinated and brominated polychelates of similar structure.

Goodwin and Bailar[78] obtained thermally stable polymers containing cobalt, aluminium, and chromium, using as chelate ligands polymeric Schiff bases formed from methylene-5,5'-bissalicylaldehyde and sulphonyl-5,5'-bissalicylaldehyde with diethylenetriamine. They assume that substances of the following structure are formed:



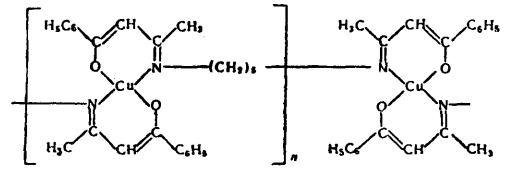
where X = $CH_2.CH_2$, SO_2; M = Co^{3+}, Al^{3+}, Cr^{3+}; and Y = Cl^-, NO_3^-, $\frac{1}{2}SO_4^{2-}$.

Marvel and Bonsignore[79] obtained macromolecular chelate compounds

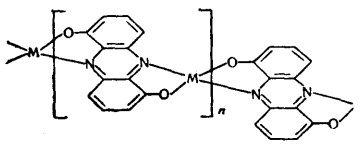


by the reaction of salicylideneazine with salts of copper, nickel, zinc, cobalt, and cadmium. The polymeric structure of such compounds is suggested by their insolubility in water and organic solvents, and also by their appreciable thermal stability.

Several Schiff bases of 1-phenylbutane-1,3-dione give resins and rubberlike products with copper acetate[80], this being explained by the formation of chelate polymers having the structure

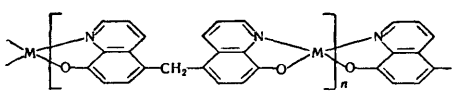


Another good compound for complex formation was phenazine-1,6-diol, which yielded polychelates



with Cu^{2+}, Fe^{3+}, Hg^{2+}, and other metals [81].

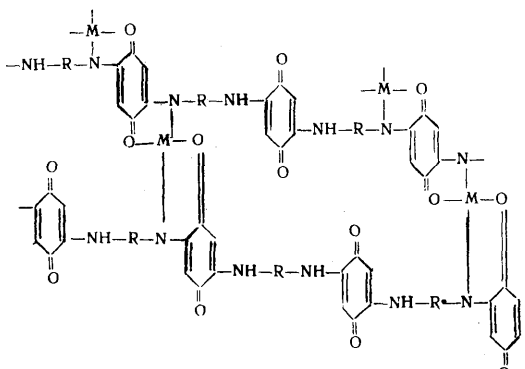
Korshak *et al.* [82] described polychelates of methylene--5,5′-bisquinoline-8,8′-diol with metals. Reaction of this compound with the acetylacetonates of Cu, Ni, Zn, Co, Cd, and Mn gave chelate polymers of molecular weight not exceeding 9000



These workers also obtained interesting unsymmetrical polychelates, using either two different chelate ligands with the same metal or two metals with the same chelate ligand. Besides the above quinoline derivative, quinizarin was also used as ligand. The unsymmetrical coordination compounds were found to have similar properties to those of the homogeneous polychelates. All these compounds were coloured powders. The thermomechanical curves indicate that the polymers undergo degradation at 250°–400°.

The work on polybisazaoxachelates of Berlin and his collaborators is also of great interest. Reaction of a chloramine with benzidine and some other diamines enabled these workers to obtain infusible, almost black polymers which were insoluble in the usual organic solvents [83–85]. These compounds were soluble in concentrated sulphuric acid and partly soluble in formic acid and dimethylformamide. End-group determinations showed their molecular weight to be 2000.

The presence in polyaminoquinones of *ortho* C=O and NH groups made it possible to obtain a series of chelate polymers of copper, magnesium, cadmium, and other metals of general structure

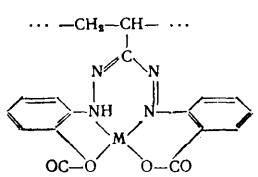


The low metal content (6–12%) compared with the theoretical indicates that cross-linking involves some of the C=O and NH groups. This hypothesis is supported also by the presence of a hydrogen bond, revealed by the infrared spectrum.

The electron paramagnetic resonance spectra of the synthesised polyaminoquinones contained asymmetric lines, although the latter appeared only when the molecular weight of the polymer had become fairly high. The concentration of unpaired electrons in these cases was 10^{20}–10^{21} g^{-1}. When the temperature was lowered to 80°K, the electron paramagnetic resonance absorption disappeared, recalling the behaviour of paramagnetics having antiferromagnetic properties. The corresponding chelate polymers of copper exhibited an electron paramagnetic resonance spectrum practically identical with that of the original highly polymerised metal-free compound. It is interesting that the entry of copper not only intensifies the signal but also preserves it down to the temperatures of liquid nitrogen. The above workers suggest, however, that this phenomenon is due to further cross-linking, not with the presence of actual unpaired *d* electrons on the metal ions.

Several investigators have obtained polybisazaoxachelates by introducing chelate groups into a carbon-chain polymer. Thus Maynard [86] treated a 47% solution of a 10 : 2 : 1.1 butadiene–methacrylonitrile–styrene copolymer in decalin with ethylene glycol, and then aminated the resulting mixture with ammonia. He treated the polyamine thus obtained, containing about 10% of total nitrogen and 2.5% of amine nitrogen, with salicylaldehyde in benzene solution, distilled off 5 parts of the condensed water, and treated the resulting rubberlike product with metal salts, obtaining insoluble polychelates with the ions Cu^{2+}, Zn^{2+}, Co^{2+}, Fe^{3+}, Hg^{+}, Sn^{2+}, and Sn^{4+}.

Interesting polychelates were obtained by Schulz [87], who found that polypropenal can react with the usual reagents for aldehydes, forming oximes, hydrazones, and phenylhydrazones. *o*-Hydrazinobenzoic acid yields a poly(propenal *o*-carboxyphenylhydrazone) containing 70 mole % of hydrazone groups, which with diazotised anthranilic acid forms a polymeric formazan more readily. Like the formazans of low molecular weight, this polymer forms very stable metal complexes, for example with Cu^{2+} and UO_2^{2+}, but not with Ni^{2+} or Mn^{2+}.

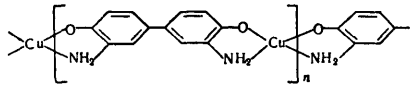


Schulz correctly assumes that this property of the polymers can be utilised in the construction of columns for the selective separation of these ions.

Polybisazaoxachelates have attracted the attention of many American research workers. Apart from the papers mentioned above, several technical reports on the synthesis and properties of chelate polymers have been published in the USA. This work has been carried out in Ohio under the direction of well-known specialists in the field of coordination compounds (Bailar, Fernelius, and others) [88,89]. However, we have no knowledge of the exact contents of these reports‡. It is noteworthy that it is in Ohio, which contains one of the scientific research centres of the United States Air Force, that the principal American investigations on the properties of chelate polymers have been carried out, the main purpose being to find new thermostable materials. Characteristically, properties of polychelates other than their thermal properties have been studied

‡ Copies of these reports are not held by the Lenin State Library, in the Library of Foreign Literature.

extremely superficially in this work. Nevertheless, several papers and lectures by various American scientists give some information on the polychelates which have been investigated in Ohio. Thus Shaw[5] reported in particular that a polychelate of the structure



had been synthesised and studied in Ohio, but he did not give the properties of this compound.

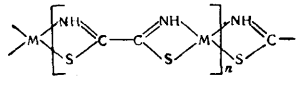
Atlas and Mark[4] have more recently written a brief survey of thermostable polymers. On the basis of information presented at the Conference on High-Temperature Polymers held in May 1959 at Dayton (USA) they give structures for a few new polybisazaoxachelates synthesised in Ohio by Bailar, who obtained a series of chelate polymers by fusing biquinolyl-8,8'-diol with zinc, copper, and nickel salts. Other chelate ligands used included bisdiphenols, bissalicylic acids, and derivatives of *o*-aminophenols. All the substances obtained were thermostable coloured powders.

3. Polybisazathiachelates

Possibly the most interesting polymers having the chelate loop 2(N, S)–M are the compounds formed by metals with rubeanic acid, for which as early as 1926 Rây and Rây[90] proposed the following structural formula:

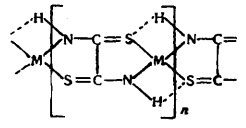


This formula was regarded as correct until 1944, when Jensen[91] concluded from an investigation of the chemical properties of a series of internal complexes that the salts of rubeanic acid are polymers having the structure



He also showed that the old formulae for these salts were impossible owing to steric hindrance.

Almost fifteen years later Piper[92] suggested a formula for metal polyrubeanates with repeating five-membered rings in the *trans* form, based on spectroscopic and magnetochemical data. Almost simultaneously a paper by Barcelo[93] reported similar conclusions based on infrared spectra, and proposed the following formula for polyrubeanates:

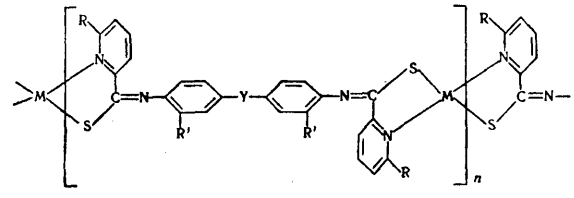


There are indications in the literature[94], however, that the polymer may exist in the *cis* form. Kubo *et al.*[69] assume further that copper polyrubeanate (other metals were not investigated) is a planar network, not a linear structure. This view is based on the low magnetic moments of copper polychelates.

Quite recently[95] polychelates of nickel with *NN'*-disubstituted dithiooxamides have been obtained (the tetrasubstituted compound does not form a polychelate). All these chelate polymers are amorphous powders, insoluble in solvents. They are stable on being heated to 300°–400°. *NN'*-Diacetoxydithiooxamide gives with nickel a polychelate which is soluble in several hot mineral oils and nitrobenzene. Such properties are probably associated with the relatively low molecular weight of this compound. The nickel poly-*NN'*-dimethyldithiooxamide derivative also probably possesses a low degree of polymerisation. It is crystalline and decomposes at a lower temperature. Measurement of the magnetic susceptibility of the polychelates showed that in several cases the magnetic moment was 2.4 μ_B, which is attributed to the simultaneous presence in the macromolecule of chelate loops with both planar and tetrahedral configurations, with the latter predominating.

Polyrubeanates have also found practical application. For example, the preparation of a molecularly oriented polymeric plastic which polarises light has been patented[96], the polymer containing nickel and copper polydithiooxamides as additives. The semiconducting properties of polyrubeanates have also been described[75].

Polybisazathiachelates of general formula



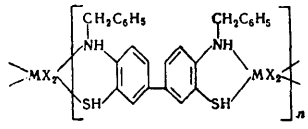
(VIII)

(where R = R' = H, and Y = SO_2, O, CO, or is absent altogether) were obtained by Martin[97] by the interaction of 2-methylpyridine, sulphur, and various diamines. These substances, while possessing two pairs of donor groups, readily undergo polycoordination with the four-coordinate bivalent ions of copper, nickel, zinc, and mercury. He was unable to determine any end-group from the infrared spectra. Elementary analysis also suggests that the polymer chain is of indeterminate length. Martin assumes that his synthetic polychelates have molecular weights of about 15 000. Thermal stabilities of the polymers were determined on a thermogravimetric balance. Vigorous decomposition starts at 340°–400°. The zinc compounds show the greatest thermal stability, which is in turn affected by the nature of the group Y. Maximum thermal stability is achieved when Y = SO_2. Thus the various polychelates of zinc decompose above 400°, but when Y = SO_2 the polymer is so stable that its infrared spectrum shows no change in structure after heating in air at this temperature for 6 h. Introduction of the bridging groups Y = O and CO into the original molecule does not lead to the production of plastic polychelates.

Terent'ev *et al.*[98] also investigated the properties of chelate polymers having the structure (VIII) with R = H or CH_3, R' = H or OCH_3, and Y absent. It was found that introduction of methoxy-groups increases the solubility of

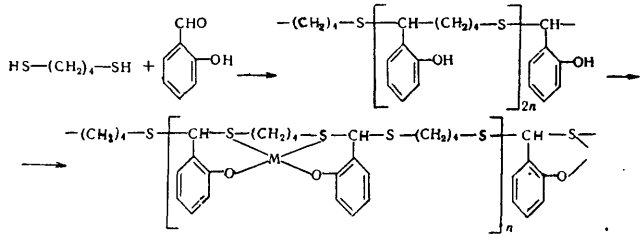
the compounds, while their molecular weights do not exceed 40 000–45 000. Magnetochemical examination showed that the polymers had chelate loops of tetrahedral structure.

Eirich and Mark[99] have reported the preparation of a chelate polymer having the structure



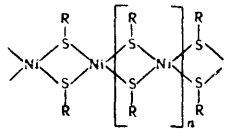
where X represents Cl^- or other substituent attached to the metal. The polychelate was synthesised by the interaction of toluene, benzidine, and sulphur, followed by treatment with a salt of the metal. However, the above formula seems extremely doubtful to us. The hydrogen of the thiol group is sufficiently acidic to be replaced by a metal. It can only be supposed that, since this work was merely reported at a conference, it contained some unverified results.

Atlas and Mark[4], at the Conference on High-Temperature Polymers held in Dayton in May 1959, mention that Drinkard (University of California) has described the reaction between alkanedithiols and aldehydes, leading to the formation of polymeric mercaptals. If any coordinate groups still remain in such a molecule, chelate polymers can be formed. The following reaction is cited as an example

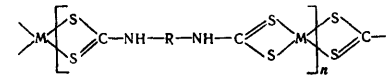


4. Polybisdithiachelates

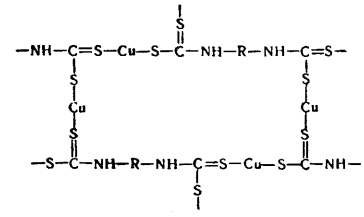
The first investigator to obtain polybisdithiachelates was probably Jensen[91]. While studying the mercaptides of nickel, he turned his attention to the extraordinarily close similarity in properties between the nickel compounds of benzoquinoline-8-thiol and of 2-methylquinoline-4-thiol. The former compound, unlike the latter, can yield a non-polymeric internal complex. From a comparison of the colour, solubility, and magnetic properties of benzoquinolinethiols, benzothiazole-2-thiol, and several other thiol derivatives, he concluded that these compounds contain a planar chelate loop with four-coordinate bivalent nickel having the structure 2(S, S)–Ni. Jensen hence decided that nickel mercaptides are highly polymerised compounds of the type



For a long time after this no one took an interest in polybisdithiachelates. It is only recently that a few papers by Terent'ev and his coworkers have appeared describing the synthesis[100] and properties[75,101,102] of chelate polymers containing the chelate loop 2(S, S)–M. These are compounds formed by several metals with biscarbamodithioic acids, and have the general formula



where R = $[CH_2]_2$, $[CH_2]_3$, p-C_6H_4, p-$C_6H_4.C_6H_4$-p'; M = Ni^{2+}, Zn^{2+}, Co^{2+}. Polychelates having this structure were obtained by the reaction of aqueous solutions of the corresponding sodium biscarbamodithioates with the metal acetates. These workers were able to show[100] that, in the case of copper(II) salts, such reaction is accompanied by reduction of the latter to copper(I) with simultaneous formation of a polymer having a two-dimensional network structure



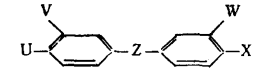
where R has the same significance.

Polybisdithiachelates are fine powders of various colours. They are extremely difficultly soluble and are infusible. The chelate polymers are thermostable, decomposing above 350°. They most probably possess a network structure. Their electrical properties are especially interesting[75]; several substances have been found to possess semiconductor characteristics. These same polybisdithiachelates proved to be strong catalysts for the decomposition of hydrazine[102].

5. Polybisdiazachelates

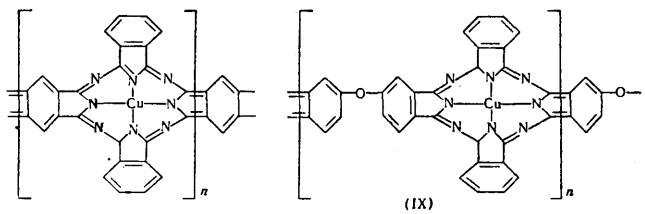
Polybisdiazachelates form a distinctive group of chelate polymers. They include firstly polymers which to a certain extent repeat the structure of such important and interesting compounds as the phthalocyanines, haemin, and chlorophyll.

As early as 1949 Ciba Ltd. patented[103,104] the preparation of polymeric phthalocyanines having a relatively low degree of polymerisation. A phthalocyanine dye is obtained by reaction of the substance



(in which Z is the radical of a simple dibasic acid, for example carbonic or sulphuric acid, and U, V, W, and X represent CO or CN groups) with copper halides and dicyanoaryls or o-dicarboxylic acids in the presence of urea. Ammonium molybdate is used as catalyst. The product is a black powder, practically insoluble in organic solvents, but dissolving in concentrated sulphuric acid to form a green solution.

Since copper phthalocyanine possesses high thermal stability and can be sublimed in a current of nitrogen at 560° without decomposition, it and its analogues have attracted the attention of chemists not only as excellent dyes but also as possible polymers of astonishing thermal stability. Marvel and Rassweiler[105] obtained polymeric phthalocyanines by the interaction of pyromellitic acid, phthalic anhydride, and urea, and also from the 3,3′,4,4′--tetracarboxylic acid of diphenyl ether, phthalic anhydride, and urea. The metal ion used was copper(II). The infrared spectra of the resulting polymers showed that their structure was in fact similar to that of phthalocyanine:



(IX)

however, they were of low molecular weight.

This paper gives references to some American work done under contract in 1952 and 1956, which also had the purpose of obtaining polymeric phthalocyanines. Thus in 1956 Bailar and Drinkard prepared a phthalocyanine-like polymer from pyromellitic acid and urea, but the product was insoluble and could not be investigated further.

Marvel and Rassweiler[105] obtained the substances as blue-green or greenish powders. The polymers were soluble (although with difficulty) in dimethylformamide, which enabled them to be separated from the phthalocyanine formed as a byproduct under these conditions. The polychelates could be reprecipitated from the dimethylformamide with chloroform, but these workers were unsuccessful in estimating the molecular weight of the compounds. The chelate polymers are similar to phthalocyanine in thermal properties, but in air they slowly decompose at 350° and above.

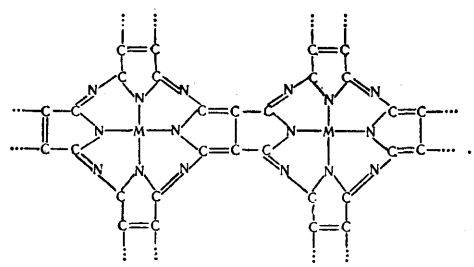
Somewhat later Marvel and Martin[106] described the preparation of a polymeric phthalocyanine of structure (IX) by a different method, based on the use of phthalonitrile and 3,3′,4,4′-tetracyanobiphenyls with copper bronze. These substances in various proportions were fused together at 275° for 3 h. The products were purified by extraction with acetone followed by agitation with sulphuric acid for 20 h. The insoluble residue dissolved in sulphuric acid on heating, but was not reprecipitated on cooling again. All these substances were dark blue with ametallic lustre. The infrared spectra, viscosity measurements, and analytical data show that the products have an extremely low degree of polymerisation. Such phthalocyanines decompose at 350° within 24 h.

Drinkard and Bailar's paper[107] also describes a polymeric copper phthalocyanine, obtained by the interaction of pyromellitoyl anhydride, cuprous chloride, and urea in the presence of a catalyst (ammonium molybdate) at 160° for 30 min. It is assumed that both linear (ribbon) and network structures are formed. Determinations of molecular and equivalent weights on the basis of elementary analysis and potentiometric titration give a mean molecular weight of about 4000, approximately corresponding to octameric phthalocyanine.

Epstein and Wildi[66] investigated the electrical properties of the polymeric copper phthalocyanine obtained by heating pyromellitonitrile with cuprous chloride and urea. They determined the Hall effect of the polychelate, and found that the compound has *p*-type conduction. The polymer is characterised by two states, one having an activation energy of 0.26 eV and a carrier density of 10^{16} cm^{-3}, while the second state, also characterised by *p*-type conduction, has a corresponding value after heat-treatment of 10^{18} cm^{-3}.

Joiner and Kenney[108] synthesised six-coordinate germanium phthalocyanine, in which two coordination positions were occupied by chloride anions. Hydrolysis led to the exchange of the anions for hydroxyls. This substance became appreciably darker on being heated. Examination of the infrared spectra showed that –O– bridging groups were formed with the production of polymeric germanium oxyphthalocyanine, for which the formula $(C_{32}H_{16}N_8GeO)_x$ was given.

Berlin *et al.*[109] synthesised very interesting and distinctive chelate polymers, which obviously contained only carbon, nitrogen, and metal atoms, while being close to the phthalocyanines in structure. The polymer was assumed to have a parquet structure:



Such polymers were obtained by reaction of the metals or their compounds with ethylenetetracarbonitrile in a vacuum at 160°–300°. An especially interesting phenomenon is the formation of films of polychelates having the above structure on the surface of metal strips when the latter are heated in ethylenetetracarbonitrile vapour under reduced pressure at 150°–400° for 5–20 h.[110]

The polymers are insoluble, infusible black materials, stable to the action of alkalis and dilute acids. It is interesting that the infrared spectrum exhibits no intense absorption bands in the range 700–3000 cm^{-1} apart from that at 2224 cm^{-1}, corresponding to the CN group.

The polychelates possess very intense broad electron paramagnetic resonance lines. Examination of the electrical properties of such polymers[111] shows them to have *p*-type conduction, while the dependence of the logarithm of the conductivity on the reciprocal of the temperature is similar to that for semiconductors possessing impurity conduction. Interaction of an equimolecular mixture of a metal acetylacetonate, ethylenetetracarbonitrile, and phthalonitrile yields copolymers which presumably have a ribbon structure[109].

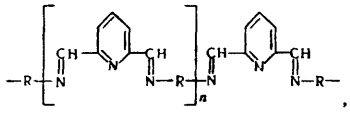
A further group of polybisdiazachelates, similar in structure to haemin and chlorophyll, have been described in a series of papers by Lautsch and his coworkers[112–114], who obtained various polymers and copolymers containing in the side-chains groups allied to the above compounds. Such chelate ligands were introduced into the polymer molecule either purely synthetically, by copolymerisa-

tion, or by incorporating prosthetic groups during polycondensation. As a result, polymers were obtained in which the main chain consisted of a linear or cross-linked ethyleneimine group and a polystyrene skeleton. Polycondensates of the type of polypeptides were finally obtained. In all cases the quantity of prosthetic groups was 0.01–1.0% of the main polymerised component. Several chelate polymers of these compounds with iron(II) were also obtained. Polychelates of this structure with a mesohaemin prosthetic group acted as oxidative catalysts.

Minne and Rochow[115] described the formation of polybisdiazachelates of copper with organosilylamines. Dimethylchlorosilane reacts with ethylenediamine to form a linear polymer of silylamine, treatment of which with anhydrous copper(II) chloride leads to rearrangement of the polymer chain with the formation of a silazane and simultaneous separation of ethylenediaminecopper chloride. Further treatment of the silazane with excess of $CuCl_2$ produces a cross-linked chelate polymer.

Similarly, beryllium chloride gives chelate polymers with the same silazane[116], one-third of the nitrogen atoms present in the original polymer taking part in the formation of chelate loops.

A synthesis of chelate polymers of distinctive structure has been effected also by Lions and Martin[117], who obtained polymeric Schiff bases from pyridine-2,6-dialdehyde with ethylenediamine, hexamethylenediamine, and benzidine. These were hard and infusible, their monomeric unit containing a terdentate group of nitrogen atoms

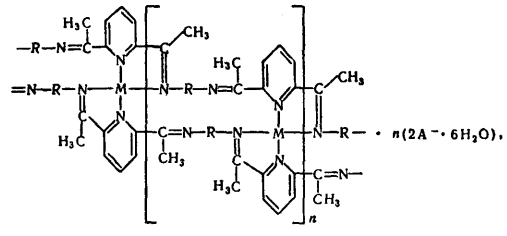


where R = $[CH_2]_2$, $[CH_2]_6$, p-C_6H_4.C_6H_4-p'. The first two polymers formed polychelates with bivalent salts of iron and cobalt, and the third with copper(II) salts. The chelate polymers, in contrast to the original Schiff bases, dissolved quite well in water, and were separated with difficulty from solution as the perchlorates or iodides Partial hydrolysis of the compounds might take place in solution, with separation of the metal hydroxides.

The structure of the substances remained obscure. Although these workers were inclined to the view that they had obtained polybistriazachelates, they pointed out[117] the possibility of such polymers existing as tetracoordinated compounds, *i.e.* as polybisdiazachelates. In this case one of the three nitrogen atoms in the terdentate group is not involved in the formation of coordinate links. Such a view seems to us the more correct, since the magnetochemical results obtained by these workers cannot give an unambiguous answer in the above cases, while the formation of a sexidendate chelate polymer is made extremely improbable also as a result of steric hindrance.

Depending on the conditions, polychelates varying in composition can be isolated, with a metal ion in all or in only a proportion of the chelate groups. A noteworthy polymer, isolated as the sulphate, is that of iron with the polymeric Schiff base from pyridine-2,6-dialdehyde and ethylenediamine, in which iron ions occupy all the coordination sites of the original macromolecule. It possessed appreciable ferromagnetism, its high molar magnetic susceptibility (0.15) being explained[117] by intermetallic interaction. However, it seems to us that the ferromagnetism of the polychelate is more likely to be due to contamination with the ferromagnetic oxide Fe_3O_4 than to interatomic interaction of the electron spins of the iron atoms. The likelihood of such a conclusion is supported also by the precipitation, observed by the American workers, of metal hydroxides from solutions of such polychelates and from solutions of non-polymeric complexes of analogous structure.

Compounds related to the above substances have been prepared by Terent'ev *et al.*[118] Starting from 2,6-diacetylpyridine, they synthesised a series of polyketimine derivatives of nickel, iron, and cobalt of the following structure:



where R = $[CH_2]_2$, $[CH_2]_6$, o-C_6H_4; M = Ni^{2+}, Fe^{2+}, Co^{2+}; $2A^-$ = Cl_2, SO_4. The resulting polybisdiazachelates were coloured powders, in most cases soluble in water or methanol.

Determination of the instability constants of several of the synthetic materials confirmed the structural formulae suggested for them, which were supported also by the magnetochemical results and the spectral characteristics of the polymers. Solutions of such compounds have anomalous viscosity, attributed primarily to dissociation of the macromolecular aggregates. Examination of the electrical properties of the polybisdiazachelates[75] showed that several of them possess a conductance which is typical of organic semiconductors.

6. Ion-Exchange Resins

A large and interesting group of polychelates are located on the borderline between two branches of chemistry — organic polymer and analytical chemistry. They are the macromolecular ion-exchange compounds. In some cases ion-exchange resins — more precisely cation-exchange resins — are able to segregate certain metal ions by forming coordinate bonds with ions of heavy metals. Here we shall give only a brief account of the main characteristics and methods of synthesis of cation-exchange resins, since several monographs and reviews have been published on this topic[119–128].

Among all the cation-exchange resins, we are interested only in those which form chelate loops. We shall not consider here cases in which the metal forms an insoluble salt of a macromolecular acid. We have already encountered representatives of this group of polymers. Without claiming to give a complete survey of chelate ion-exchange resins, we shall merely cite below a series of characteristic examples of polychelates having this structure.

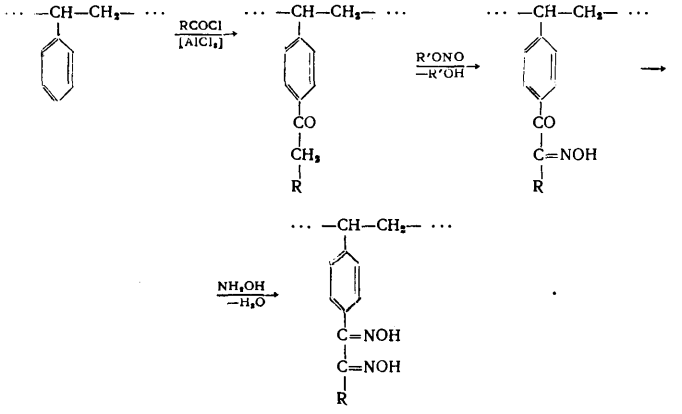
In the process of ion exchange, chelate compounds are usually formed only with feebly acidic cation-exchange resins. Nevertheless, these compounds possess enhanced

selectivity towards certain ions. For example, Smirnov and Blushvein[127] obtained a cation exchanger by the polycondensation of pyrogallol and formaldehyde, the selectivity of this compound for nickel and lead exceeding that for iron and calcium by a factor of 200. Selective cation-exchange resins of similar structure have also been prepared[128] from resorcinol, formaldehyde, and arsenic pentoxide with additions of cross-linking agents.

Despic and Kasanović[129] have describe the synthesis and polymerisation of an unsaturated β-diketone, methacryloylacetone (5-methylhex-5-ene-2,4-dione). In the presence of small quantities of ethylene glycol dimethacrylate as cross-linking agent, and after treatment with aqueous alkali, such a polymer forms polychelates with the uranyl and ferric ions. The resin loses its coordinated ions under the influence of acidic reagents. Similar behaviour is shown by resins obtained by the copolymerisation of methacroylacetone with methacrylic acid in the proportions 1 : 1 and 1 : 2 with additions of 10% of ethylene glycol dimethacrylate.

Cation exchangers based on cross-linked polystyrene or its copolymers are most widespread at the present time. For example, the Annual Report of the Chemical Research Laboratory at Teddington for 1954 [130] quotes data on the synthesis of polystyrene cross-linked with various substances containing chelate ligands. Such resins are capable of ion exchange. In particular, an investigation has been made of the possibility of complex formation by resins, containing amino-, carboxy-, amino-carboxy-, and sulpho-groups, with salts of bivalent copper, nickel cobalt, manganese, magnesium, calcium, and barium, tervalent lanthanum, and the alkali metals. Copper and nickel ions were shown to form the most stable chelates.

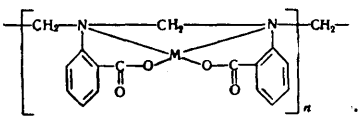
Štamberg *et al.*[131] obtained an ion exchanger based on cross-linked polystyrene, selective with respect to nickel, by the following scheme:



The structure of this cation exchanger is very similar to that of dimethylglyoxime, Chugaev's famous reagent for nickel ions.

Of course, it is not only cross-linked polymers and copolymers of styrene that are applicable as ion-exchange resins. Thus in 1957 a Czechoslovak patent[132] described the preparation by treatment of cross-linked chloromethylated copolymers of hydrocarbons with excess of amino-carboxylic acids, of a selective cation exchanger for the extraction of complexing ions. Another patent[133] claims the production of an ion-exchange resin which forms complexes selectively with copper and with palladium. Such a cation exchanger is obtained by condensing dihydroxybenzaldehyde with formaldehyde and then converting the polyaldehyde into a polyaldoxime.

An interesting complexing ion exchanger has been obtained by the polycondensation of anthranilic acid with formaldehyde[134,135]. The resulting polymer obviously contains chelate loops having the structure:



By the interaction of anthranilic acid, certain aromatic diamines, and formaldehyde, Gregor *et al.*[136] succeeded in obtaining a series of cation-exchange resins which gave stable polychelates with Cu^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, and Co^{2+}.

Bayer[137,138] investigated the relative stability of the complexes formed by copper, nickel, cobalt, zinc, cadmium, manganese, and uranium with the bis-*o*-hydroxyanil of glyoxal, and found that the metals can displace one another, at least partly, in the following sequence:

$$Cu > UO_2 > Ni > Co > Mn > Zn > Cd;$$

the further to the left is a metal in this series, the stronger the acid required to isolate it from its complex.

Bayer continued his investigation by studying polyaminophenols[139,140]. He condensed di- and tri-aminophenols with glyoxal, and obtained Schiff bases of high molecular weight. An especially interesting product was obtained by the polycondensation of 2,4,6-triaminophenol with glyoxal, yielding an insoluble black powder. Excess of glyoxal gives granular products, which is particularly valuable in view of Bayer's results. As in the case of glyoxal bis-*o*-hydroxyanil, the polymeric Schiff bases form macromolecular chelate compounds, which are able to yield back the metal on treatment with acids. Such Schiff bases are not hydrolysed by mineral acids of pH > 0.5. Nevertheless, such a resin proved to be extremely selective. Over the pH range 0–7 it does not bind alkali or alkaline earth metals at all. Bayer established that the polymer retains best of all the ions Cu^{2+}, UO_2^{2+}, and Ni^{2+}, even in the presence of a large excess of ions of other heavy metals.

Bayer also presented a paper on the preparation of these and similar macromolecular complexing agents[141] at the International Symposium on Macromolecular Chemistry, Wiesbaden (Germany), October 1959, where he described in particular the preparation of polyhydroxamic acids from a polymethacrylate. Such polymers formed stable polychelates with copper, iron, and uranium. Nevertheless, the selectivity of such ion-exchange resins was considerably lower than that of the resins described above. It is true that they possess higher mechanical and chemical stability than the polymeric Schiff bases, but their capacity for metals is rather lower.

It is interesting that chelate polymers can themselves extract ions from solutions, and then act as anion exchangers. Such an exchanger has been obtained[142] by the interaction of copper(II) and cobalt(II) salts with cross-linked polyethyleneimine. The chelate polycation was so stable that its combined copper could not be replaced by zinc, nickel, or cobalt. Only in strongly acid medium did this polymer lose its metal ions.

Nonogaki has subsequently obtained another anion-exchange resin of the same type[143]. A copolymer of polyethyleneimine and dichloroethane gave a stable complex with copper salts. Such a polychelate can be used as a strongly basic anion-exchange resin. Similar results were obtained in the synthesis of chelate polymers of cobalt with copolymers of *o*-bis-2-aminoethylaminomethylbenzene and dichloroethane.

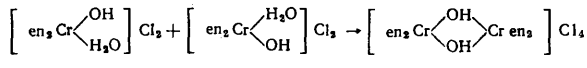
7. Hydroxo-Bridged and Related Compounds

The work discussed above does not exhaust the chemistry of chelate polymers. The small but distinctive group of hydroxo-bridged compounds and their structural analogues should, in our opinion, be included among polychelates. These chelate polymers lie on the borderline between the chemistry of inorganic polymers and the chemistry of polychelates. Here, too, we shall deal only with a few of the most important examples of compounds of this type.

These compounds are complexes in which metal atoms are linked together by hydroxo-bridging groups. Their formation may be accompanied by substitution by anions, or by conversion of hydroxo- into oxo-bridging groups. These processes may take place simultaneously.

Hydroxo-bridged and related compounds provide an example of those rare cases in which a chelate polymer is formed with molecules containing less than two pairs of donor groups.

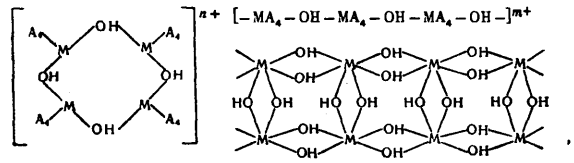
The first chemists to isolate hydroxo-bridged compounds were probably Gentele[144] and Jörgensen[145]. During the early 1890's these compounds were investigated by Pfeiffer[146,147], who suggested that the two metal atoms in them could be linked by hydroxo-groups. On the basis of modern ideas, the reaction which he described can be written as follows:



where en represents an ethylenediamine molecule.

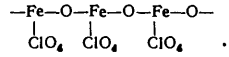
Subsequently, the amount of work done on hydroxo-bridged and related compounds increased markedly. Thus by 1930 Gmelins Handbuch, for example, listed[148] many tens of such compounds of cobalt, but consideration was confined to bridged complexes containing not more than four central atoms. Mellor[149] also cited a large number of papers describing hydroxo-bridged and related compounds, devoting more than fifteen pages, for example, to cobalt compounds having this structure.

In fact, the process of hydroxo-bridge formation may not be completed at a definite stage. Pfeiffer[150] suggested that the first stage in such a process is hydrolysis of the salts. A little later Kullgren[151] showed that the degree of hydrolysis increases with rise in temperature. It is affected also by the pH of the solution and the nature of the anion[152]. If insufficient alkali for complete neutralisation is added to such a solution, polymerisation occurs instead of precipitation of a hydroxide or a hydroxo-salt. For example, Bjerrum showed in a series of papers[153–155] that the resulting structures are of similar size to colloidal particles. Riess and Barth[156] found that Bjerrum's solutions contained substances of ionic weight 400–1000, and postulated the existence of polyhydroxo-compounds of three types, with cyclic, linear, and network structures. Thus the following structural formulae can be written in the case of six-coordinate tervalent metals (M), which most often form such compounds:

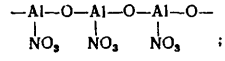


where A is a coordinated molecule or ion.

Hydroxo-bridging groups can be converted into oxo-groups under the influence of heat. Such a process can occur also on the slow addition of alkali to solutions of hydroxy-compounds. Jander and Jahr[157] found that addition of alkali to ferric perchlorate solutions produces dimeric compounds, first hydroxo and then oxo. A large quantity of alkali leads to the formation of such substances as:



These workers found that the addition of two moles of ammonia to one mole of aluminium nitrate results in the formation of the structure:



addition of alkali does not precipitate the hydroxide, but the degree of polymerisation is increased. Zirconium perchlorate behaves similarly.

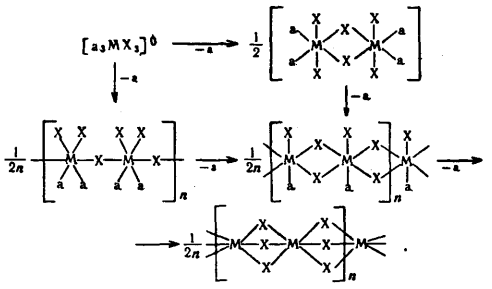
More recently Bradley[158] has discussed, on the basis of some earlier work[159], the three-dimensional structure of metal alkoxides. All such compounds of general formula $M(OR)_n$ (where n is the valency of the metal) form polymers corresponding to the coordination number of the metal. In several cases Bradley indicates the minimum degree of polymerisation (x) of such alkoxides $[M(OR)_n]_x$: depending on the valency of the metal, x varies from 2 to 8. He also states that, with the same radicals R and in the same group of the Periodic System, the degree of polymerisation x increases with increase in size of the metal atom.

Thus most of the known hydroxo- and oxo-bridged compounds are macromolecular. From the point of view of coordination theory, hydrous metal oxides can be included in this class of substances. For example, Graham and Thomas[160] assume the compounds to be complexes of zero charge. On this basis it is easy to explain such properties of hydrous oxides as the diminution in their reactivity produced by the aging of solutions with time or on heating, and also their ability to retain certain anionic impurities even after prolonged washing. It must be noted, however, that this theory has been subjected to serious criticism based on X-ray investigations[161].

In this section we have repeatedly used the term "hydroxo-bridged and related compounds". Among these "related compounds" must be included complexes in which metal atoms are linked by bridging atoms of oxygen, sulphur, nitrogen, or halogens, or by some of their simplest

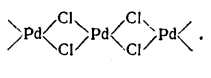
derivatives. We have just described above a series of oxo--compounds belonging to this group of polymers. Jensen's mercaptides[91], which have been discussed earlier (p. 675), should probably be included in this group of substances. Let us consider some other work on compounds related in structure to hydroxo-bridged polymers.

Substances of this type can be formed in some cases, for example, in the synthesis of amido-complexes. In general a complex $[a_3MX_3]^0$ can undergo the series of reactions:



A comprehensive investigation of the conditions for such a reaction has been undertaken by Schmitz-Dumont[162], with $[Co(NH_3)_6](NO_3)_3$ and several other substances as examples. He obtained a series of amido, hydroxo-amido, and amido--alkoxo complexes of tervalent cobalt and chromium having the above structure (X = NH_2, OH, O, OR, or combinations thereof; M = Co^{3+}, Cr^{3+}). The products were amorphous powders, similar in properties to other macromolecular coordination compounds.

The interesting paper by Shaw[5] states that X-ray studies of complex compounds have shown that the simple formula AB_n cannot be used to determine the coordination number of the central atom A, which often exceeds n. For example, ferric chloride in the solid state is a polymer of coordination number 4. Palladium chloride molecules have a similar structure, forming a planar polymer in which chlorine atoms form bridges



Caesium copper(II) chloride $CsCuCl_3$ contains the ion $[CuCl_3]_n^{n-}$ of indefinite chain length. Shaw considers that a similar structure is possessed by HgI_2, MoS_2, WS_2, and several other compounds.

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Several chelate polymers containing various chelate loops have been discussed. Research has been concerned mainly with the thermal properties of polychelates, and most of the experimental work on the chemistry of chelate polymers has been on these lines. Unfortunately, little published information can be found on the electrical properties of chelates; reports on the structure of the chelate loops in the polymers, the overall structure of the macromolecules, or their spatial arrangement are few.

Nevertheless, a few conclusions on the properties of chelate polymers can be reached from an examination of the literature. The thermal stability of polychelates greatly depends on whether the metal ion is located in the main polymer chain, when relatively thermostable materials are formed, or in side-chains, in which case no appreciable increase in thermal stability is observed. The properties of polychelates are greatly affected by the structure of the chelate loop. For example, among polybisdioxachelates the beryllium polymers are the most interesting, while among the bisdiaza-compounds it is the iron and copper derivatives. In several cases films and filaments can be obtained from chelate polymers, but they are sometimes quite unsuitable for industrial processing.

Chelate polymers having interesting electrical properties, those of semiconductors, catalysts, etc., are attracting attention. These specific characteristics are usually inherent in polychelates containing a system of conjugated bonds, and also in compounds which are in some way ordered as a planar or three-dimensional network. But work on these lines is at present only sporadic.

The chemistry of chelate polymers forms a new branch of polymer chemistry. The immediate difficulty is to visualise the mechanism by which polychelates are formed. The physicochemical properties of such compounds are not always clear; difficulties will undoubtedly be encountered in the industrial utilisation of polymers. Nevertheless, the structural characteristics of polychelates will make it possible in the future to synthesis compounds having the most varied combinations of properties.

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